U.S. Department of Energy
Office of Civilian Radioactive Waste Management

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Modeling the Effects of Crevice Former, Particulates, and the Evolving Surface Profile in Crevice Corrosion

Presented at:
Critical Factors in Localized Corrosion 5: Symposium in Honor of Hugh S. Isaacs The 210th Meeting of the Electrochemical Society

Presented by:
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Case Western Reserve University

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Cancún, Mexico

Acknowledgement and Disclaimer

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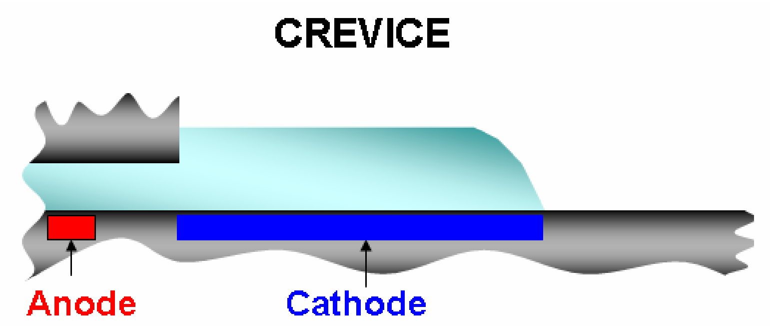
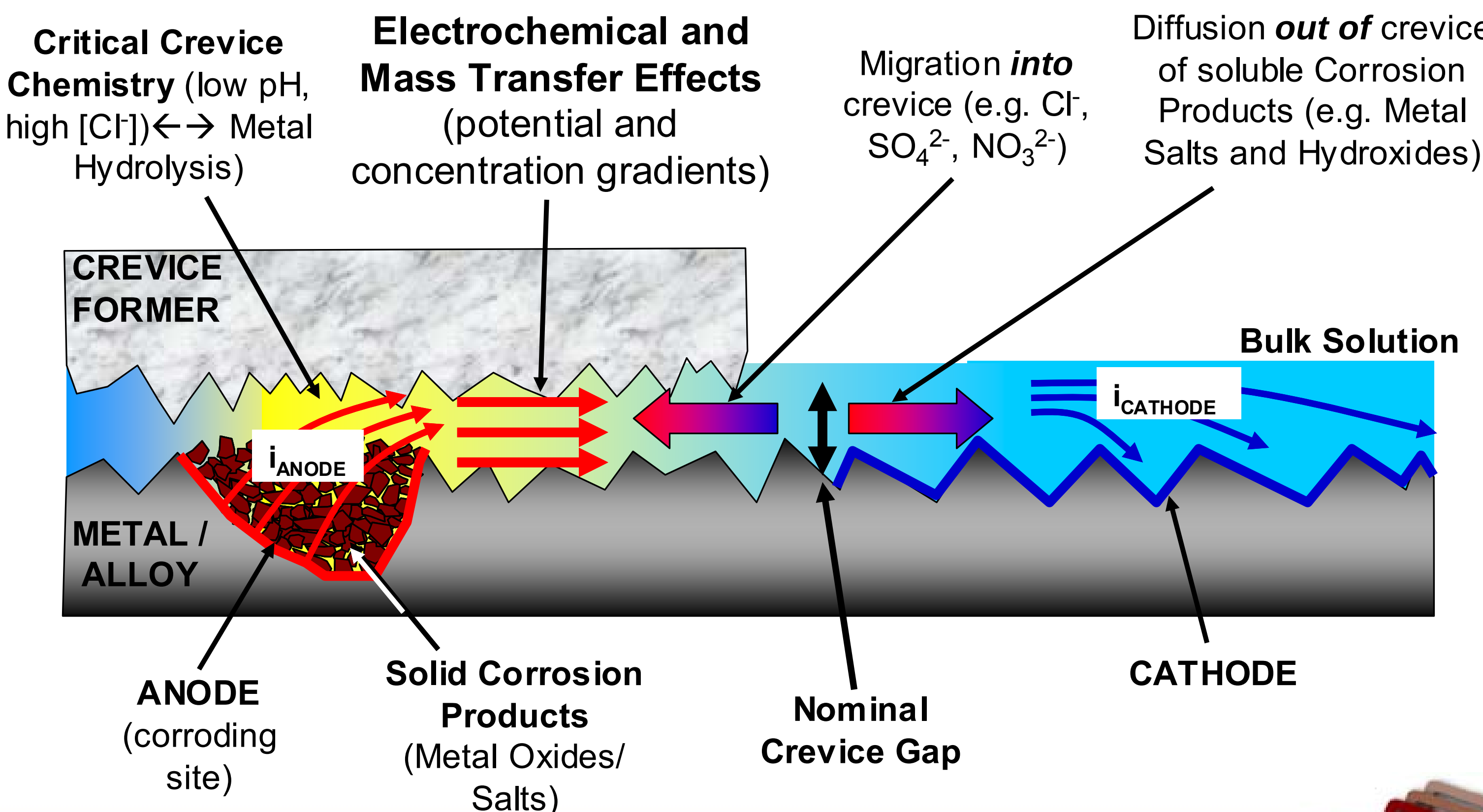
- The views, opinions, findings, and conclusions or recommendations of authors expressed herein do not necessarily state or reflect those of the DOE/OCRWM/OCS.

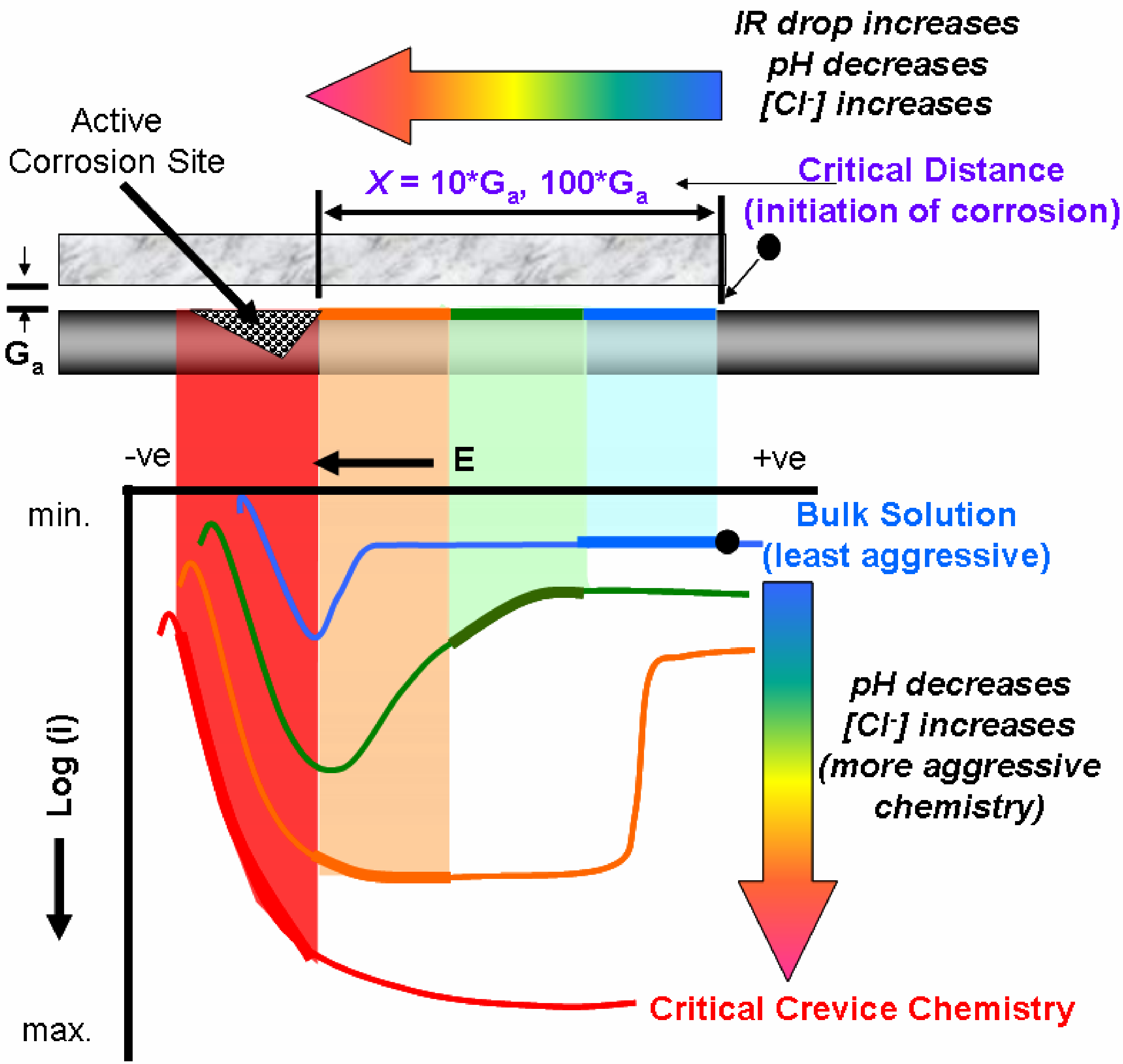
Crevice Corrosion



Crevice corrosion may occur in **restricted regions** due to **transport limitations**, followed by a build-up of a **highly corrosive chemistry**, capable of dissolving the metal. The dissolution rate is potential-dependent.



Critical Solution Chemistry within a Crevice



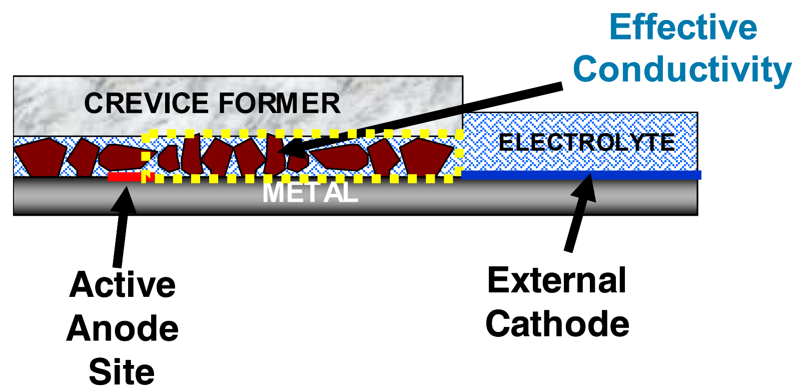
- Active corrosion starts at a "critical" distance within the crevice
- Anodic current produced by this electrode length (X) is small
- Majority of current along X is produced at the corroding site

OBJECTIVES

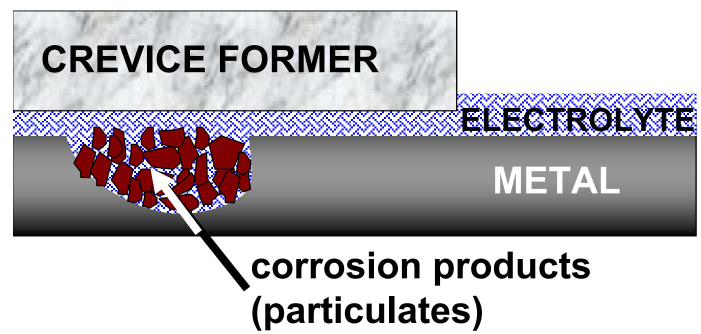
Model the **OHMIC (IR)** effects on current & potential distributions:

1. Crevice former irregularities (protrusions) and metal roughness

2. Effect of particles under crevice former

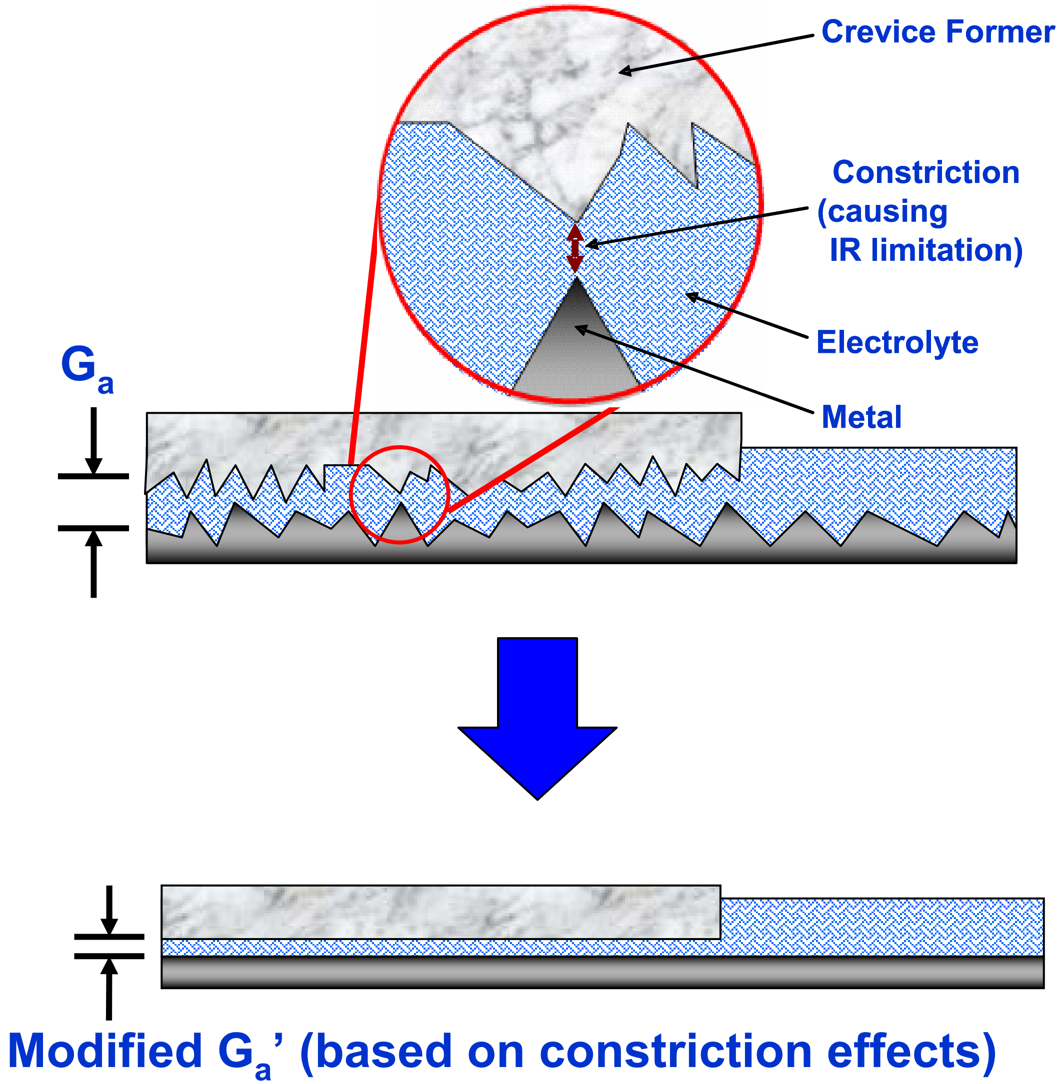


3. Particulates accumulation (corrosion products)



Changes in solution chemistry not considered in this work.

Crevice Former Irregularities and Metal Roughness

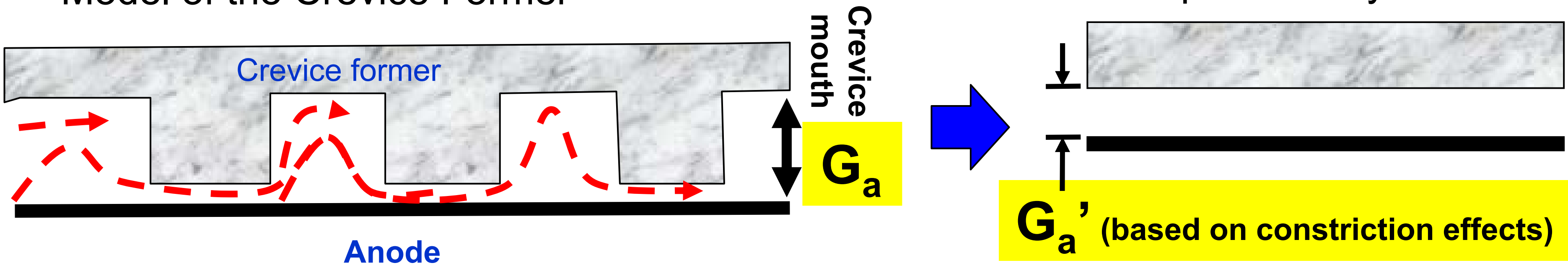


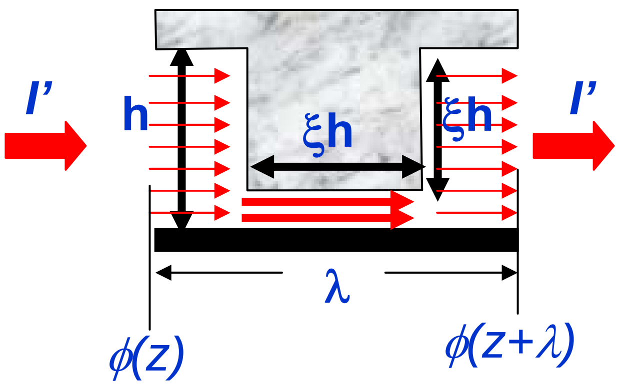
- Roughness on crevice former/ metal substrate ~ order of crevice gap (G_a).
- Narrow passages along the rough surface → resistance to current flow & high IR
- GOAL: An equivalent smooth crevice accounting for roughness in terms of a modified crevice gap (G_a')

Constriction Factor Accounting for Roughness

Model of the Crevice Former

Equivalent System





Constriction Factor* (τ)

- accounts for *cross sectional variations*
- determined from the geometry

$$\tau = \langle S \rangle \times \langle 1/S \rangle \quad \text{and} \quad \varepsilon = \langle S \rangle / \lambda^2$$

<S> = mean cross sectional area over a unit length, λ

ε = porosity

**Lanzi and Landau, J. Electrochem. Soc. 137, 585 (1990)*

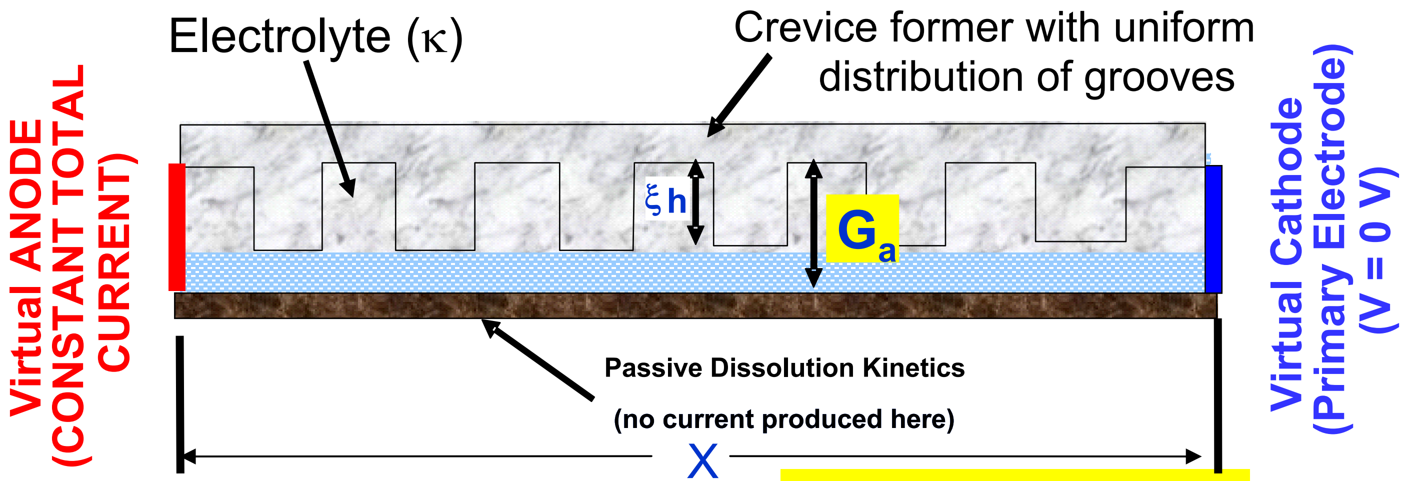
$$\frac{\phi(z+\lambda)-\phi(z)}{I'} = \frac{\langle\phi\rangle(z+\lambda)-\langle\phi\rangle(z)}{I'} = \left[-\frac{\lambda\tau}{kWG_a\varepsilon}\right] = \left[-\frac{\lambda}{kWG'_a}\right]$$

where

$$G'_a = G_a \times \frac{\varepsilon}{\tau}$$

Modified Crevice Gap (G_a') is a function of the porosity (ε) and the constriction factor (τ).

Decoupled Anode Model



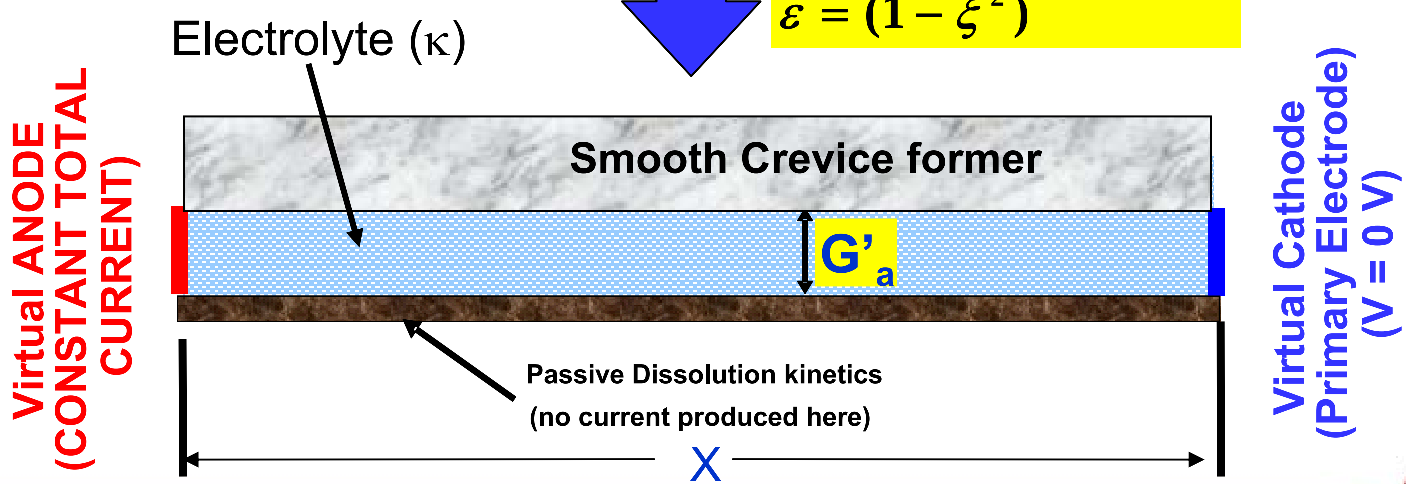
$$G'_a = G_a \times \frac{\varepsilon}{\tau}$$

where

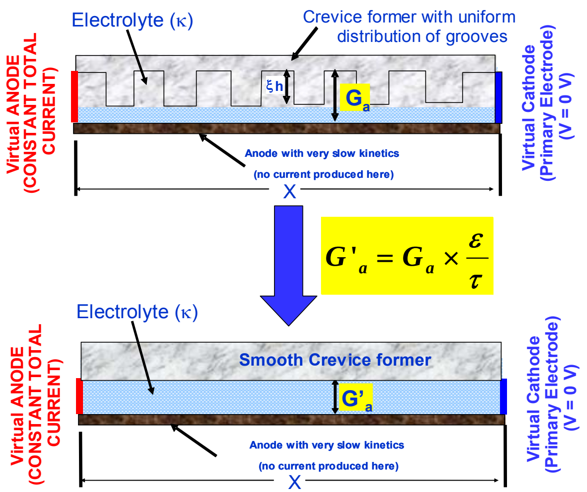
$$\tau = (1+\xi)(1-\xi+\xi^2)$$

and

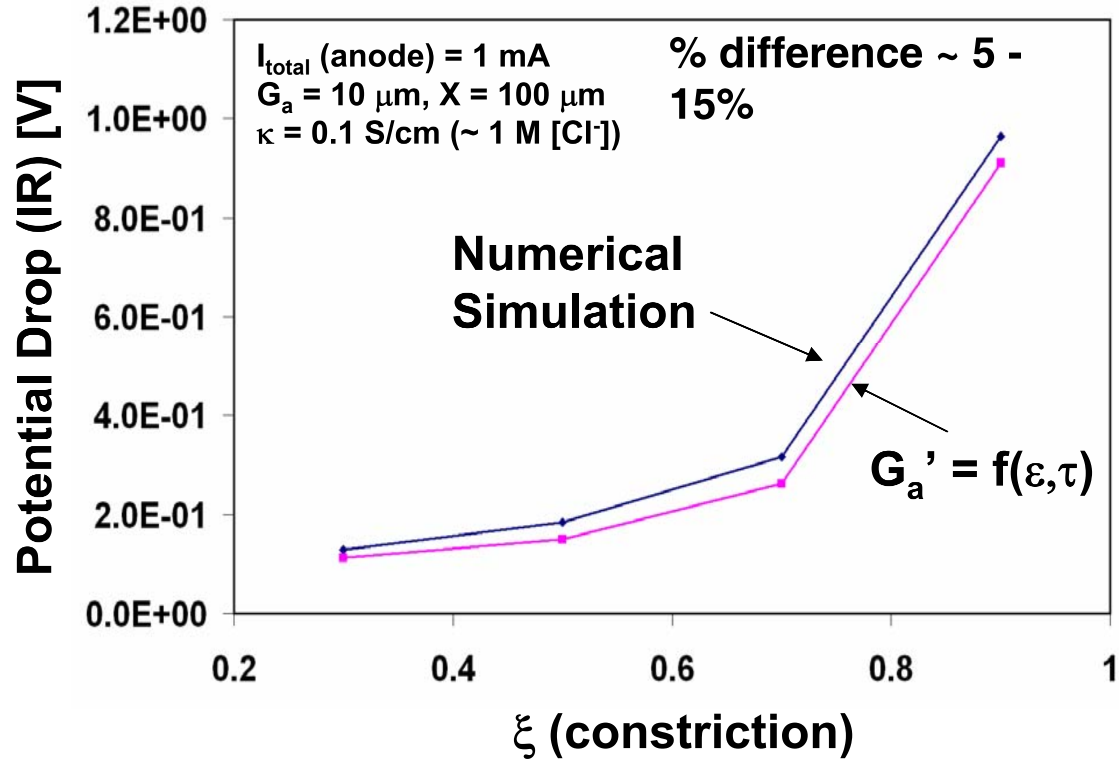
$$\varepsilon = (1-\xi^2)$$



Sample Calculations



ξ	porosity (ε)	τ
0	1	1
0.3	0.91	1.027
0.5	0.75	1.125
0.7	0.51	1.343
0.9	0.19	1.729



Critical Parameters Evaluated:

1. Effect of constriction (ζ)
2. Length, X = 10*G_a, 100*G_a
3. Total anodic current
4. Conductivity

Constriction factor analysis adequately accounts for roughness effects

Another Sample Calculation

$$G'_a = G_a \times \frac{\varepsilon}{\tau}$$

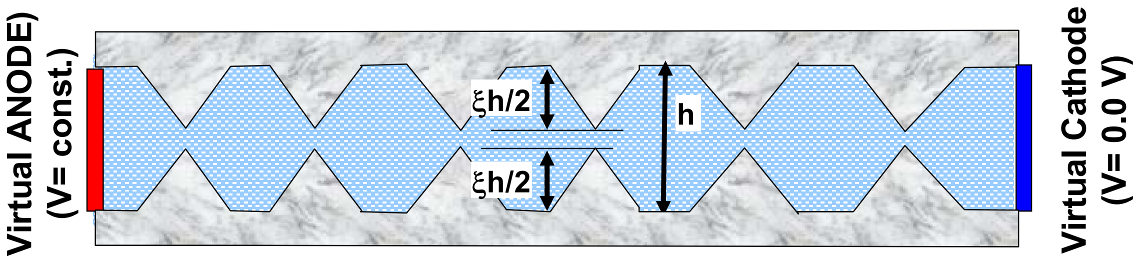
where

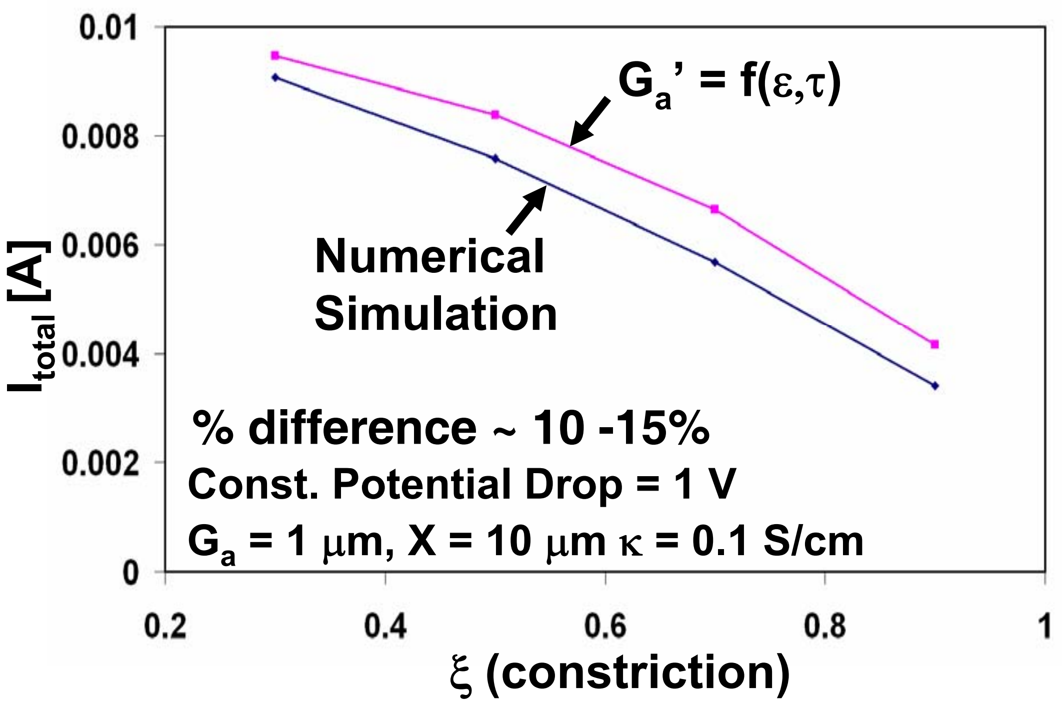
$$\tau = (1 - \frac{\xi^2}{2})\left((1-\xi) - \ln(1-\xi)\right)$$

and

$$\varepsilon = (1 - \frac{\xi^2}{2})$$

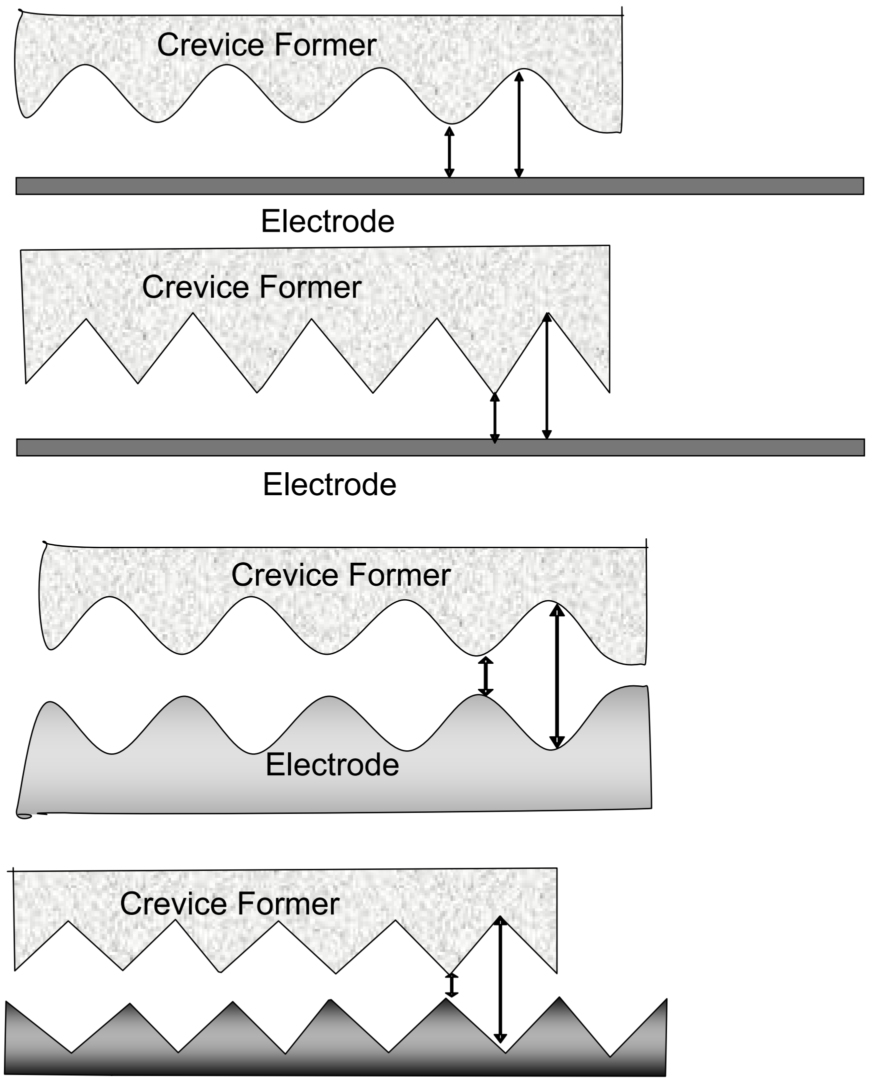
ξ	porosity (ε)	τ
0	1	1
0.3	0.96	1.01
0.5	0.88	1.04
0.7	0.76	1.14
0.9	0.60	1.43

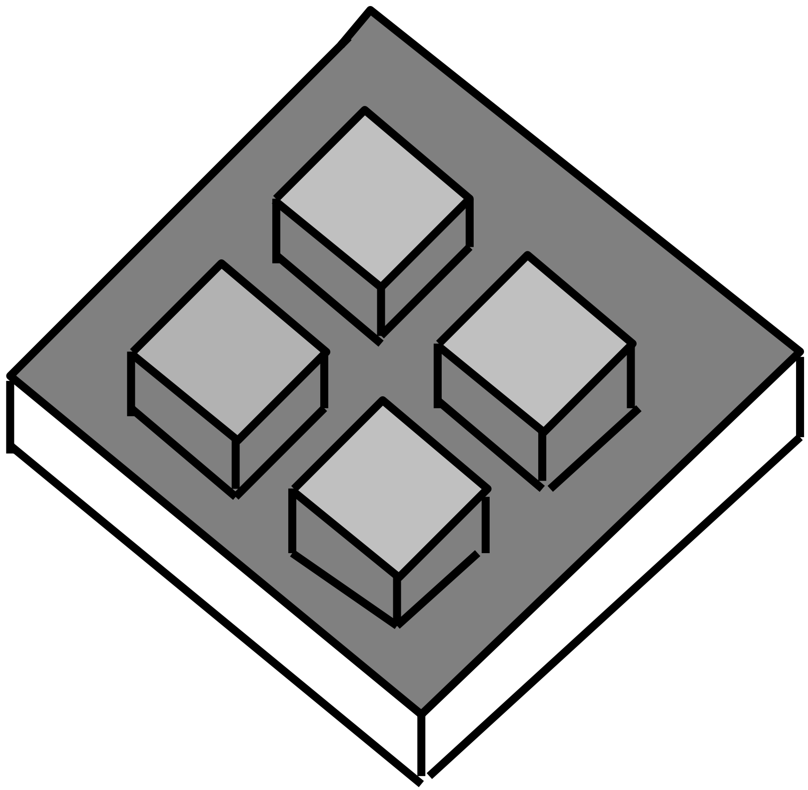




Constriction factor (τ) analysis adequately accounts for roughness effects

Other Complex Systems can be Analyzed



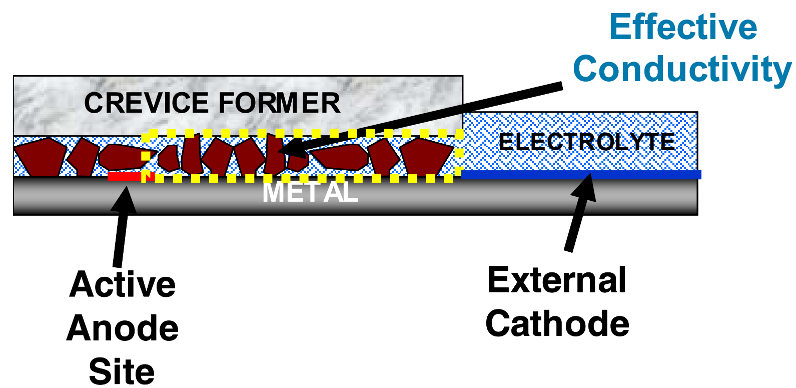


OBJECTIVES

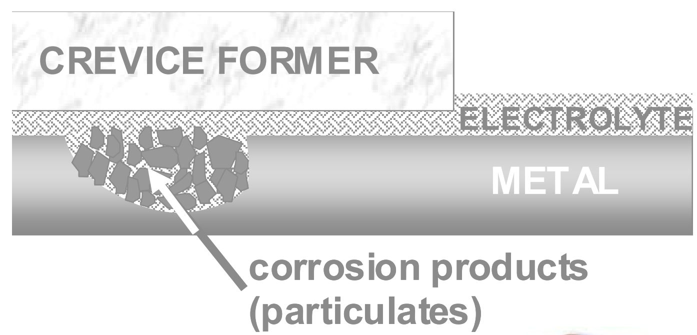
Model the **OHMIC** (**IR**) effects on current & potential distributions:

1. Crevice former irregularities (protrusions) and metal roughness

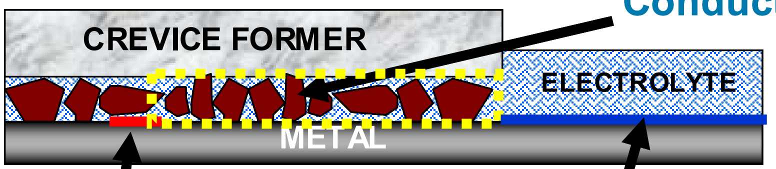
2. Effect of particles under crevice former

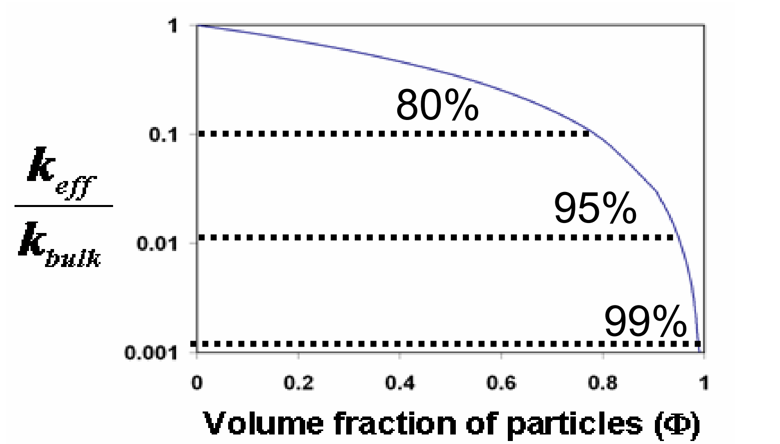


3. Particulates accumulation (corrosion products)

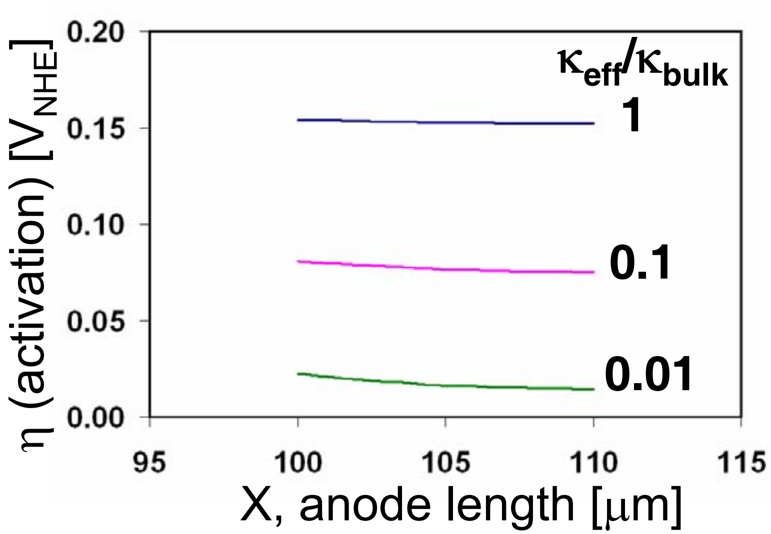


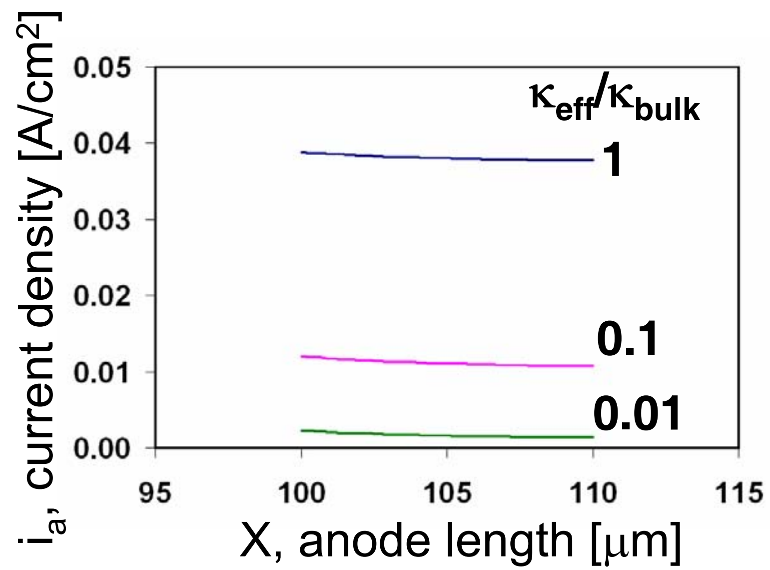
Effect of Particles Under Crevice Former





Bruggeman's Equation: $\kappa_{\text{eff}} = \kappa_{bulk}(1 - \phi_{\text{sand}})^{\frac{3}{2}}$

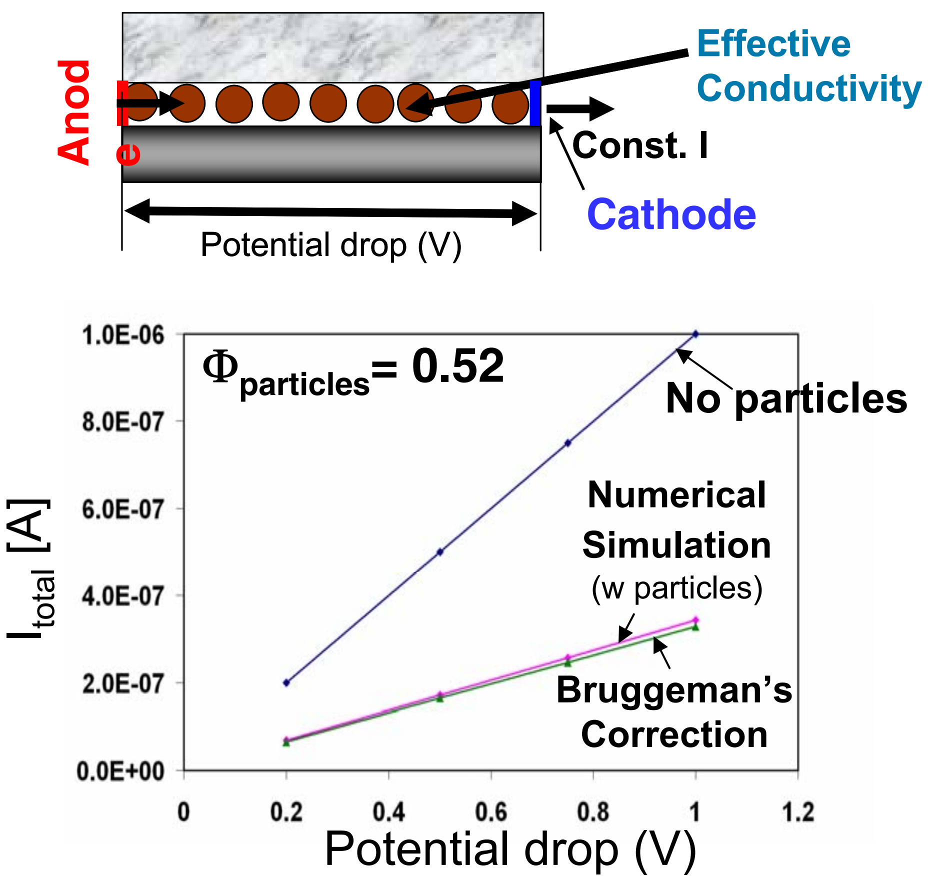




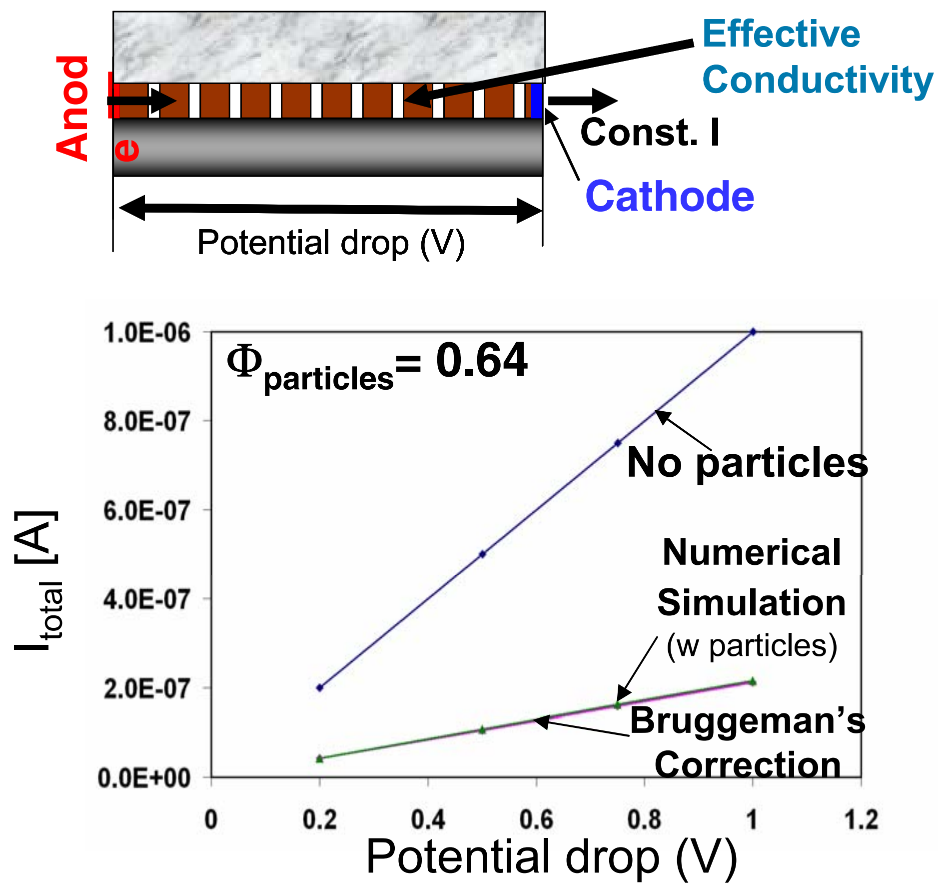
Increase in vol. fraction of particles decreases κ_{eff}, which increases the ohmic resistance and lowers the anode current

Conductivity Adjustment Accounting for Particles Under Crevice Former

Spherical Particles



Cubical Particles



Equivalent conductivity reasonably accounts for particulates.

OBJECTIVES

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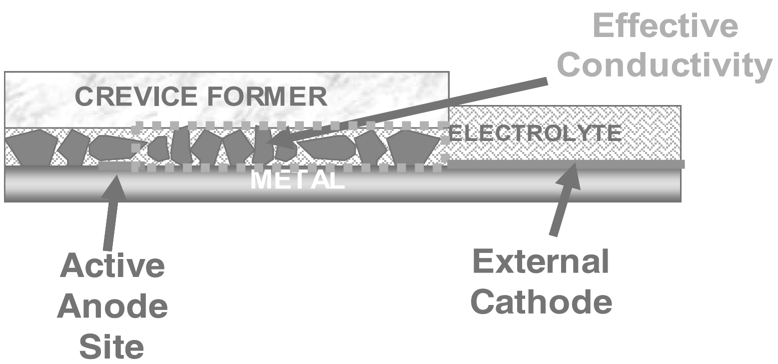
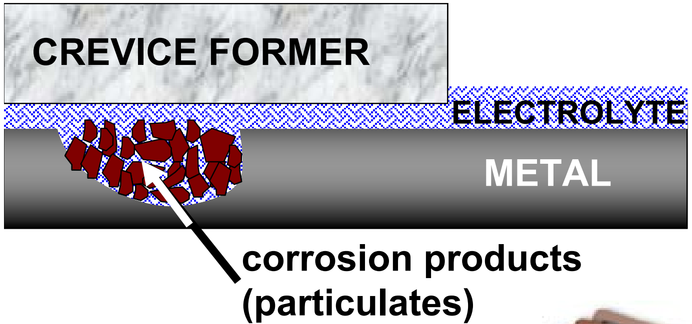


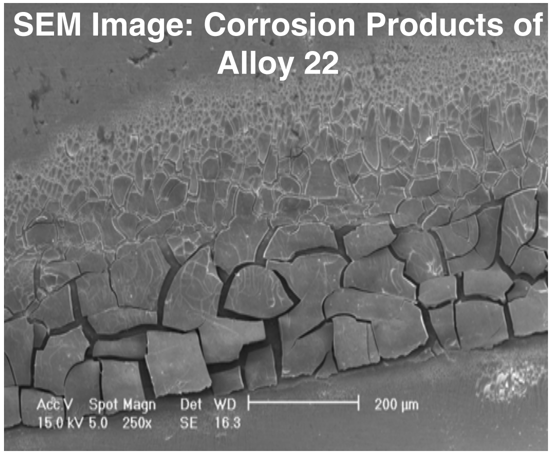
3. Particulates accumulation
(corrosion products)



Effect of Particulates (Corrosion Products)

Corrosion products (crevice corrosion tests):

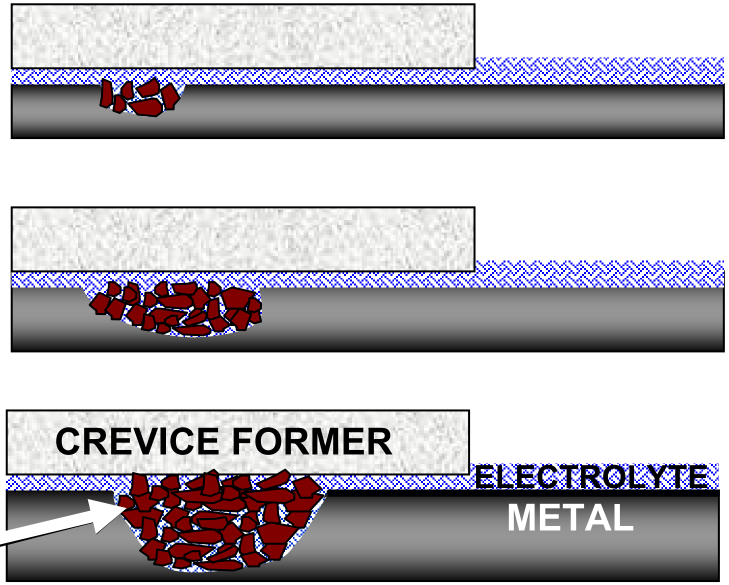
- Fine particulates (~microns)
- Loosely attached to base metal
- Consist of metal oxides (inert)



Probable effects of solid corrosion products:

- Increase ohmic resistance to corrosion of underlying metal
- Affect the corrosion evolution profile
- Form a tighter crevice gap

Schematic: Probable Anode Evolution with Solid Corrosion Products



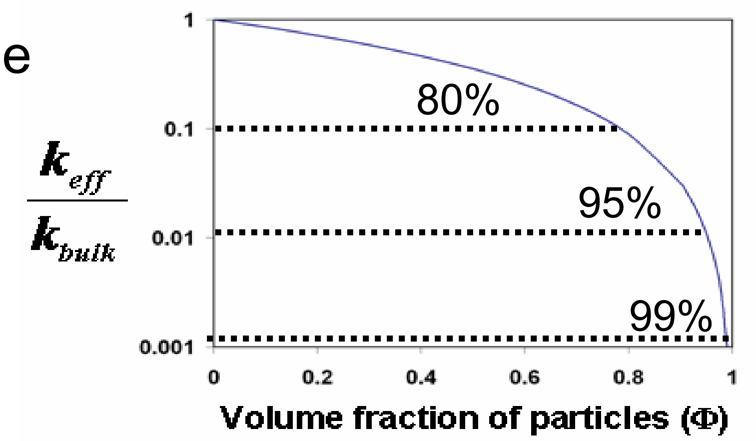
Increase in Corrosion Products would further increase the ohmic drop

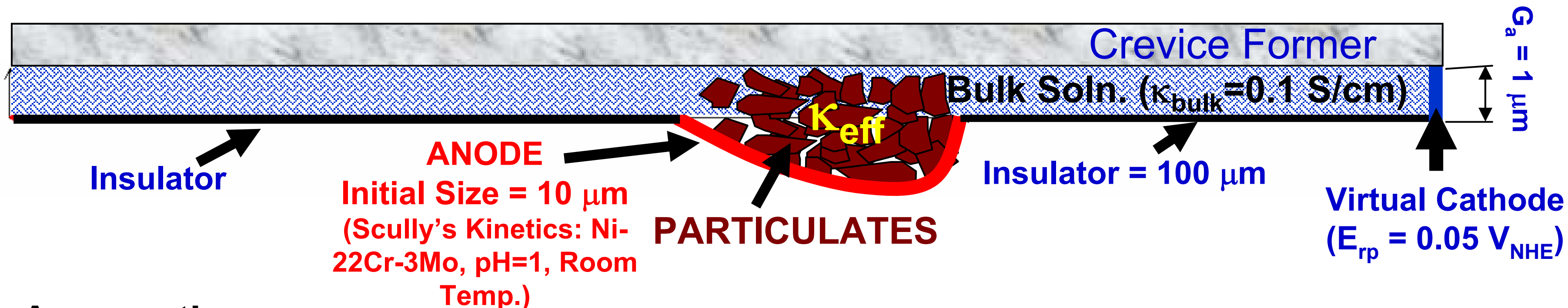
Conductivity Adjustment to Account for Particles in Corroding Site

- Particulates at corroding site increase the ohmic resistance (reduce κ)

Bruggeman's Equation

$$\kappa_{eff} = \kappa(1 - \phi_{sand})^{\frac{3}{2}}$$

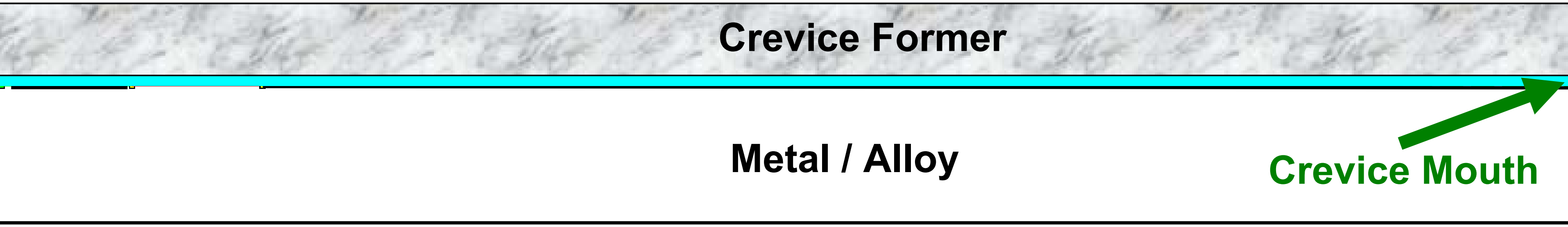


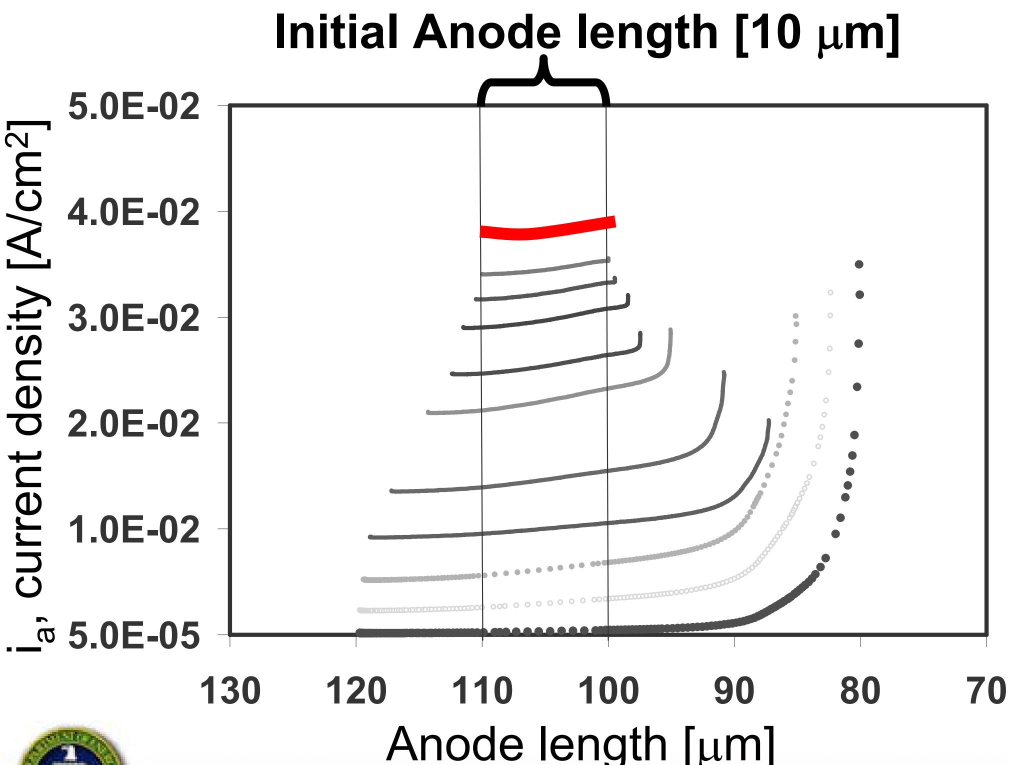


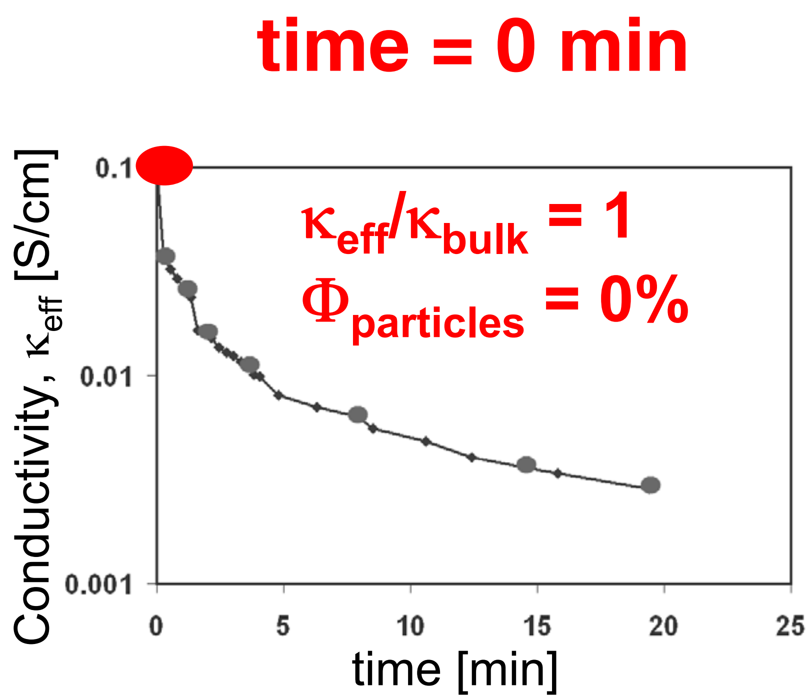
Assumptions:

- ~ 50% of the corroded metal forms insoluble inert metal oxide particles
- Density of the corrosion product ~ half of the alloy → twice the volume
- The particles are uniformly distributed in the solution within the corroding pit
- Solution conductivity within the pit is calculated using Bruggeman's Equation

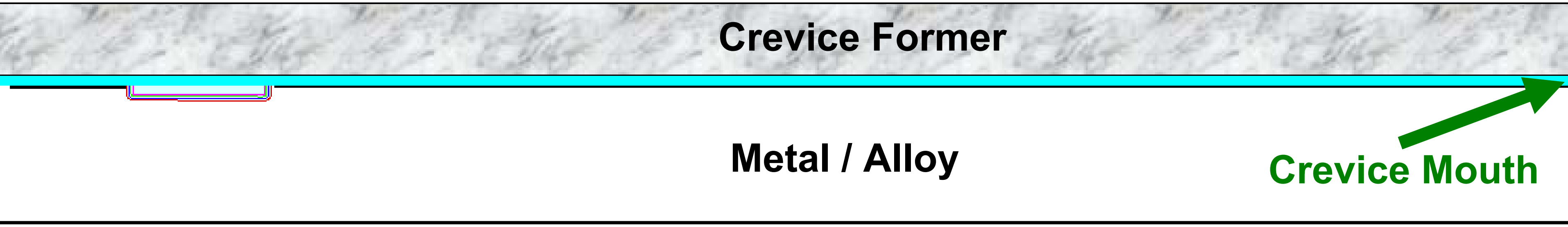
Simulation: Anode Profile Evolution

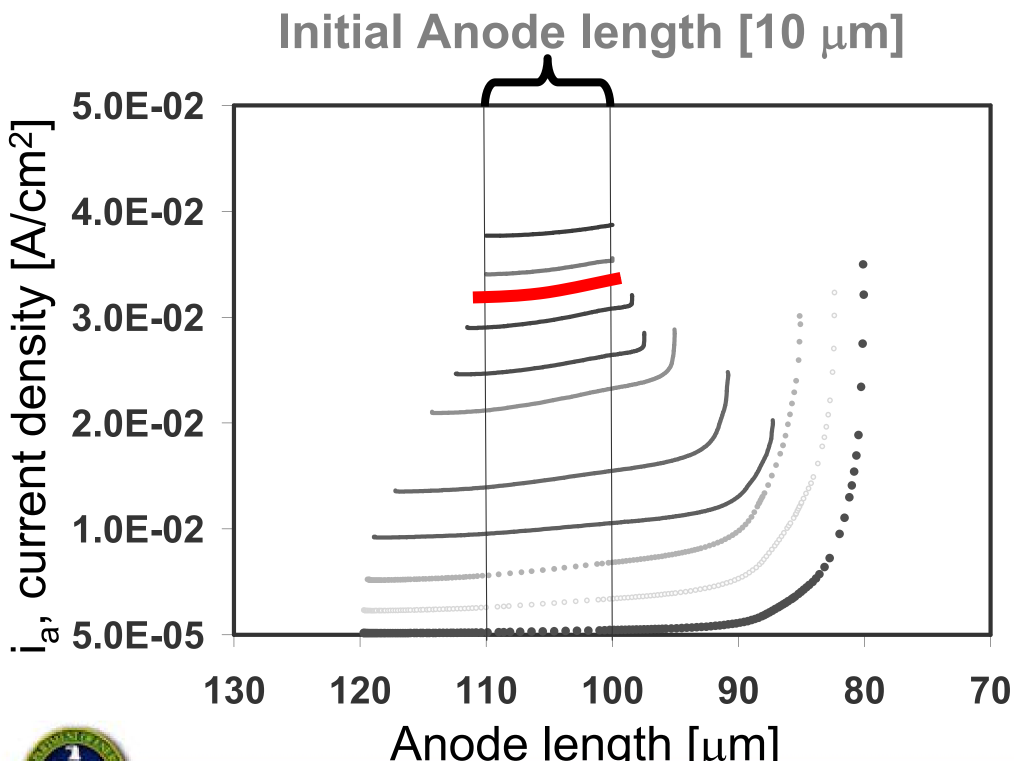




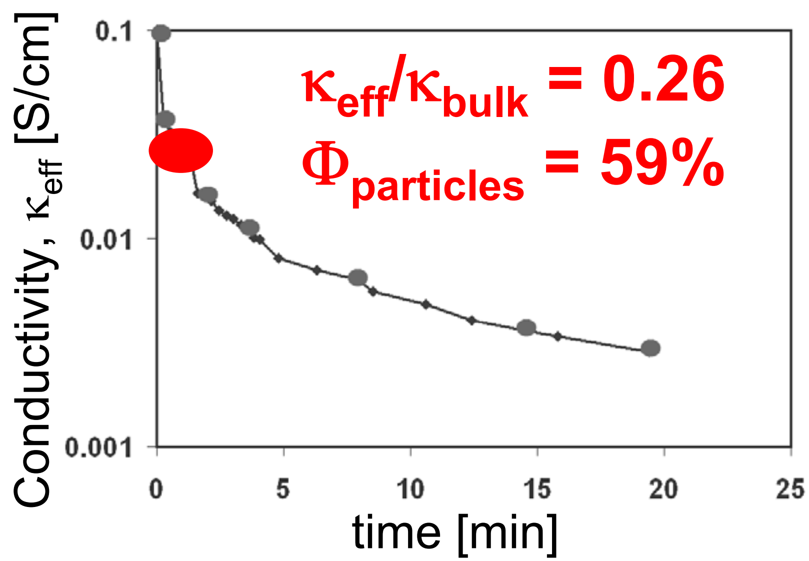


Simulation: Anode Profile Evolution





time = 1.1 min



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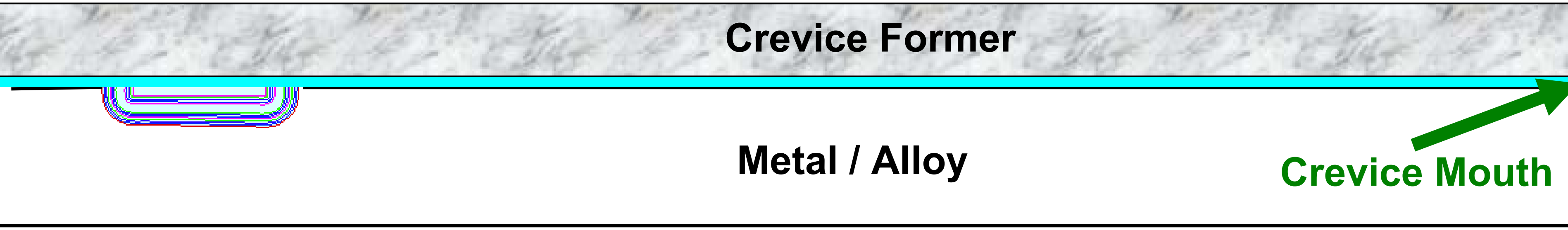

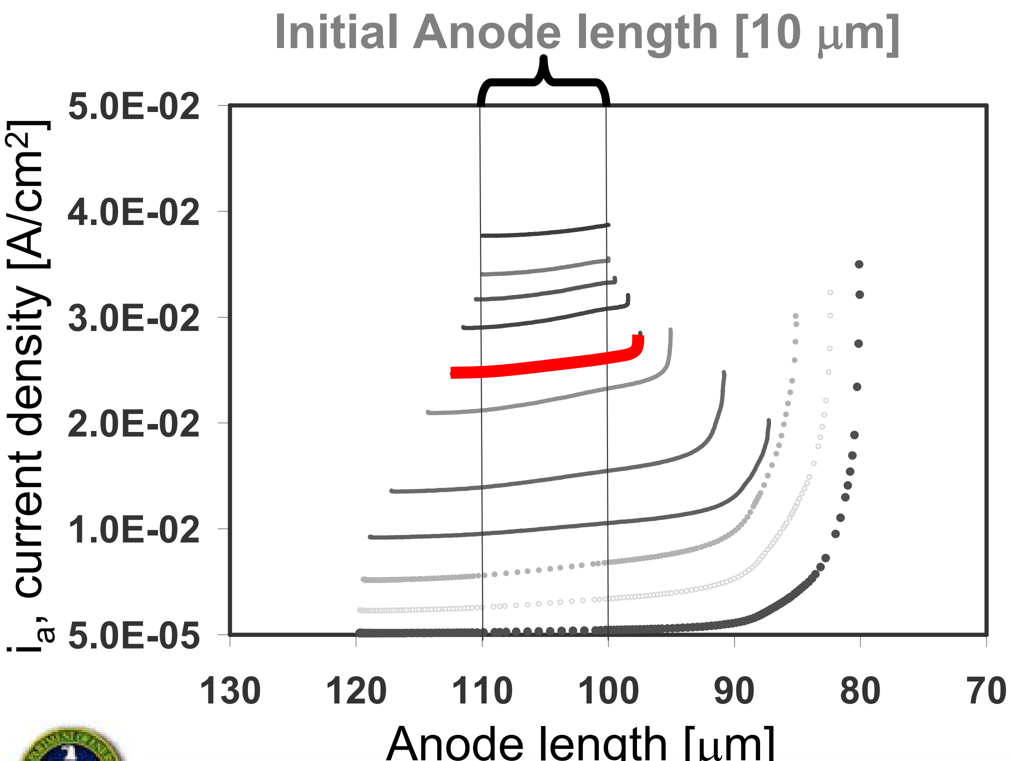

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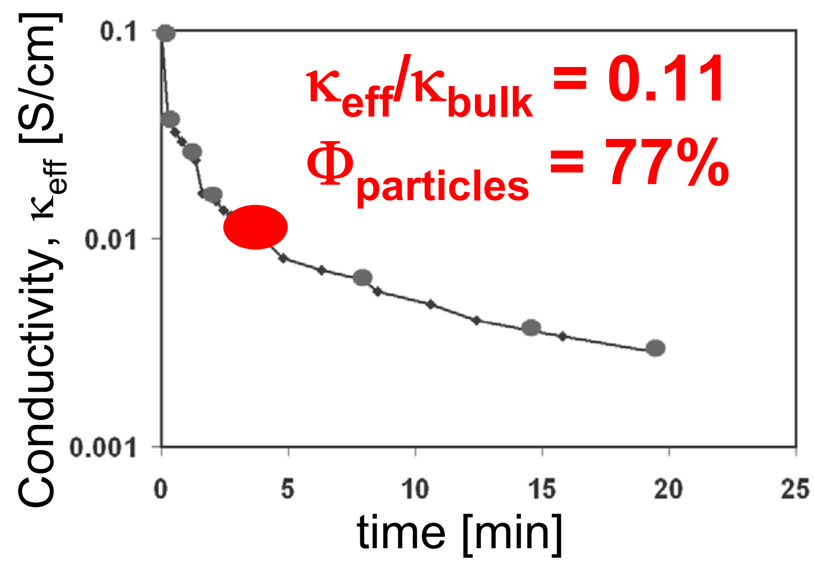
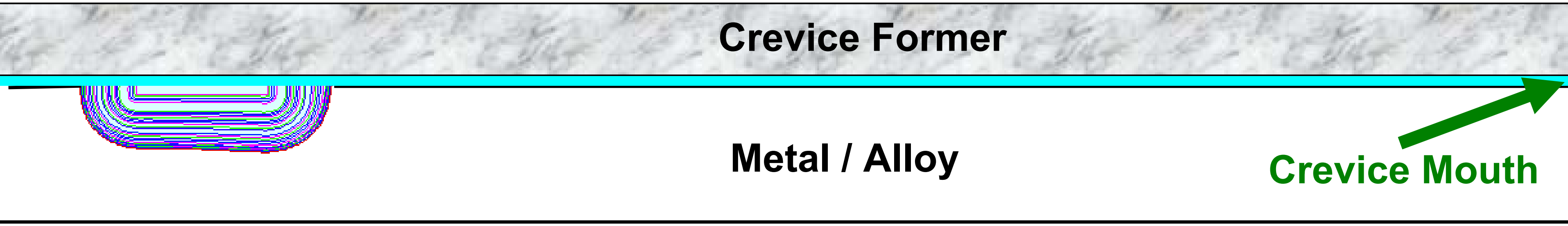
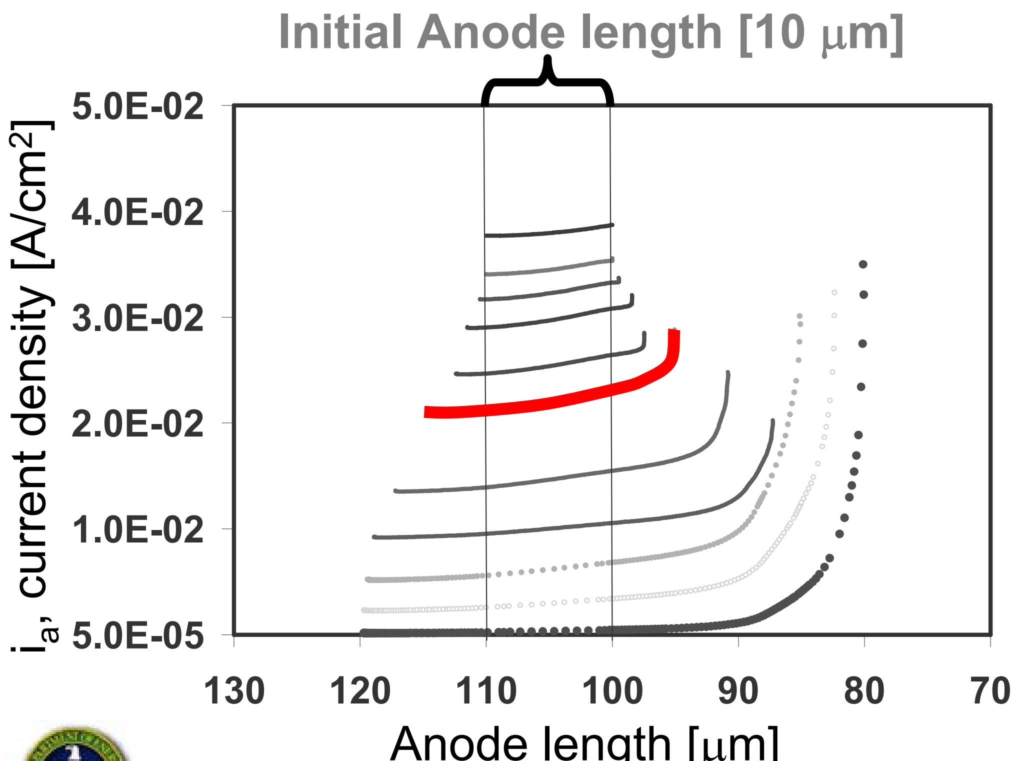
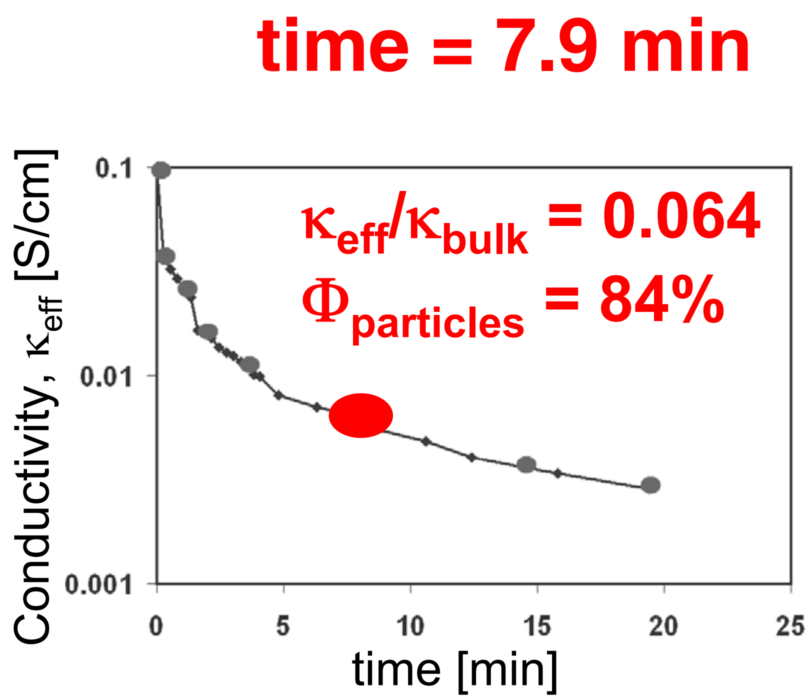


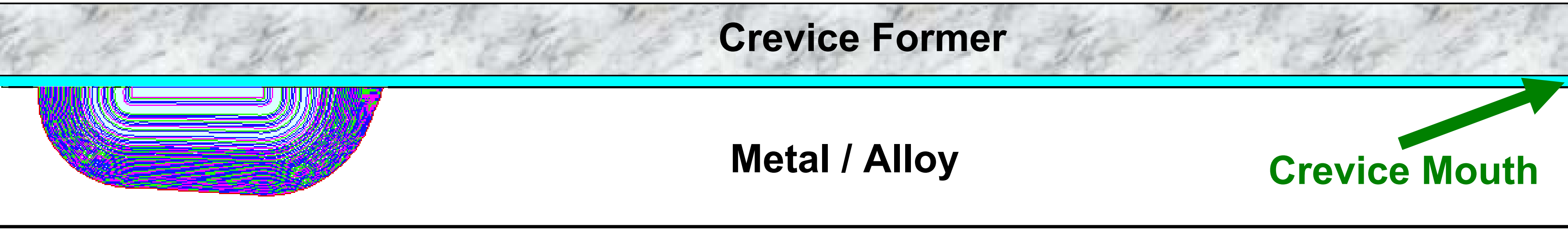
Simulation: Anode Profile Evolution

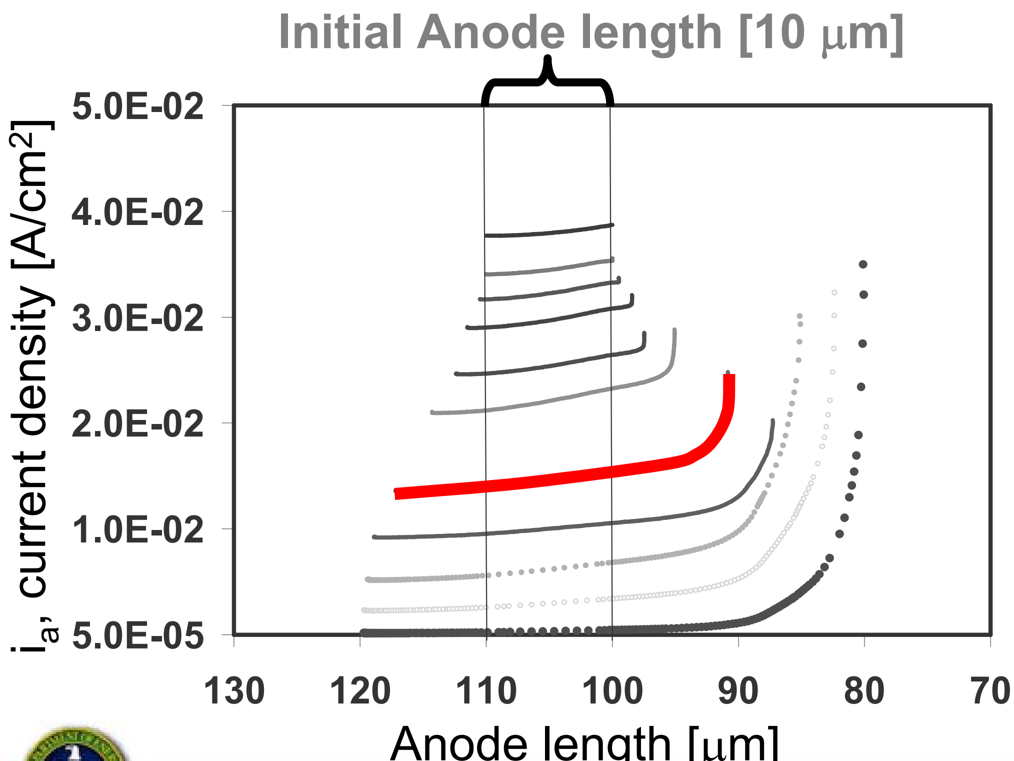


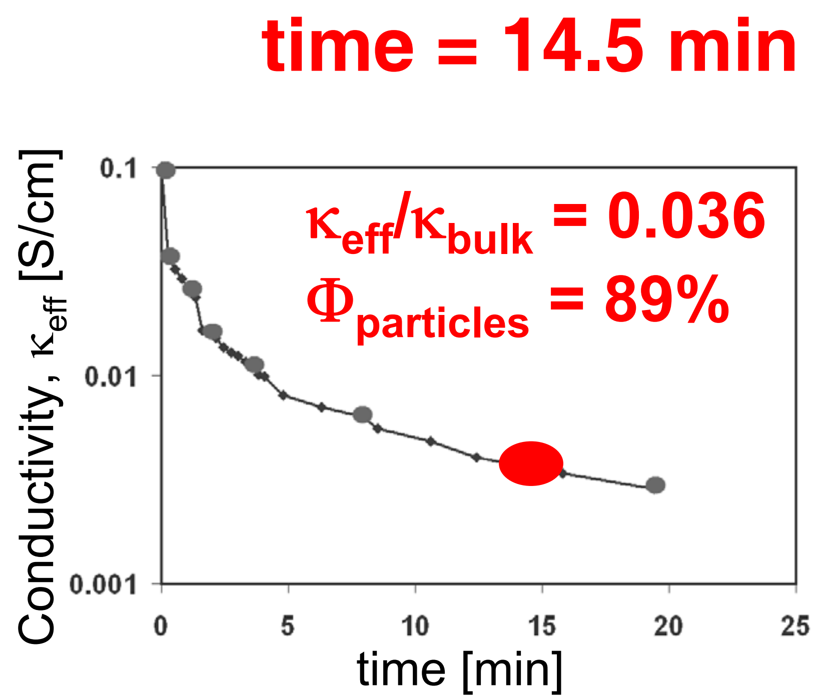




Simulation: Anode Profile Evolution







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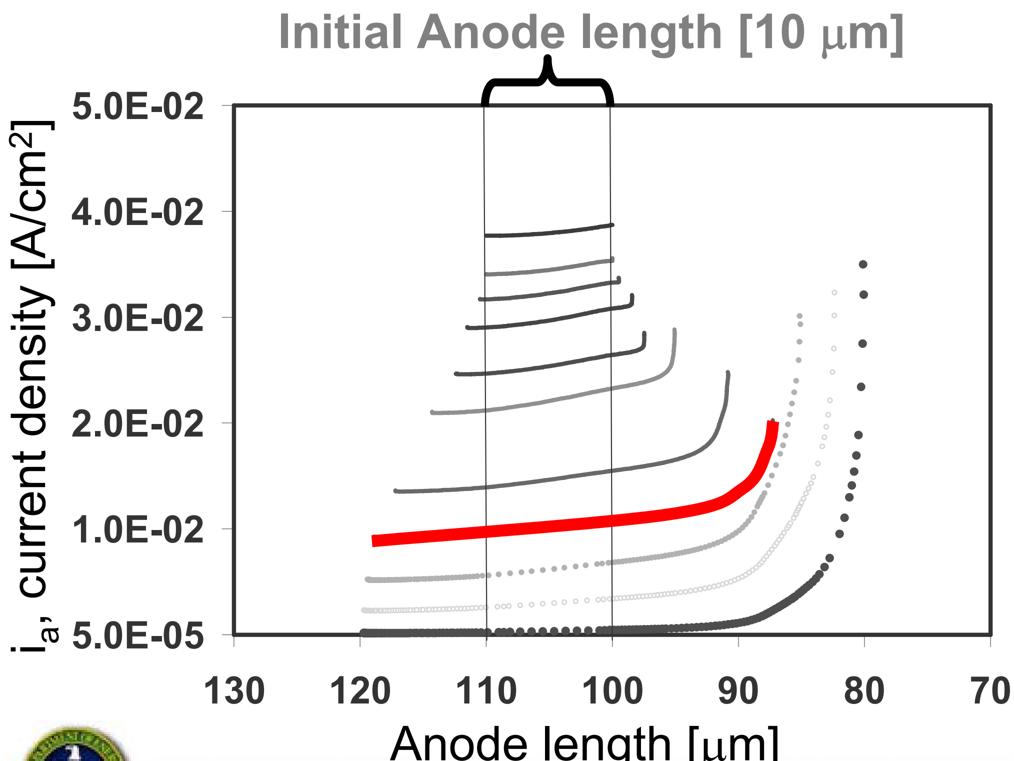

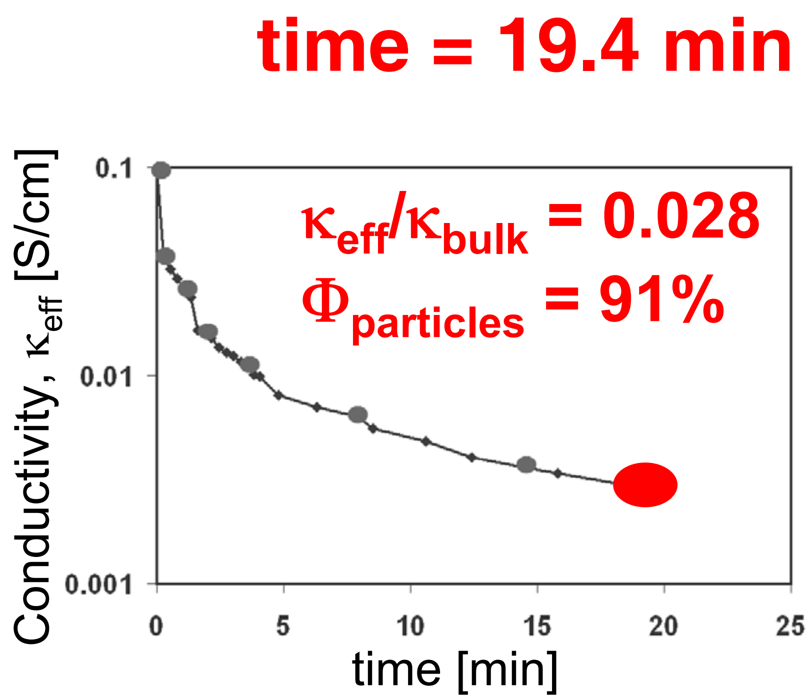

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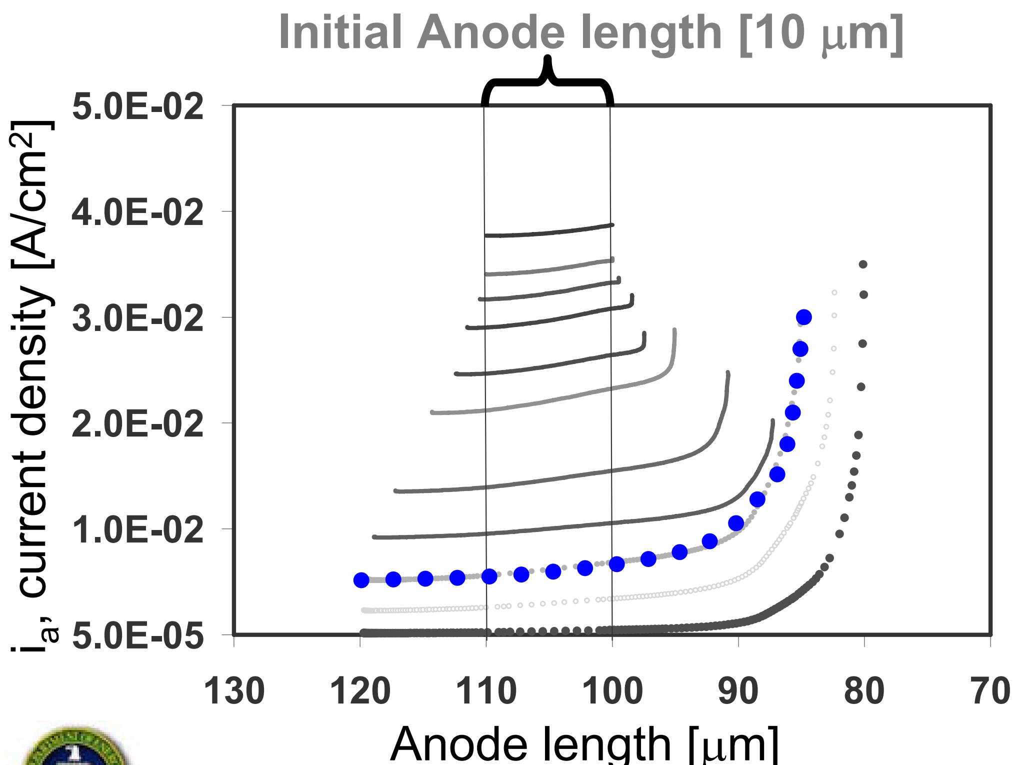

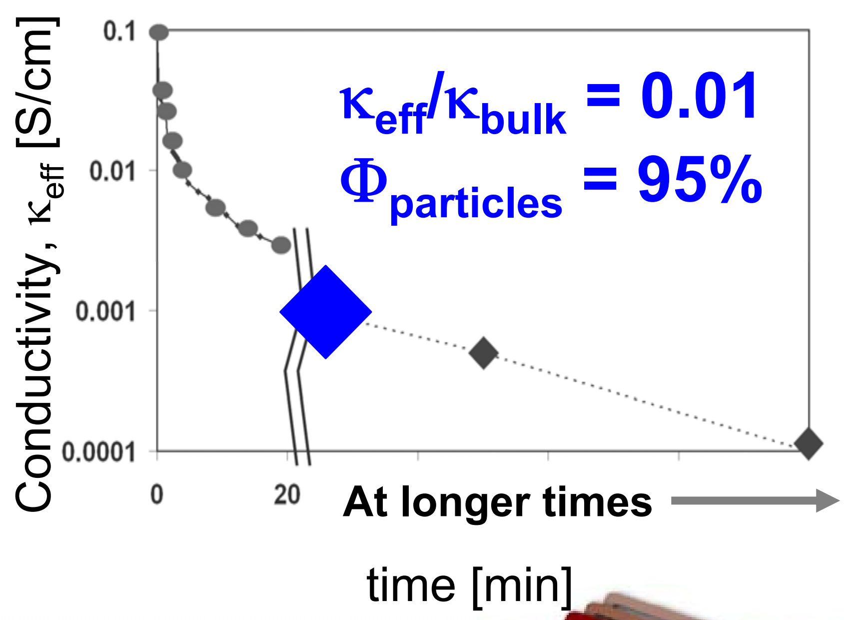

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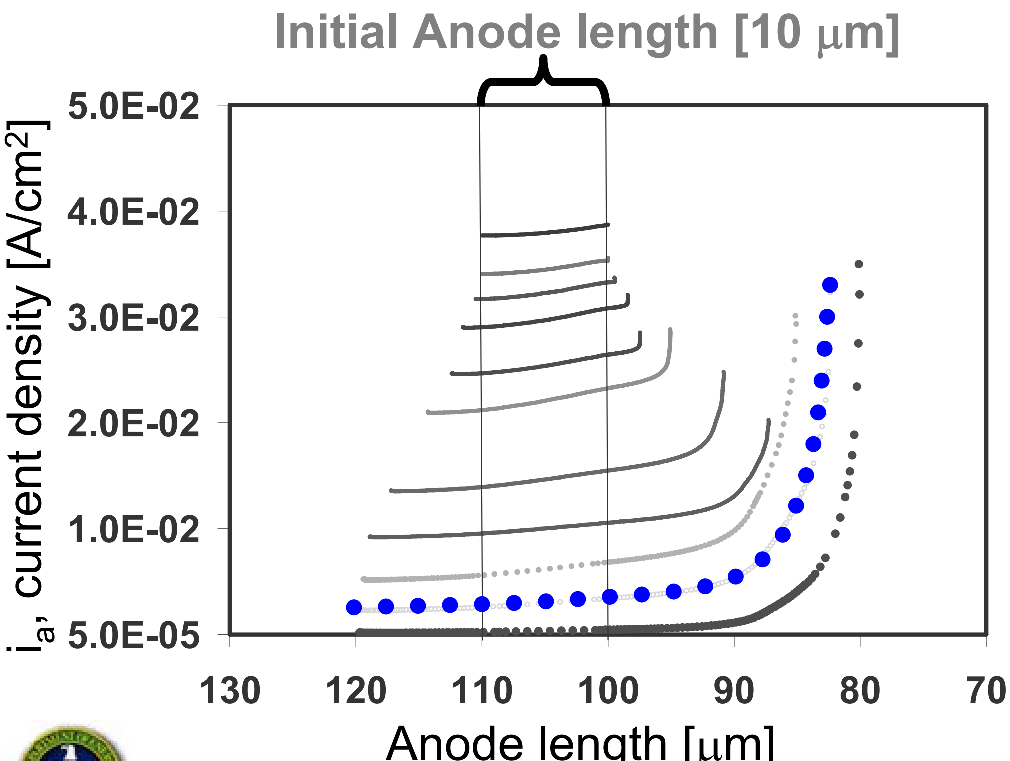
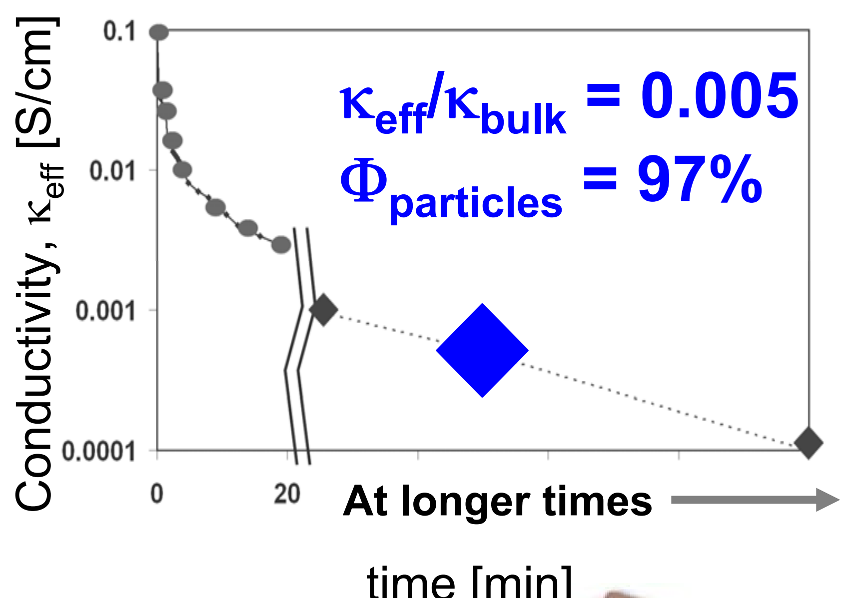
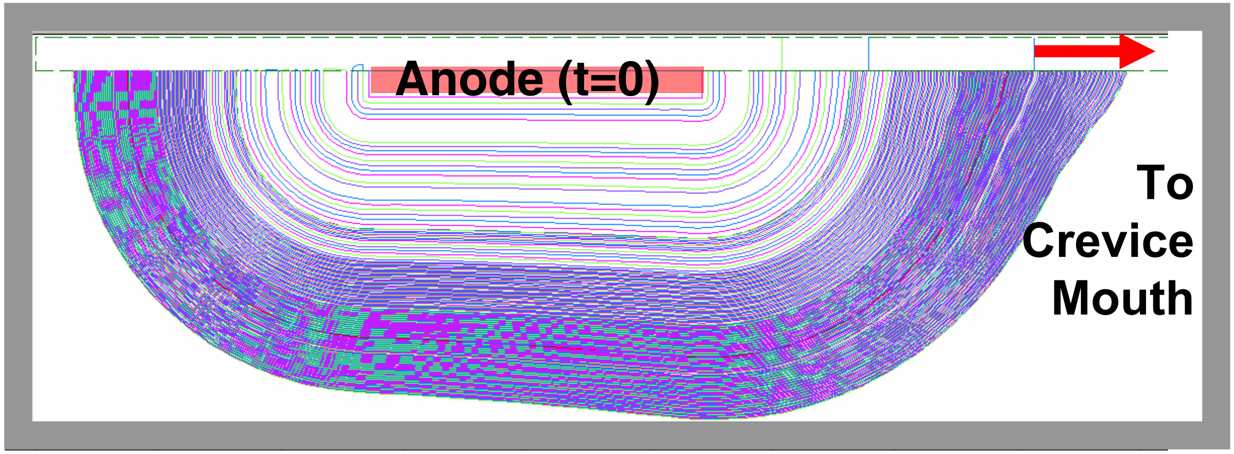


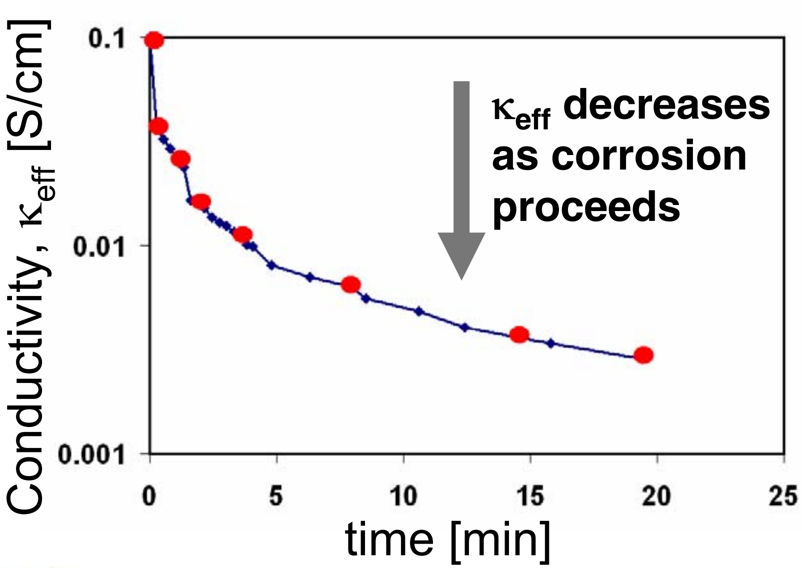


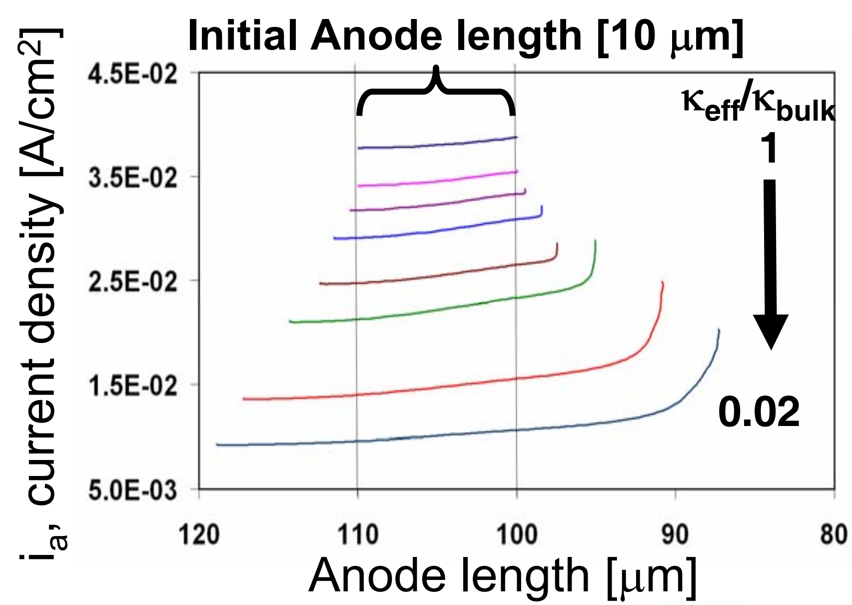
Effect of Increasing Corrosion Product Volume ($\downarrow\kappa_{eff}$)



Substantial decrease in κ_{eff} with increase in solid product volume causes:

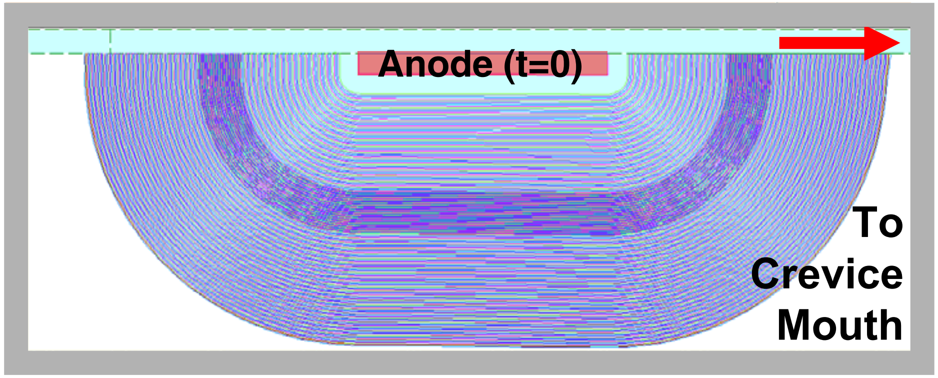
- A **tear-shaped** corroded region
- Corrosion propagates preferentially towards the crevice mouth



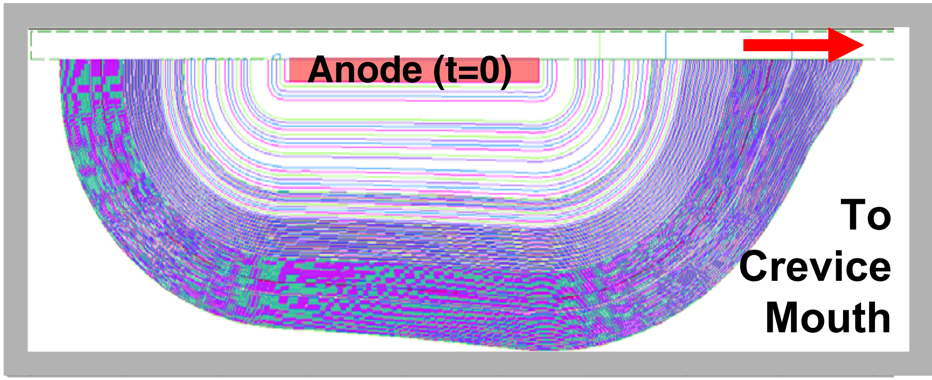


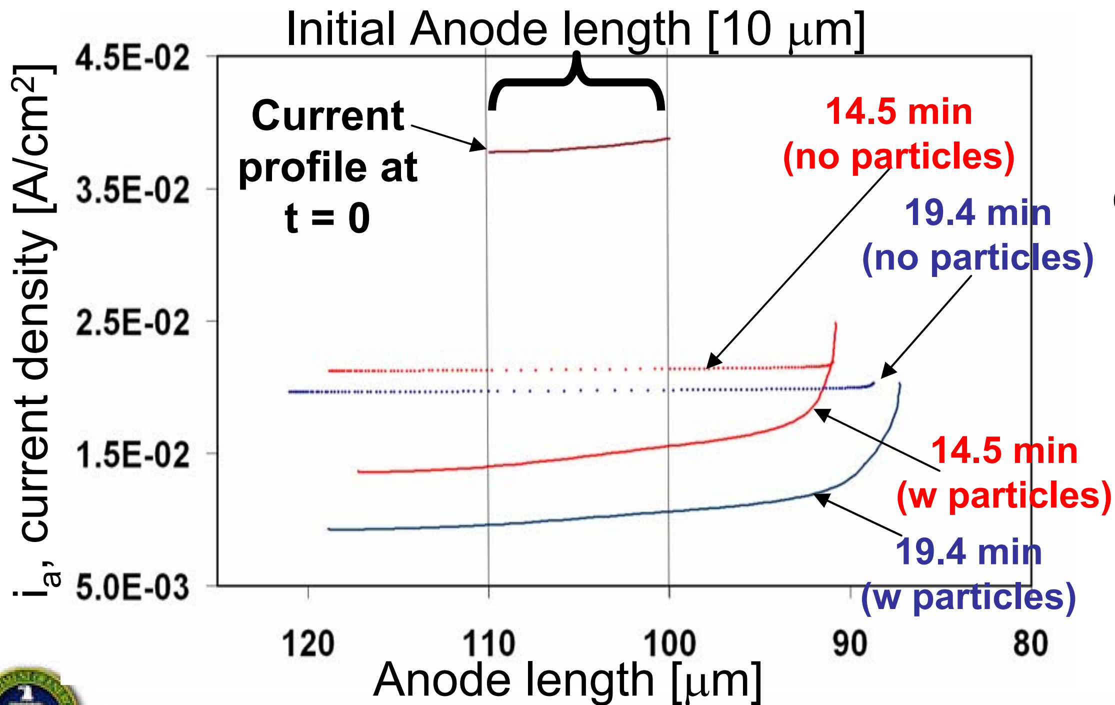
Comparison: With and Without Particulates

Without Particles: No Conductivity Variations
(κ = constant)



With Particles: Conductivity Varies
($\kappa_{eff} = f(\Phi_{particles})$)

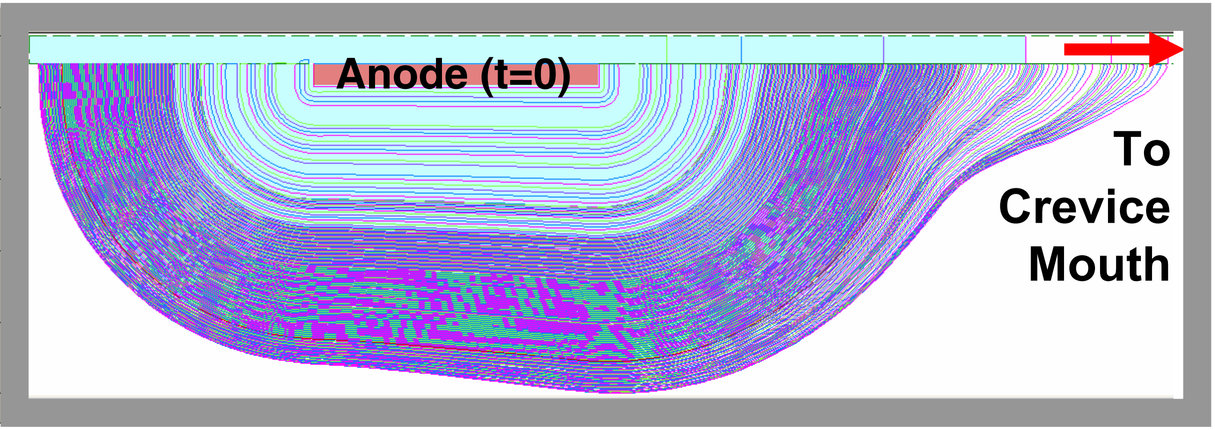




In absence of particles (no conductivity effects)

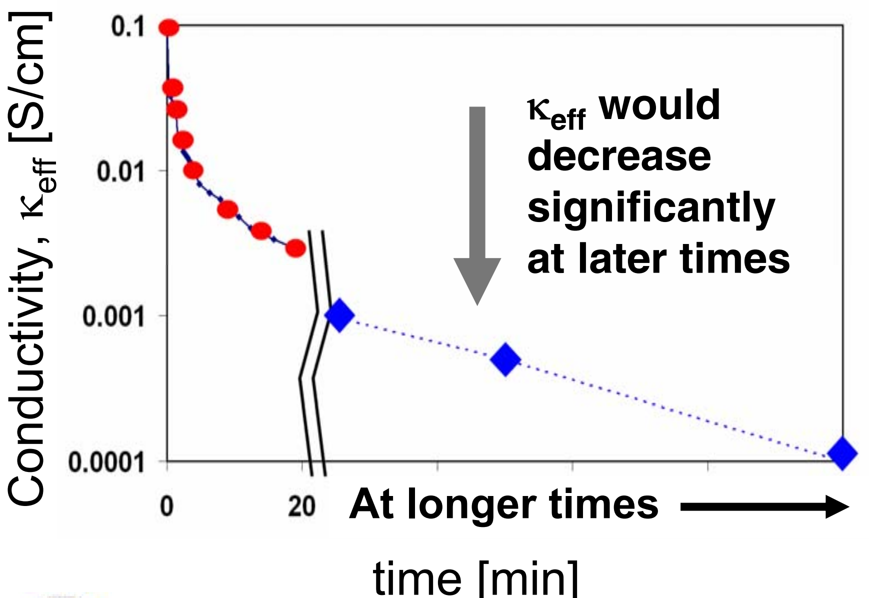
- **The corroding site propagates symmetrically**
- **Current density distribution is highly uniform, unlike the case with particulates**

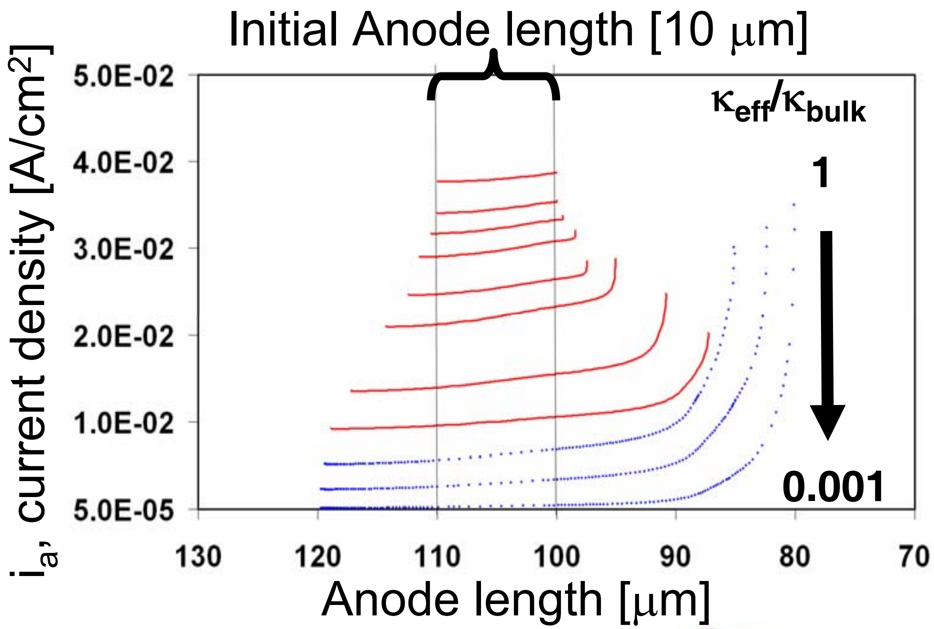
Effect of Corrosion Products on Crevice Damage Evolution



Applying lower values of κ_{eff} pertaining to longer time of corrosion:

- Substantial corrosion occurs towards the crevice mouth





Wagner No. Analysis of the Evolving Shape based on Conductivity Effects

$$R_a^* = \left|\frac{\partial \eta_a}{\partial i}\right| = \frac{RT}{\alpha F|i|} \quad (Tafel)$$

Activation Resistance

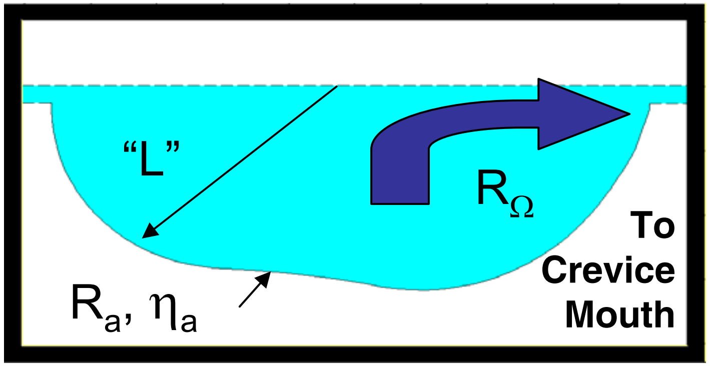
$$R_\Omega^* = \left|\frac{\partial \eta_\Omega}{\partial i}\right| = \frac{L}{\kappa}$$

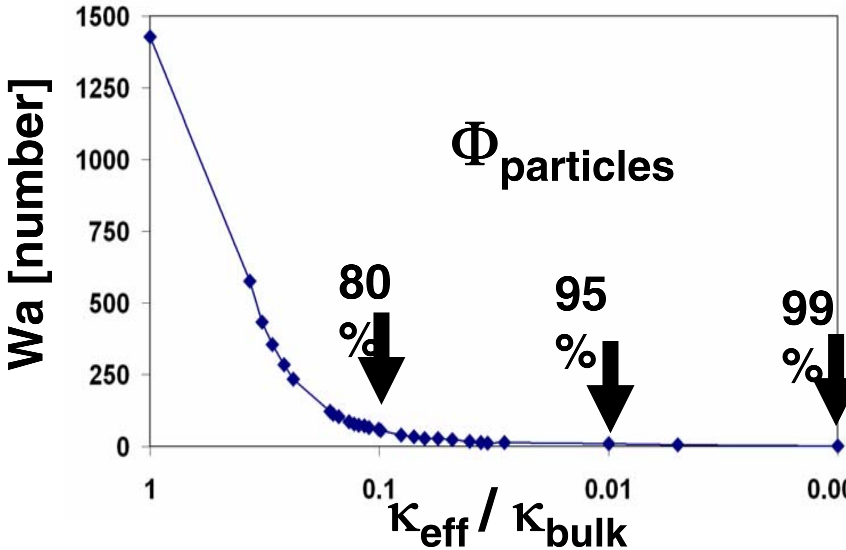
Ohmic Resistance

$$Wa = \frac{R_a^*}{R_\Omega^*}$$

(Ohmic & Activation)

- Wa > 1 → R_a dominant → symmetrical propagation
- Wa < 1 → R_Ω dominant → tear-shape, towards Crevice Mouth



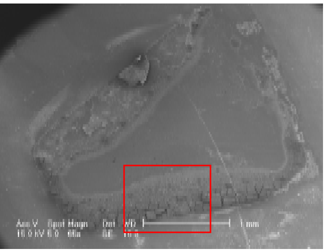


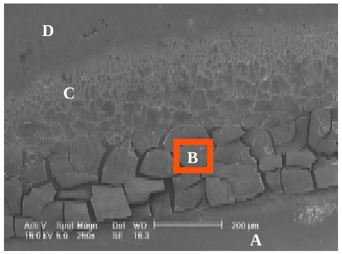
As corrosion proceeds:

- Wagner No. decreases with κ_{eff} due to more corrosion product formation
- Shift from symmetrical to non- symmetrical propagation of corroding site towards crevice mouth

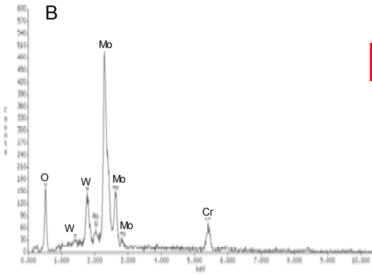
Evidence for Presence of Solid Oxides

Preliminary Analysis: EDS of C-22 corrosion product





A050 2 o'clock



	Cr (at%)	Mo (at%)	W (at%)	Fe (at%)	O (at%)	Ni (at%)
A	19.9	7.7	1.3	4.2	22.7	44.4
B	7.9	20.8	3.3	0	67.2	0.8
C	21.8	7.4	0.8	5	12.7	52.4
D	23.3	7.8	1.0	5.2	8. 5	54.3
C- 22	26.1	8.3	1	3.3	n/a	58.7

4M NaCl, 100°C, anodic polarization @ E= -0.15 volts vs. SCE, wet specimens with test solution before assemblies tightened

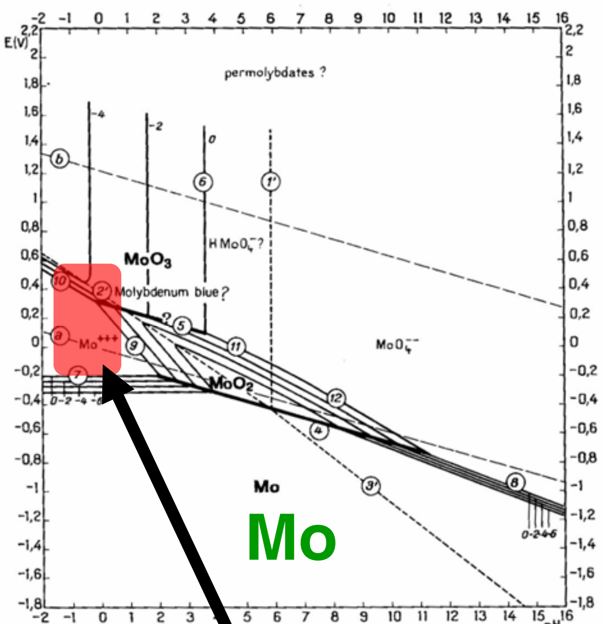


Fig. 1. Potential-pH equilibrium diagram for the system molybdenum-water, at 25°C.

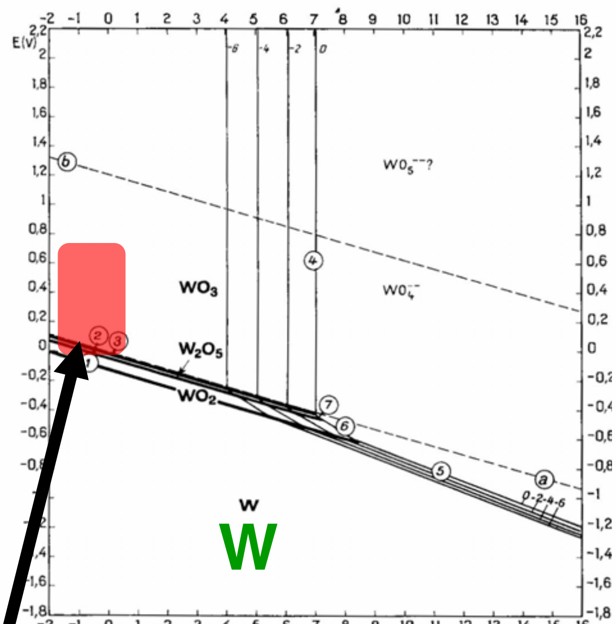


Fig. 1. Potential pH equilibrium diagram for the system tungsten-water, at 25°C.

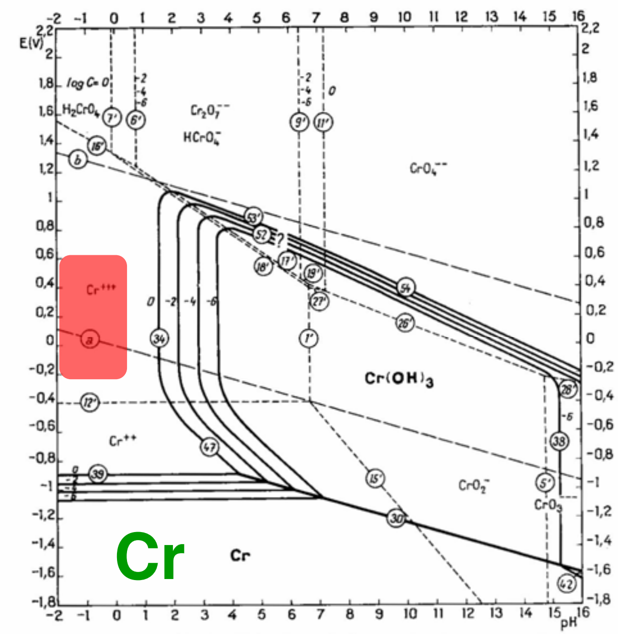


Fig. 2. Potential-pH equilibrium diagram for the system chromium-water, at 25°C.
In solutions not containing chloride.
[Figure established considering $Cr(OH)_3$.]

Mo & W have stable oxides under more acidic conditions

SUMMARY

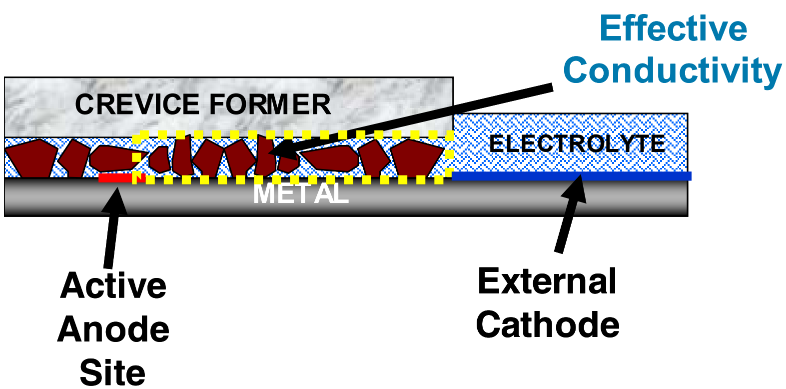
OHMIC (IR) effects on current & potential distributions were modeled.

1. Roughness elements accounted for in equivalent system →

   Constriction Factor (τ) Analysis

2. Particles under crevice former could be accounted for based on volume fraction of particles →

   Conductivity correction using Bruggeman's equation.



3. Solid corrosion products at corroding site decreases effective conductivity →

   Conductivity effects shown to propagate corroding site towards crevice mouth