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Center for Electrochemical Science and Engineering

University of Virginia

Considerations of the Role of the Cathodic Region in Localized Corrosion

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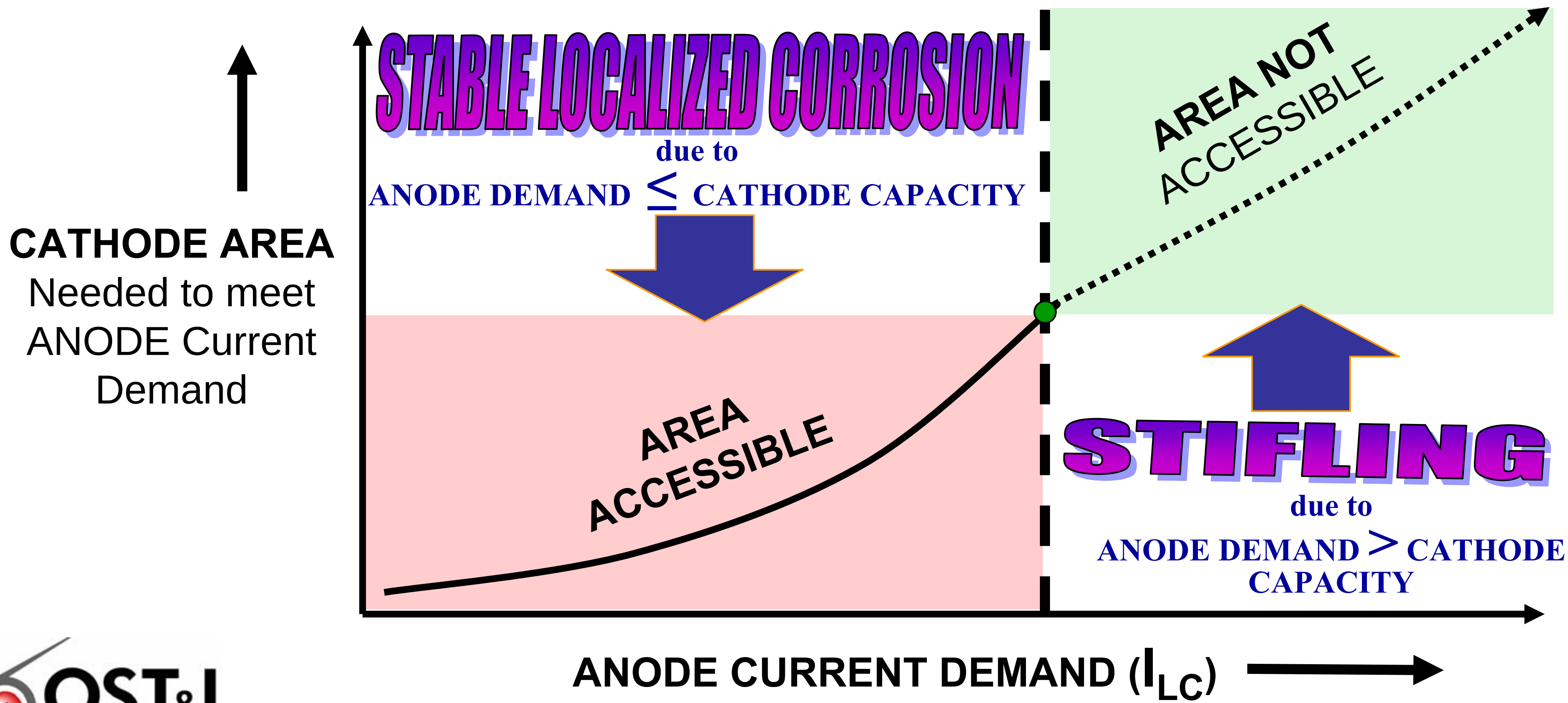
Corrosion of Waste Package Surfaces Will Occur Under Thin Film Electrolyte Conditions

- In the proposed Yucca Mountain Repository waste packages will never be fully immersed in solution
- Moisture and particulates may be present on surfaces
- Corrosion behavior in moist particulate can differ from full immersion
  - Limited size of corrosion site
  - Limited cathodic area to support localized corrosion
  - Limited cathodic kinetics could stifle corrosion

Objective

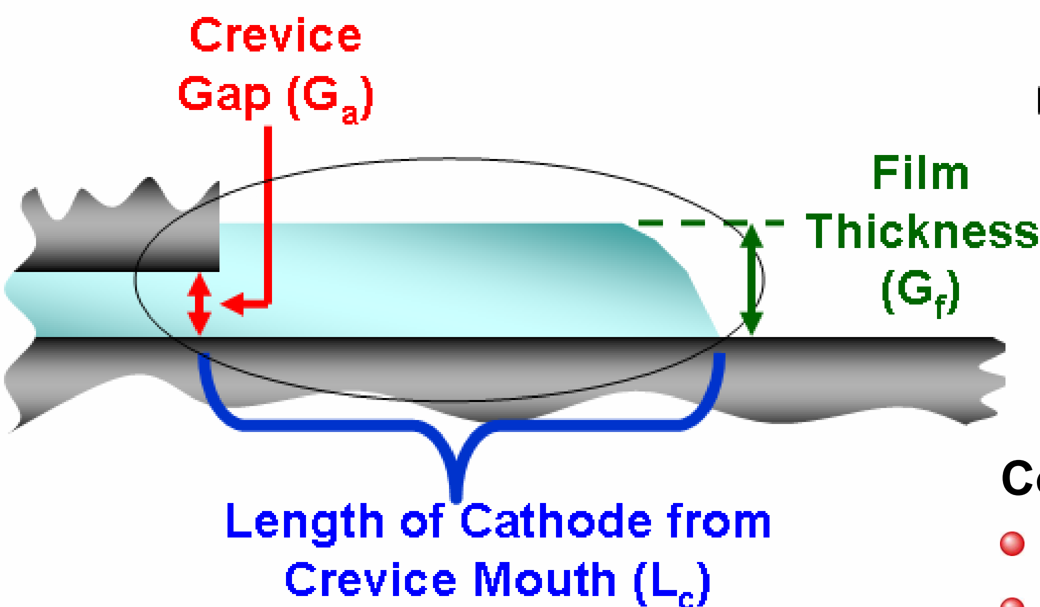
- Quantification of the total cathodic current that a wetted surface of limited area could deliver under a given set of conditions provides a scientific basis for analyses of both the maximum rate and the stability of localized corrosion.



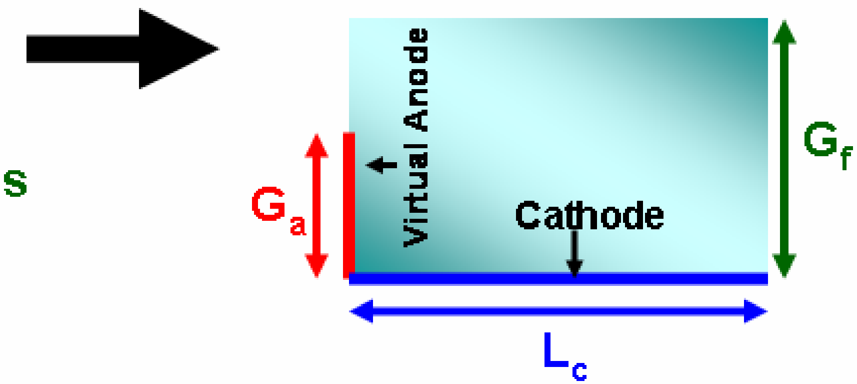
Computational Studies of Cathode Capacity

Cathodic region is <u>decoupled</u> from the localized corrosion region

<u>SCHEMATIC DIAGRAM OF A CREVICE</u>



<u>DECOUPLED CATHODE MODEL</u>



Consider the effects of:

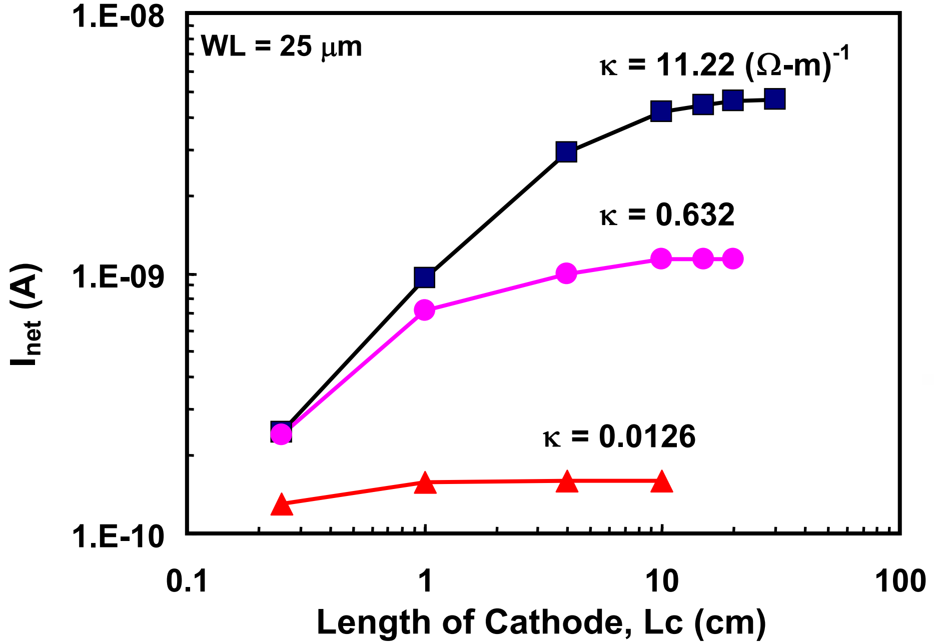
- Size of Wetted Area
- Water Layer Thickness
- Electrolyte Conductivity
- Particulates
- Temperature

Cathode Capacity

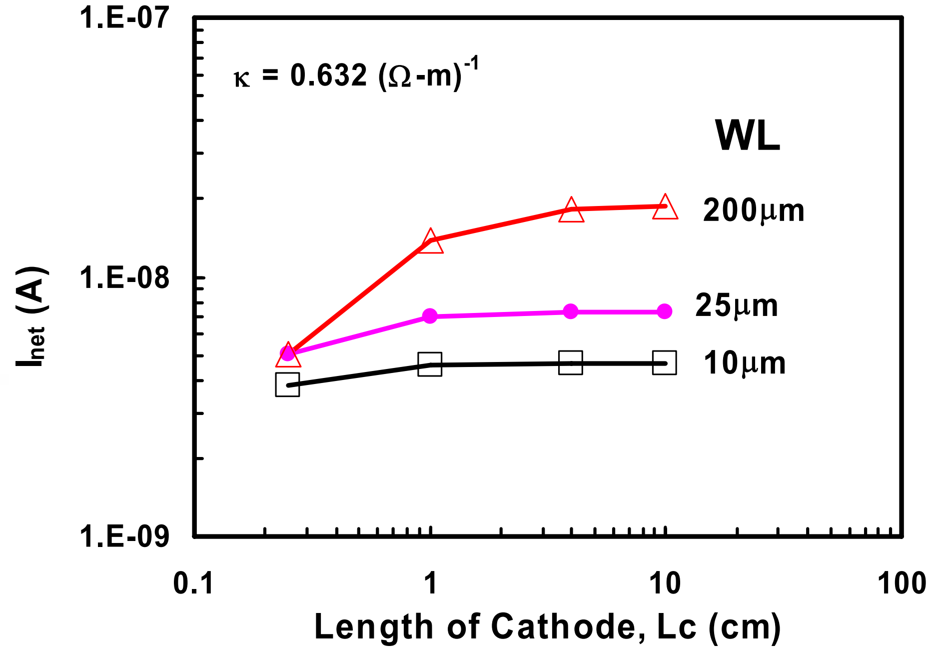
- Parameters analyzed using decoupled cathode model
  - Cathode Size (L_C)
  - Electrolyte Layer Thickness (WL)
  - Conductivity of Electrolyte Layer (κ)
  - Temperature
  - Electrolyte pH
  - Effect of Particulate in Electrolyte Layer
  - Cathodic Kinetics Mass Transfer Limitations

Total Current from Cathode Saturates with Increasing Size

Effect of Electrolyte Layer Conductivity (κ):



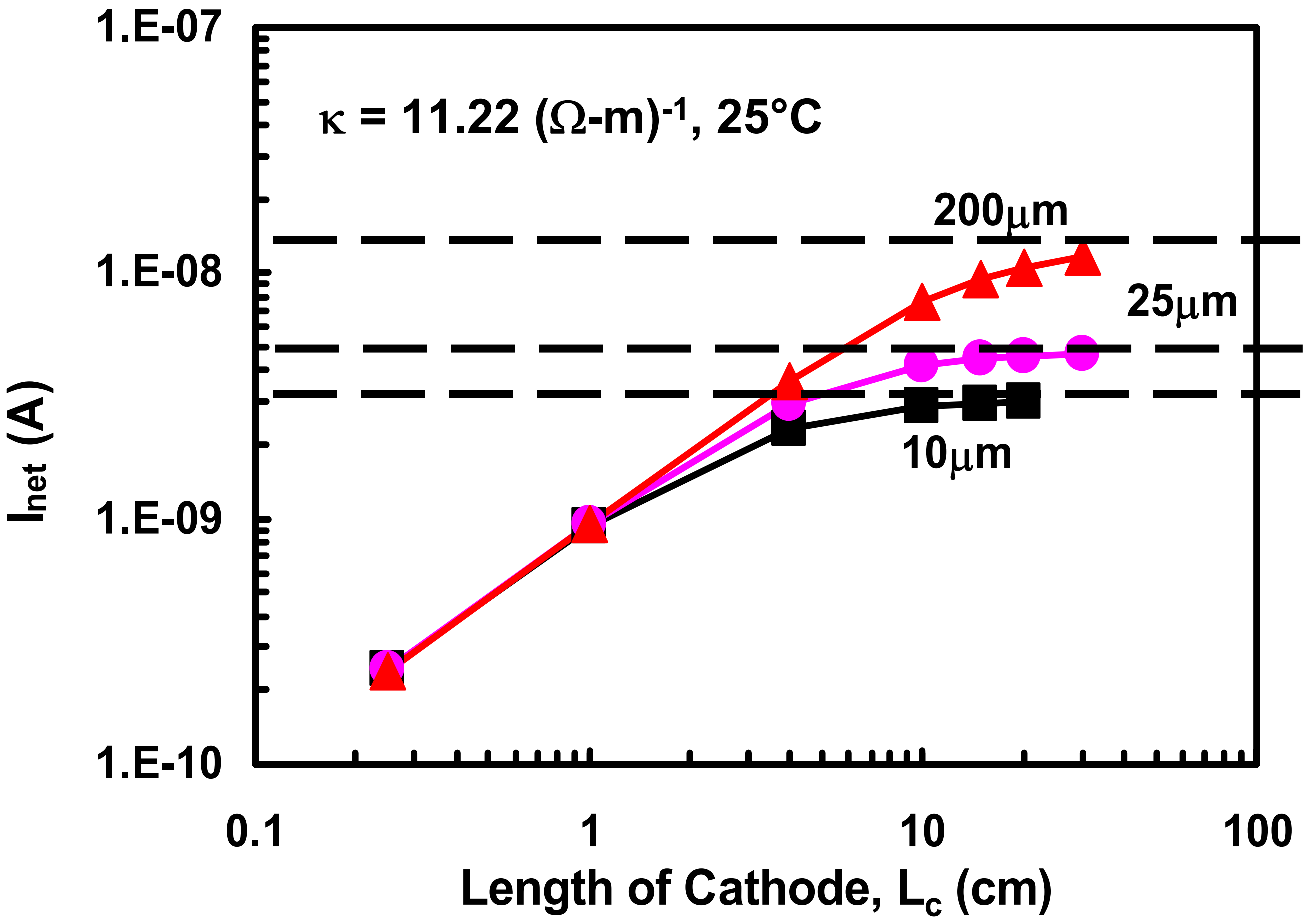
Effect of Electrolyte Thickness (WL):



As the electrolyte layer conductivity increases, Cathode Capacity (I_{net}) increases less than linearly and saturates for finite cathode size

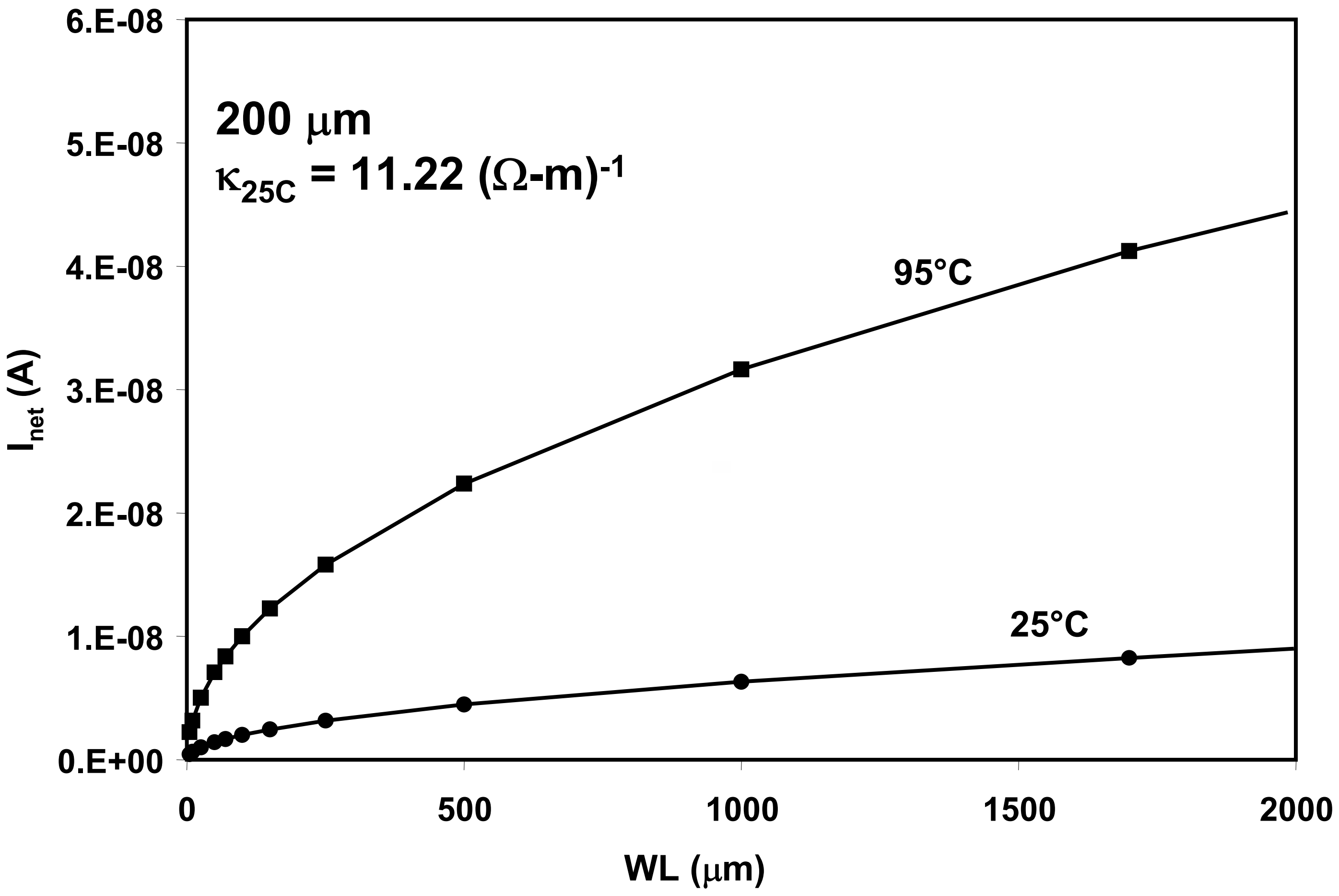
Increase in the electrolyte film thickness increases Cathode Capacity (I_{net}) more significantly for larger cathodes

Effect of Cathode Length on its Current Capacity



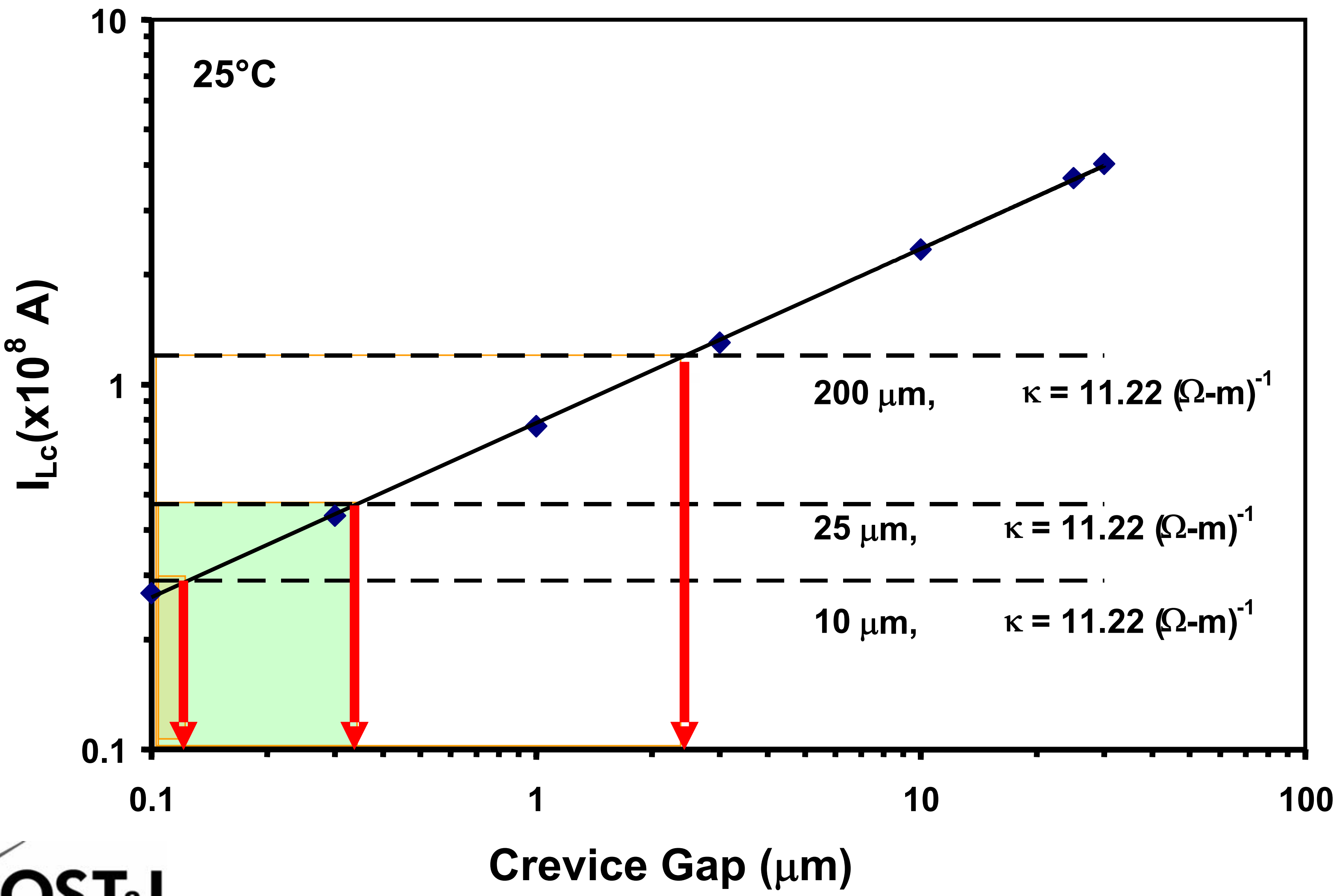
Cathode current capacity saturates for large but finite cathode size (high L_c)

Effect of Temperature on Cathode Capacity



Temperature increases current capacity, but saturation still occurs

Crevice Corrosion can be Sustained when Anode Demand less than or equal to Cathode Capacity



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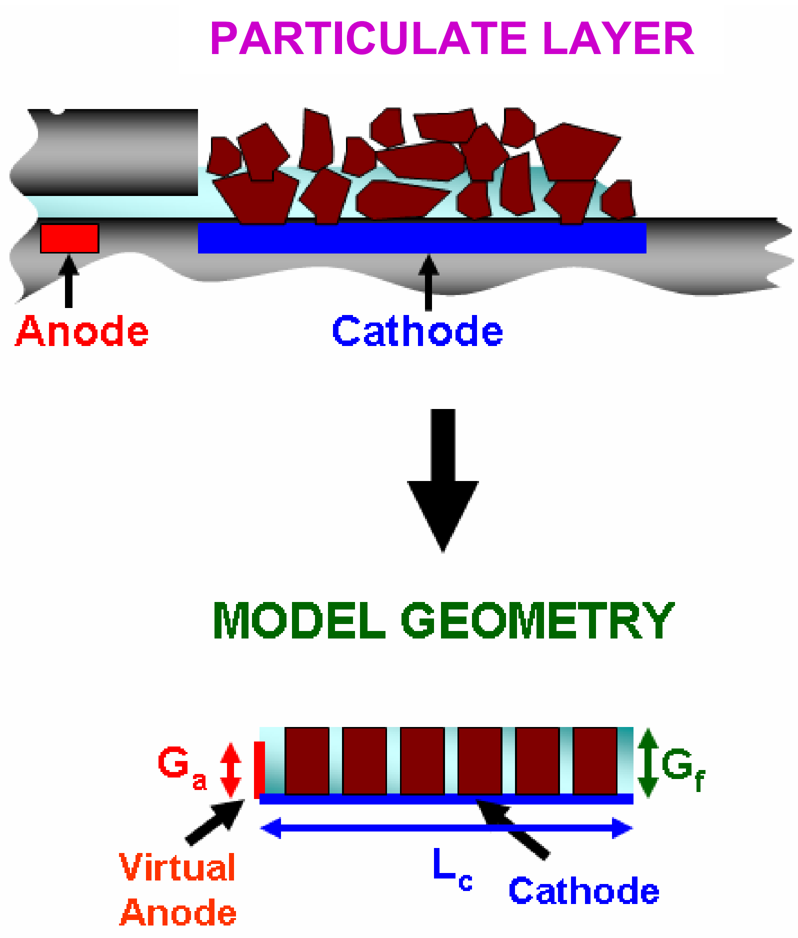
Effects of Particulates

PARAMETERS (of particulate layer)

- Particle size
- Particle arrangement
- Particle shape
- Electrode area coverage ($A_{exposed}/A_{total}$)
- Volume fraction blockage ($V_{solution}/V_{total}$)



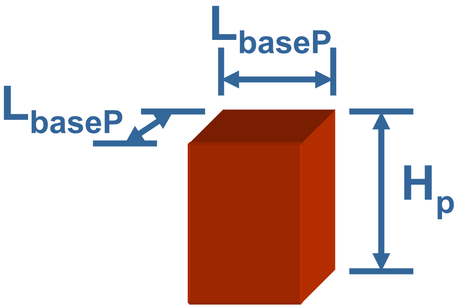
MODELING CONSTRAINTS

- Uniform particle distribution
- Steady state
- Monolayer of particles ($height_{particle}$ = $thickness_{electrolyte}$)
- No chemical changes

Methodology for Effects of Particulate

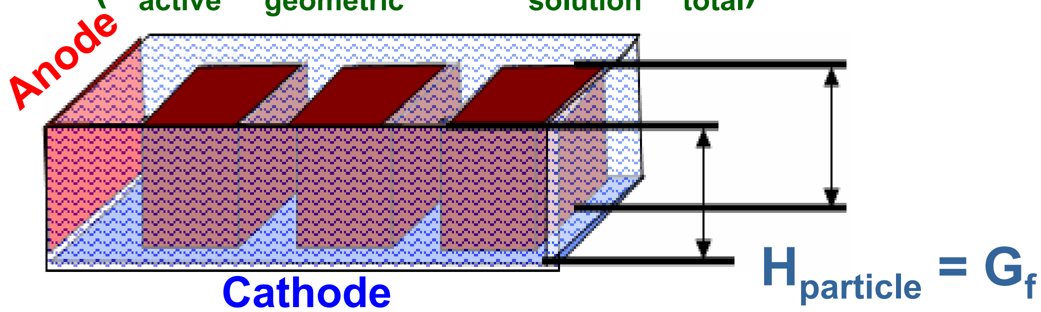
3-D Simulations based on particle shape, size & distribution

1. Select Particle (shape & size)

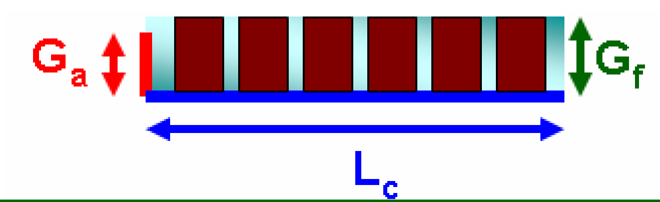


2. Fix Distribution and Arrangement

($A_{active}/A_{geometric}$ and $V_{solution}/V_{total}$)



3. Run Simulations (3-D in FEMLAB® and 2-D in CELL-DESIGN®) exploring parameters



Methodology: Bulk Solution Conductivity

Compare with homogeneous systems using simple analytical expressions accounting for particle effects

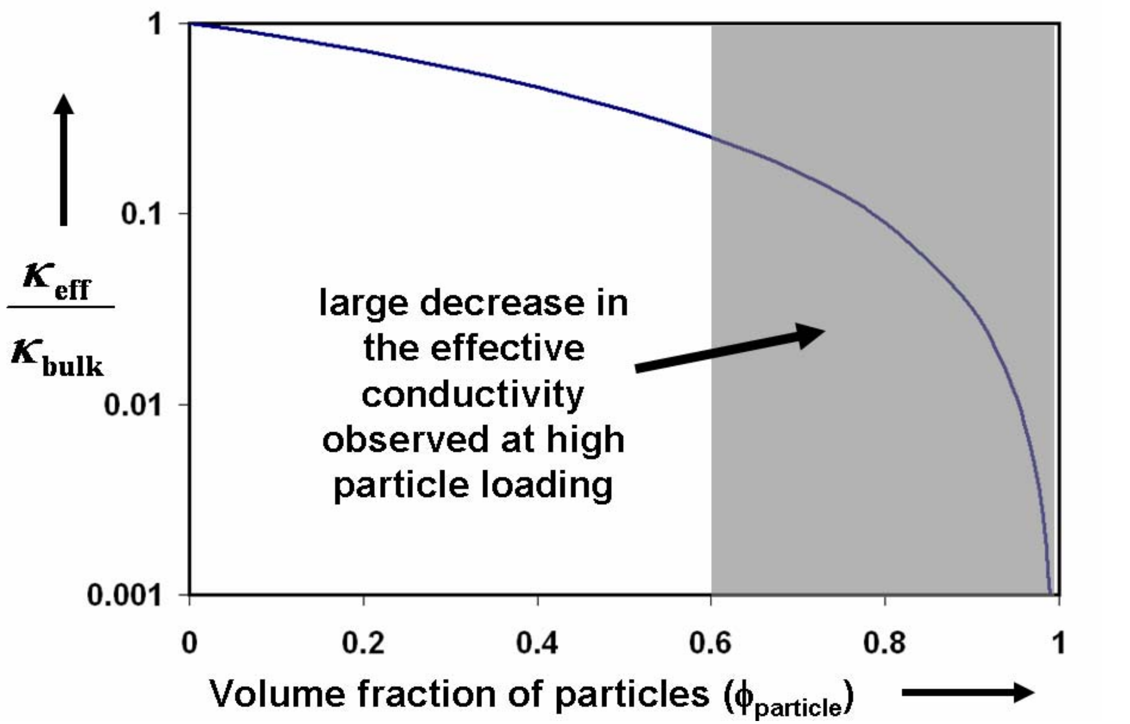
1. Particle effects on <u>bulk solution conductivity</u>

Bruggeman's Equation

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

where

$$\phi_{sand} = \frac{\text{Vol(sand)}}{\text{Vol(sand + solution)}}$$



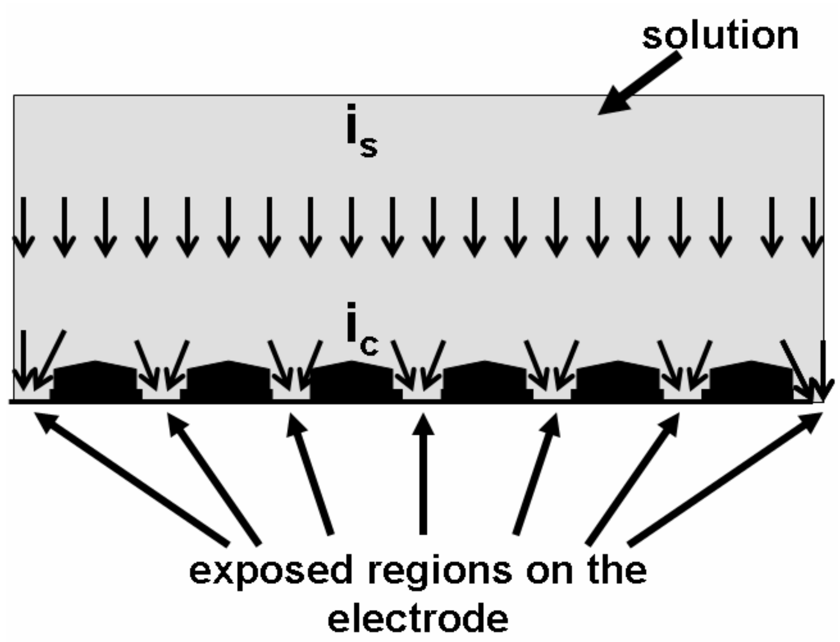
Methodology: Surface Blockage

2. Cathode surface blockage by particles

$$\frac{A_{exposed}}{A_{total}} = \frac{\text{Area(total) - Area(covered)}}{\text{Area(total)}}$$

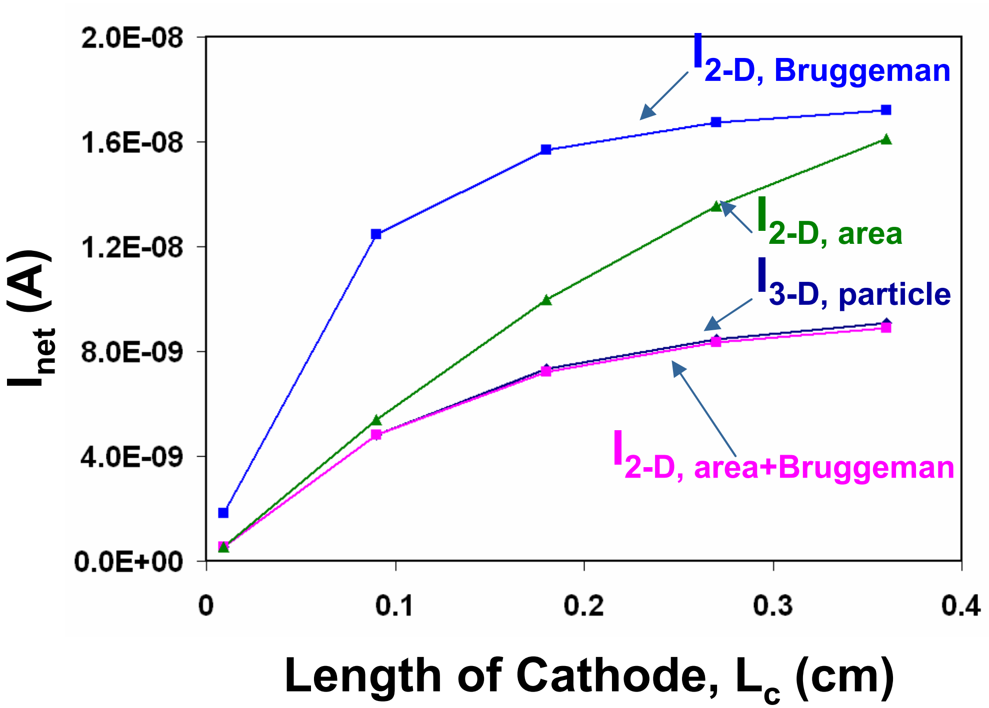
Equivalent exchange current density:

$$i_0' = i_0 \times \frac{A_{exposed}}{A_{total}}$$



3. Combination of the two effects (Bruggeman’s + area correction)

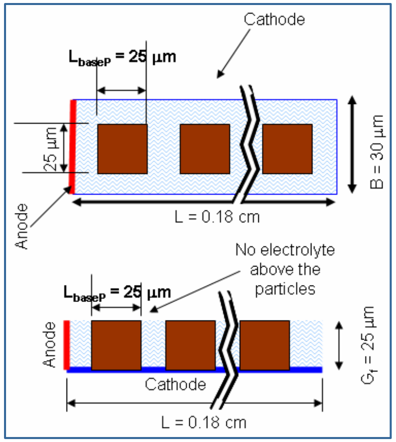
Comparison of 3-D Simulations to 2-D Volume and Area Corrections



$$\frac{A_{exposed}}{A_{total}} = 0.306$$

$$\frac{V_{solution}}{V_{total}} = 0.306$$

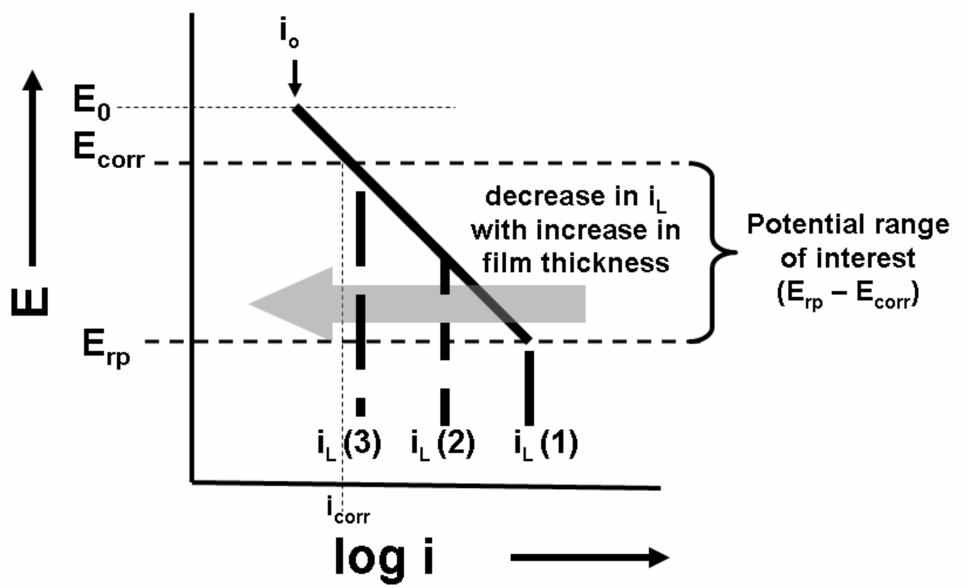
$\kappa = 12.1\ (\Omega\text{-m})^{-1}$,
$i_o = 10^{-9}\ A/cm^2$,
$\beta_c = 0.1$ V/dec,
$E_{rp} = -0.31\ V_{NHE}$,
$E_{o,c} = 0.19\ V_{NHE}$,
$i_L = 2.2e\text{-}4\ A/cm^2$

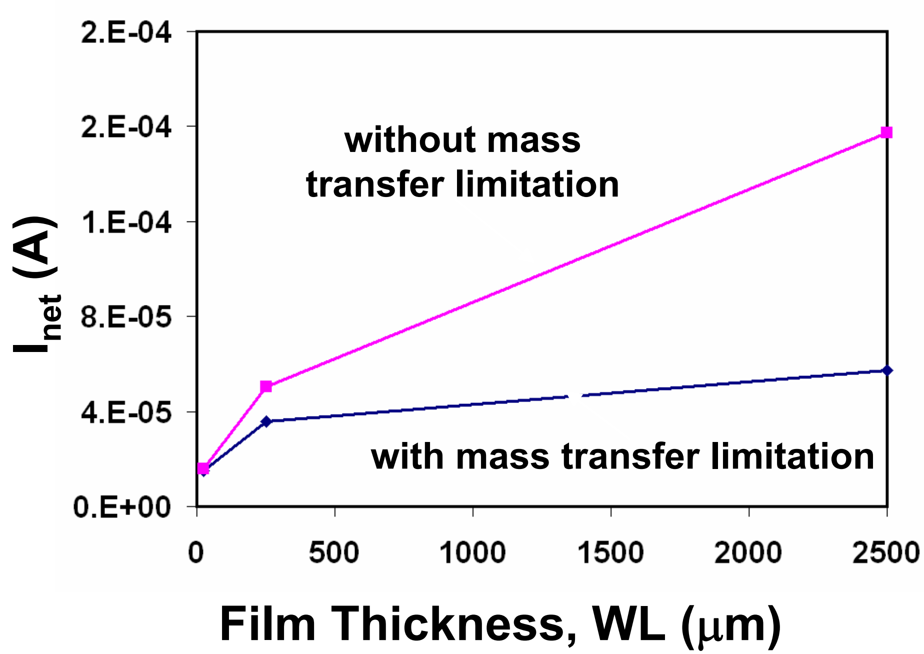


- Volume (Bruggeman) and surface coverage (area) corrections in 2-D simulations produce accurate 3-D results
- Independently area or volume correction are insufficient
- Similar results obtained without mass transfer limitations

Mass Transfer Limitation

Limiting Current: $i_L = \dfrac{nFD_{O_2} C^{sat.}{}_{O_2}}{WL}$ **; i_L decreases with increase in film thickness**



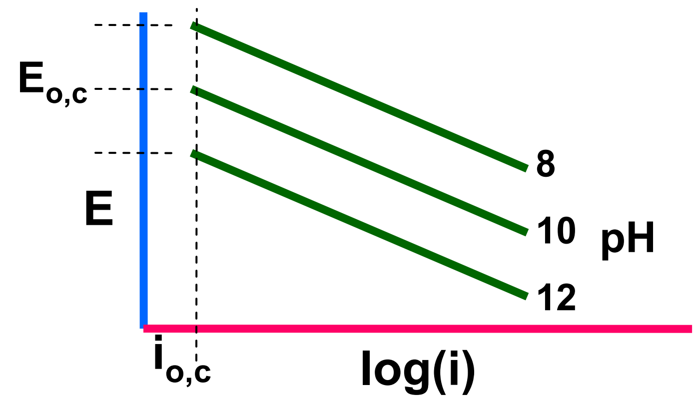


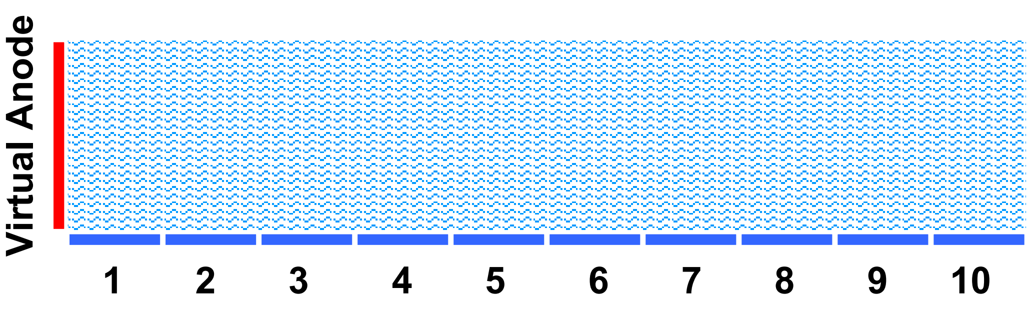
- **Cathode capacity for thicker electrolyte films is lower**
- **For thin electrolyte film the transport limitations are insignificant and the process is kinetically controlled**

pH Effect due to Cathodic Reaction Chemistry

- Cathode Reaction (oxygen reduction):
  $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
- Generation of OH- will increase the local pH in the thin electrolyte film
- Modified kinetics due to pH increase:
  $E_{o,c}pH = E_{o,c} - 0.059*pH$

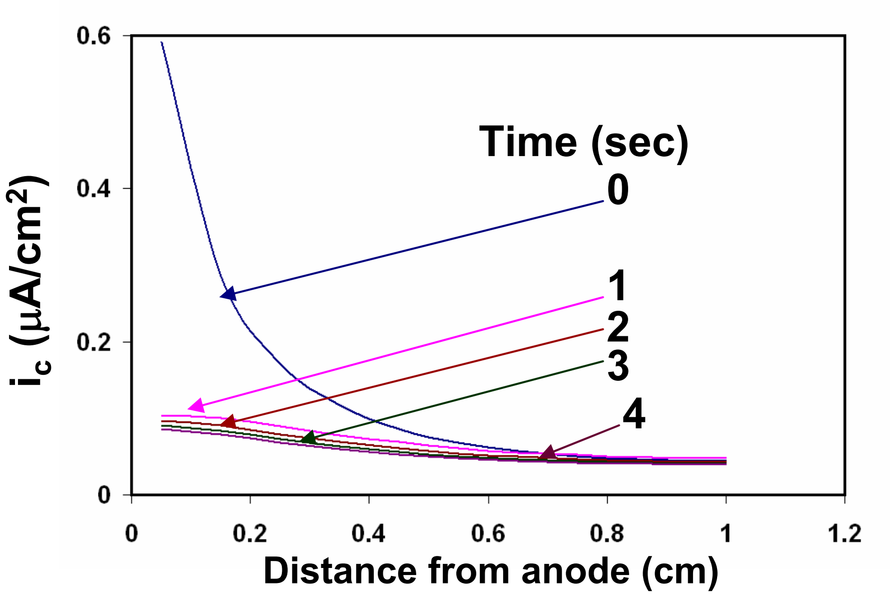
Effect of pH on O_2 Reduction Kinetics:
$E_{o,c}$ ↓ as pH ↑

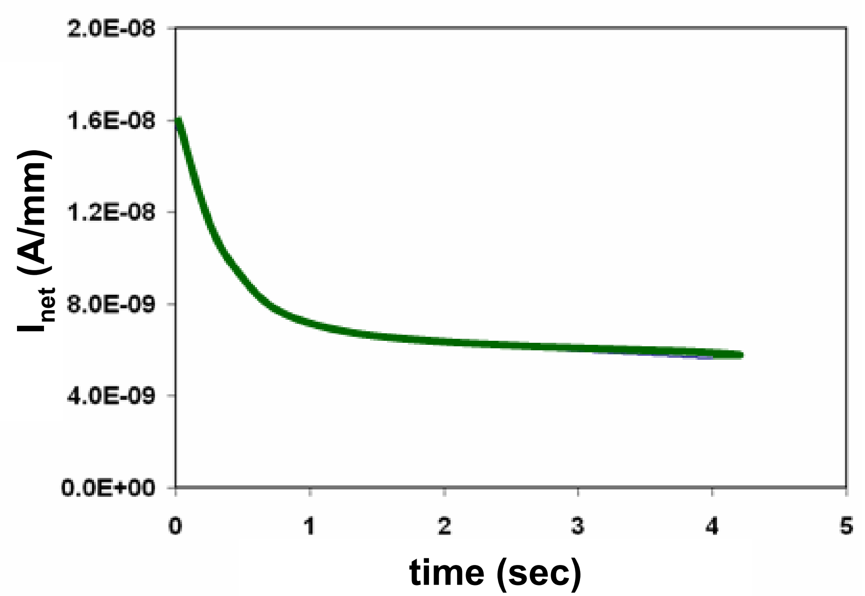




Segmented electrode geometry with varying reduction kinetics ($E_{o,c}$) based on pH is used

pH Effect due to Cathodic Reaction Chemistry





- pH increases with time causing a steep decline in i_c to occur close to the crevice opening, where the pH change is largest
- Cathode capacity decreases with time due to more sluggish O_2 reduction kinetics resulting from the pH increase

Conclusions

- Metal surfaces on waste packages may be covered with thin electrolyte layers containing particulates or deposits.
- Localized corrosion can be limited by the ability of the surrounding cathode to supply current.
- Cathode capacity strongly depends on:
  - water layer thickness
  - solution conductivity
  - electrochemical kinetics
  - temperature (affects solution conductivity and electrode kinetics)
- Presence of particulates in electrolyte decreases cathode capacity by decreasing solution conductivity and effective electrode area.
- Limited electrolyte volume under thin film conditions could lead to rapid pH increases on the surface which slows the cathodic kinetics and thus decreases the cathode capacity, making localized corrosion less likely to be sustained.