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Modeling the Cathodic Region in Crevice Corrosion under a Thin Electrolyte Film Including Particulates

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Acknowledgement

Modeling the Cathodic Region in Crevice Corrosion under a Thin Electrolyte Film Including Particulates

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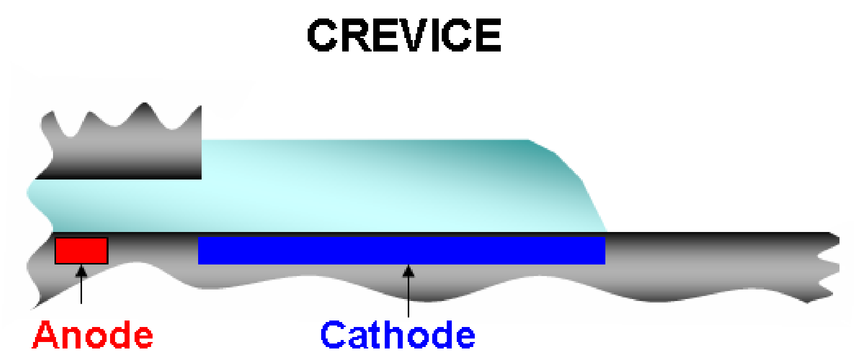
Why study the Cathode ?



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.

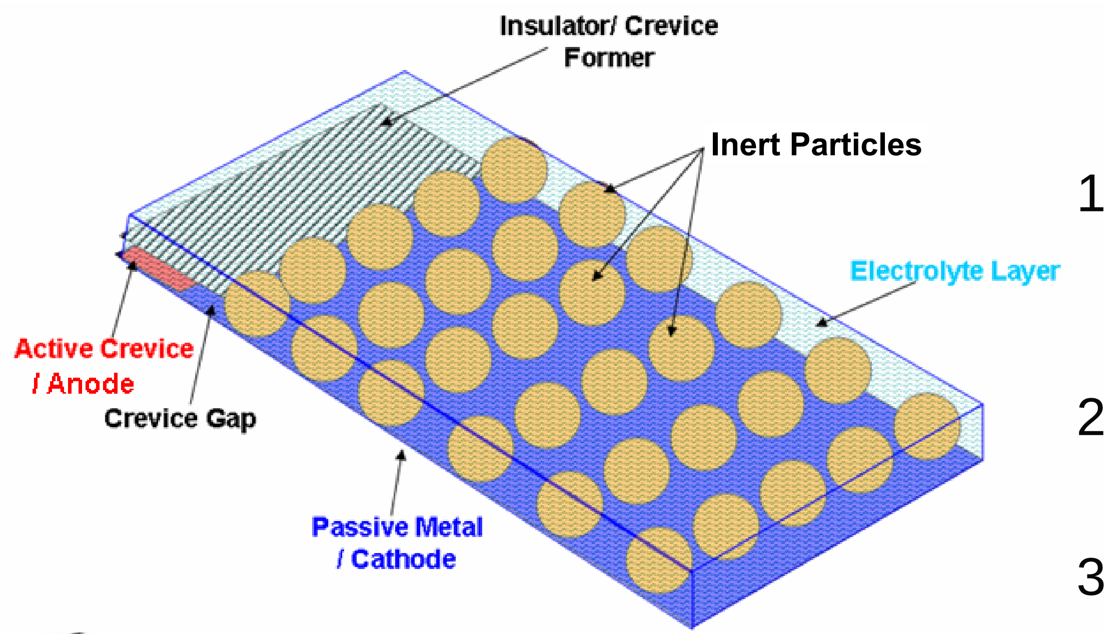
$I_{anodic} = I_{cathodic}$ ← **Anodic and Cathodic regions are coupled**

Unlike conventional corrosion, cathodic limitation to localized corrosion may exist due to :

- Presence of extremely thin (~microns) layer of electrolyte film
- Discontinuous electrolyte layer limiting the cathodic region
- Oxygen diffusion limitation in the electrolyte film due to the presence of particulates

OBJECTIVES

- Modeling and simulation (3-D) of the cathode current capacity in presence of uniform particulate monolayer (on the cathode) at steady state
- Comparison to 2-D simulation for homogeneous electrolyte incorporating approximations for effective conductivity and area coverage by particles



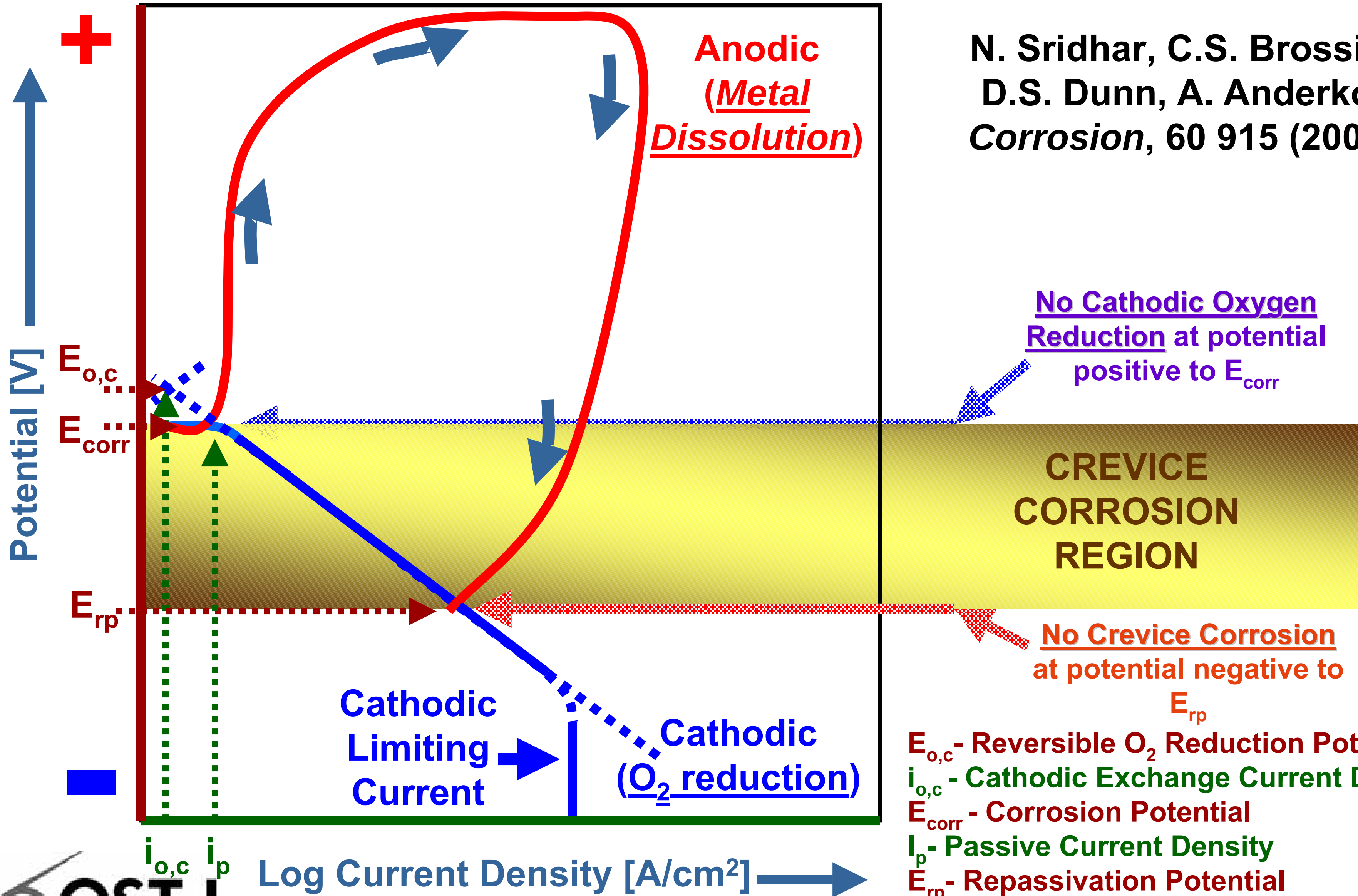
MOTIVATION

Particulates affect the current distribution and capacity (I_{total}):-

1. Increasing ohmic resistance to current flow in solution ("volume effect")
2. Decreasing electrode area ("surface effect")
3. Increasing O_2 mass transfer limitations

Schematic Diagram of Polarization Curve for Stainless Steel (SS 316)

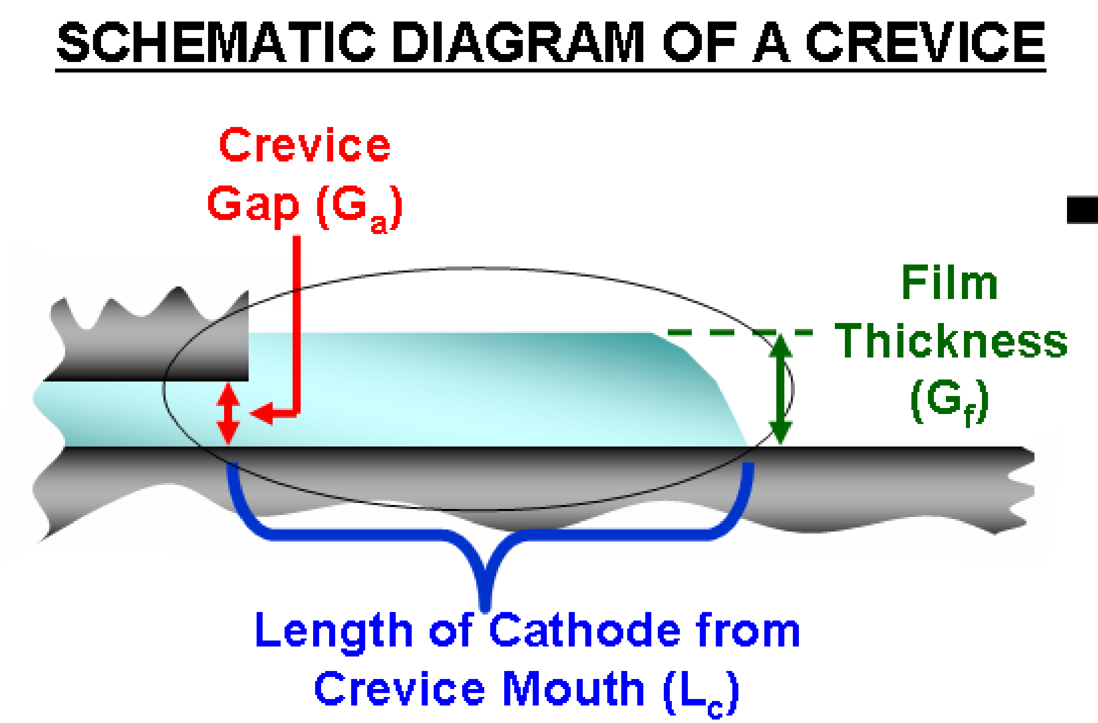
N. Sridhar, C.S. Brossia, D.S. Dunn, A. Anderko, *Corrosion*, 60 915 (2004)

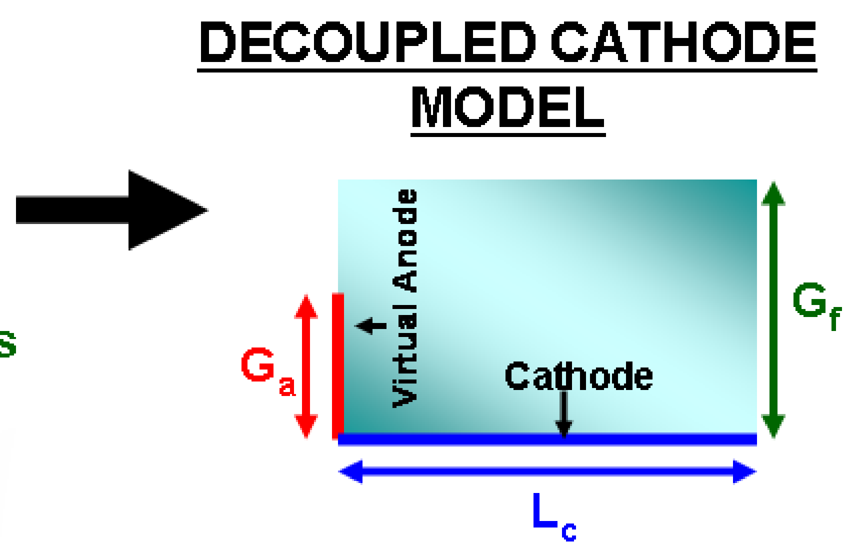


$E_{o,c}$ - Reversible O_2 Reduction Potential
$i_{o,c}$ - Cathodic Exchange Current Density
E_{corr} - Corrosion Potential
I_p - Passive Current Density
E_{rp} - Repassivation Potential

APPROACH

Cathodic region is **decoupled** from the localized corrosion region.





FACTORS FOR MODELING OF PARTICULATES

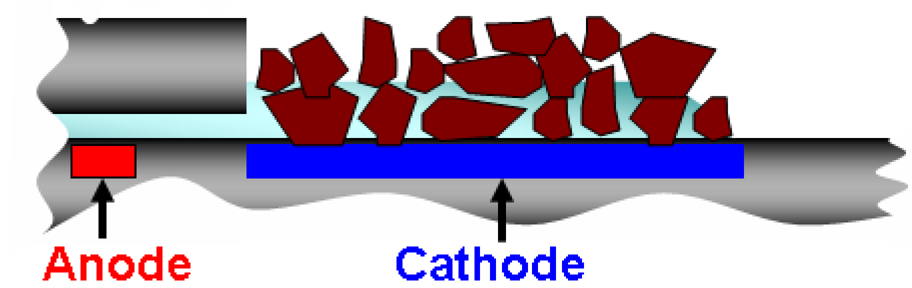
PARAMETERS (of particulate layer)

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

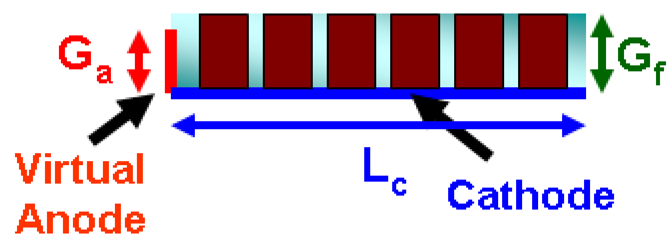
MODELING CONSTRAINTS

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

REAL SYSTEM



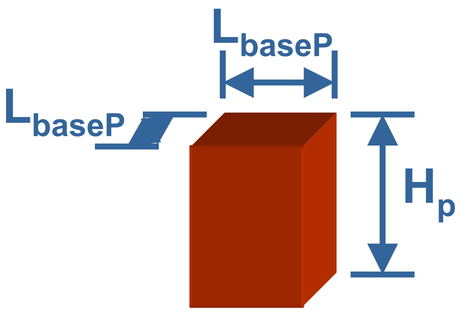
MODEL GEOMETRY



METHODOLOGY

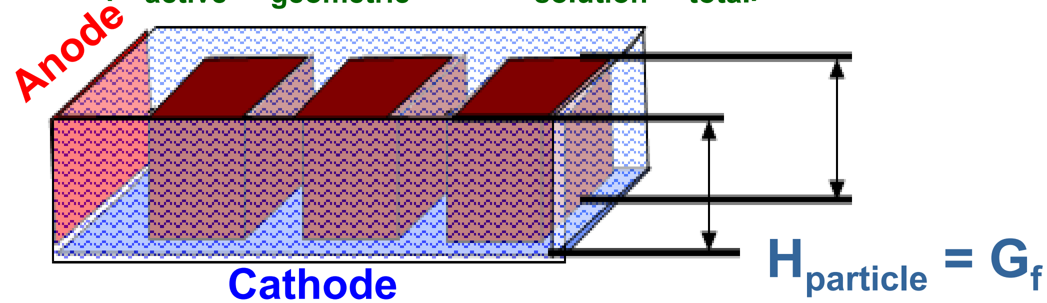
3-D Simulations based on particle shape, size & distribution:

1. Select Particle (shape & size)

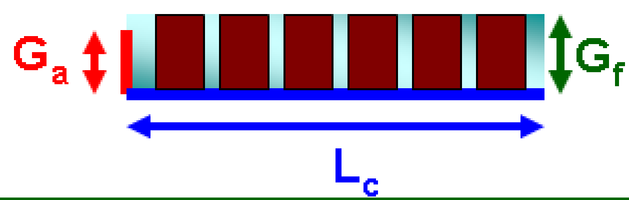


2. Fix Distribution and Arrangement

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



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



Cathode capacity is explored in the range:

a. Length of cathode (L_c : 0.01 - 0.4 cm)

b. Solution conductivity (κ : 1.21 x10^{-1} - 1.21x 10^{-3} S/cm, [1 to 0.01 M Cl^-])

c. Oxygen reduction kinetics (i_o = 10^{-7} - 10^{-11} A/cm^2)

d. Repassivation potential (E_{rp} = -0.56 to -0.11 V_{NHE})

Base Parameters: E_{rp} = -0.31 V_{NHE}, $E_{o,c}$ = 0.19 V_{NHE}, i_o = 10^{-9} A/cm^2, β_c = 0.1 V/dec, κ = 1.21 x 10^{-2} S/cm

METHODOLOGY

Compare using simple analytical expressions accounting for particle effects:

1. Particle effects on **bulk solution conductivity**

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

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

2. Cathode **surface blockage** by particles

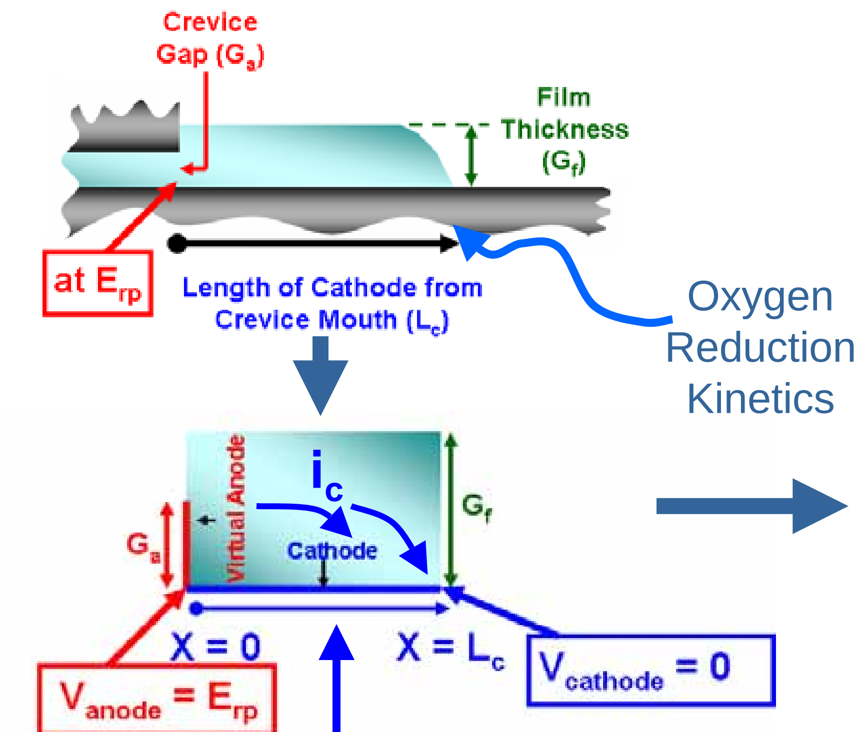
$$\frac{\mathbf{A_{active}}}{\mathbf{A_{geometric}}} = \frac{\mathbf{Area(geometric) - Area(particle\ base)}}{\mathbf{Area(geometric)}}$$

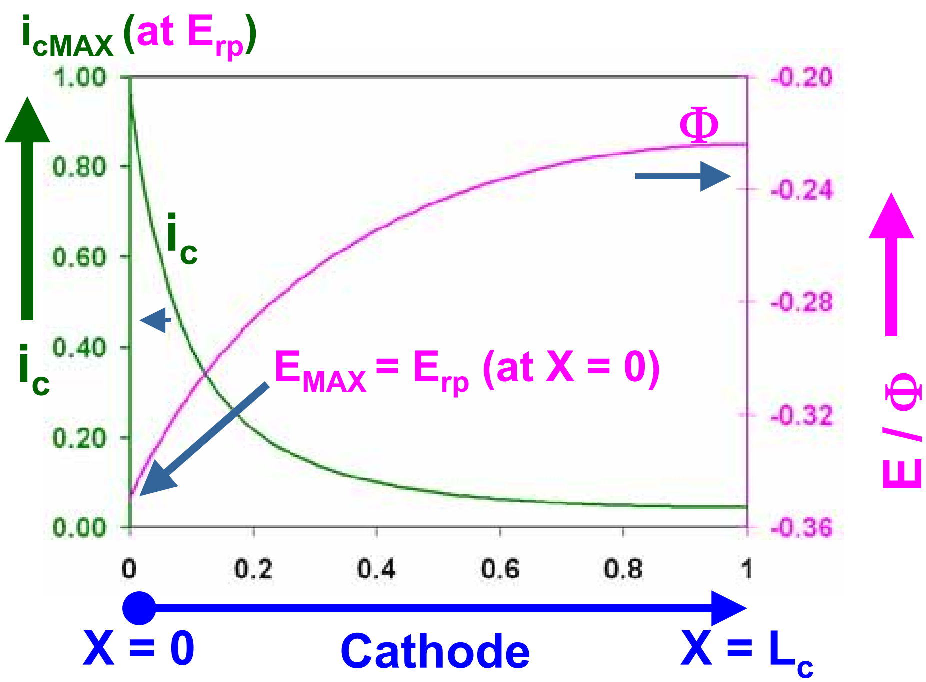
Equivalent exchange current density:

$$\mathbf{i_0' = i_0 \ x \ \frac{A_{active}}{A_{geometric}}}$$

3. Combination of the two (**Bruggeman's + area correction**)

Cathode Current Density Parameters:





KINETICS OF CATHODE:

$i_c = -i_o * \exp\{-(\alpha_c F/RT)*(V^{cathode} - E_0^{cathode} - \Phi)\}$ **[TAFEL KINETICS]**

[Φ – ohmic potential drop in solution]

$V^{cathode} = 0$ V

$E_0^{cathode} = +0.19\ V_{NHE}$ [$E_0^{cathode}$ – constant, value for SS 316 used]

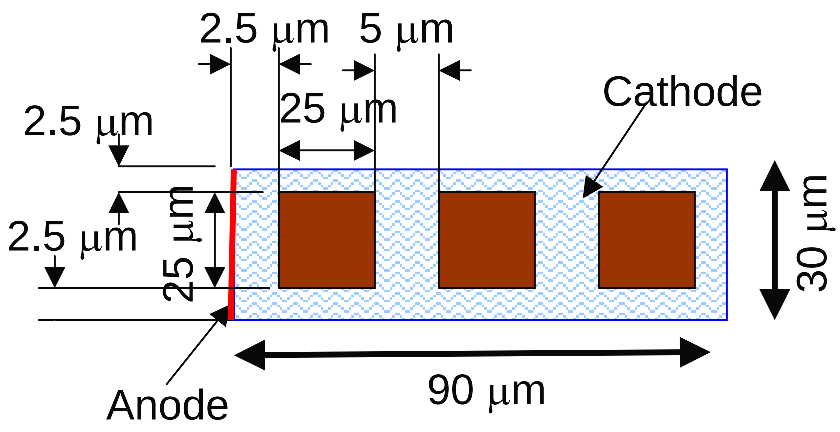
$i_c = -i_o * \exp\{(\alpha_c F/RT)(0.19 + \Phi)\}$

ANODE → A virtual anode is set at the crevice opening: $\Phi_{anode} = E_{rp}$.

Particle Distribution on Cathode:

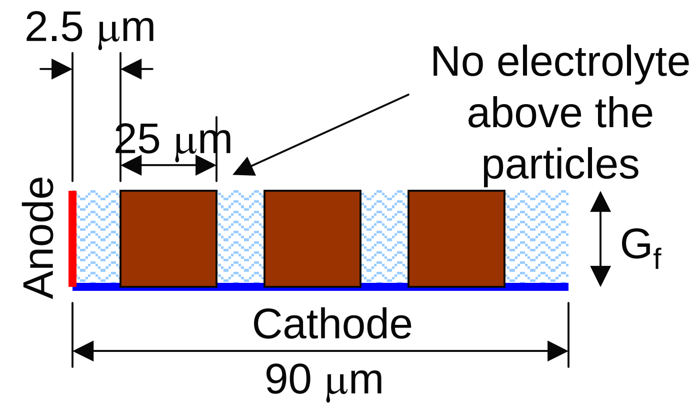
Particles represented as 25 μm cubes placed equidistant to each other and to the edges of the finite cathode:

(Top View)



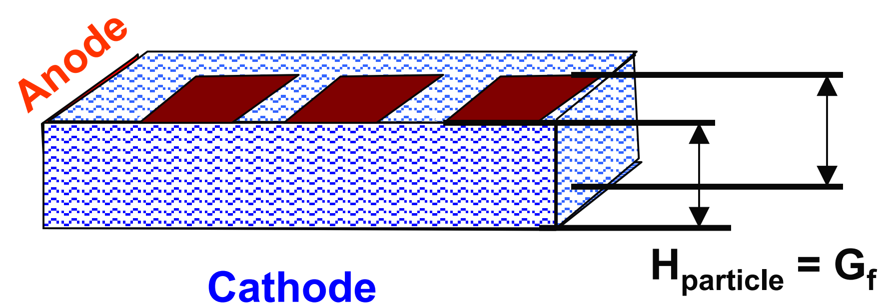
Length Increased in this direction.

(Front View)

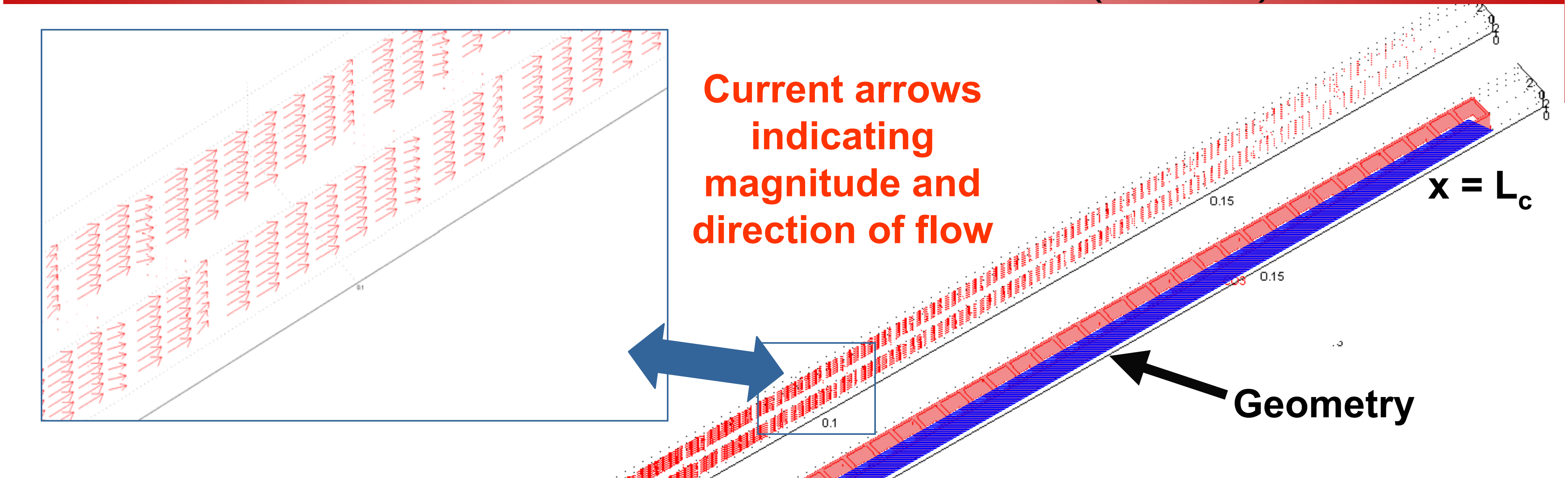


$$\frac{A_{active}}{A_{geometric}} = 0.306$$

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



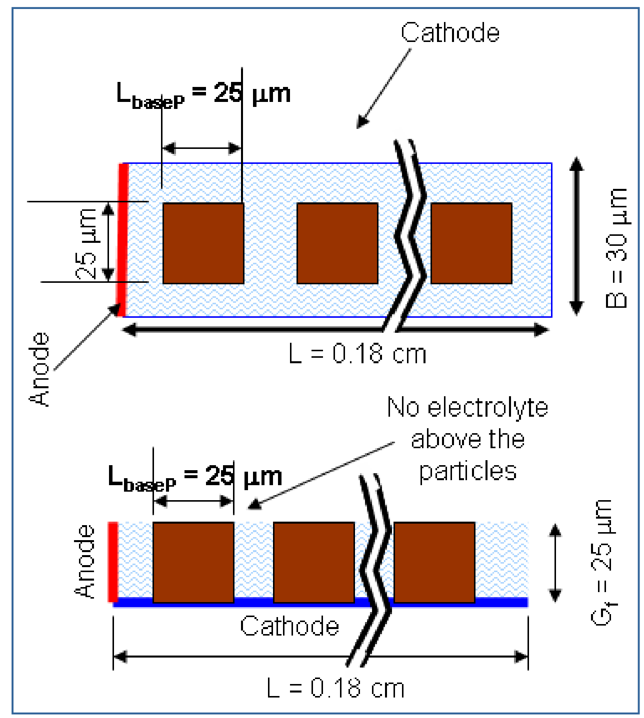
3-D Simulation of Current Flow in Solution (FEMLAB®)



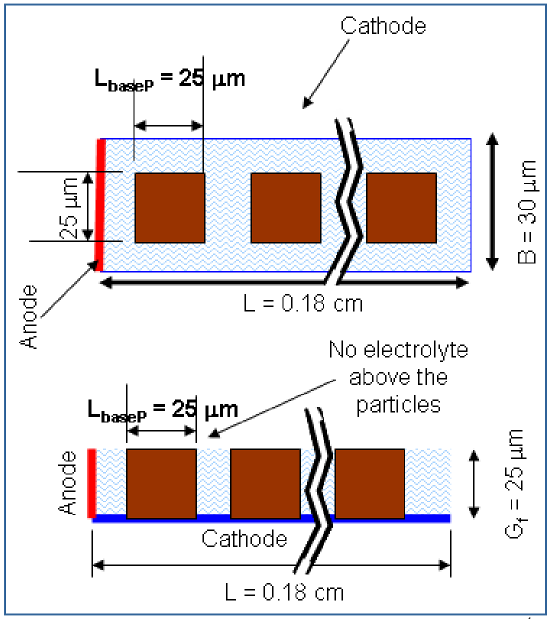
$$\frac{A_{active}}{A_{geometric}} = 0.306$$

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

κ= 1.21x10^{-2} S/cm,
i_o = 10^{-9} A/cm^2,
β_c = 0.1 V/dec,
E_{rp} = -0.31 V_{NHE},
$E_{o,c}$ = 0.19 V_{NHE},
i_L = 2.2e-4 A/cm^2,
L_c = 0.18 cm

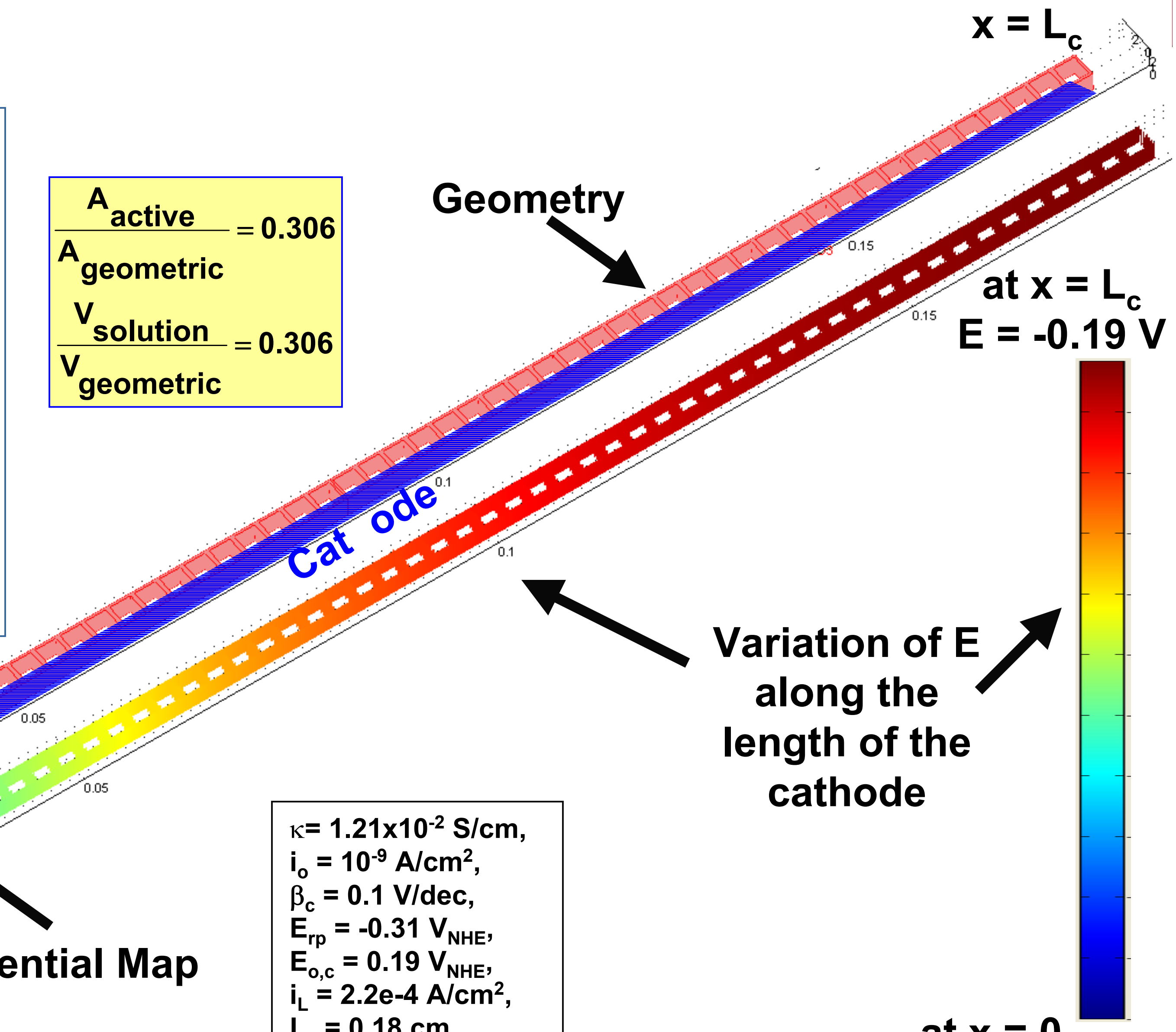


3-D Simulation of Potential Drop (E) in Solution (FEMLAB®)



$$\frac{A_{active}}{A_{geometric}} = 0.306$$

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



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β_c = 0.1 V/dec,
E_{rp} = -0.31 V_{NHE},
$E_{o,c}$ = 0.19 V_{NHE},
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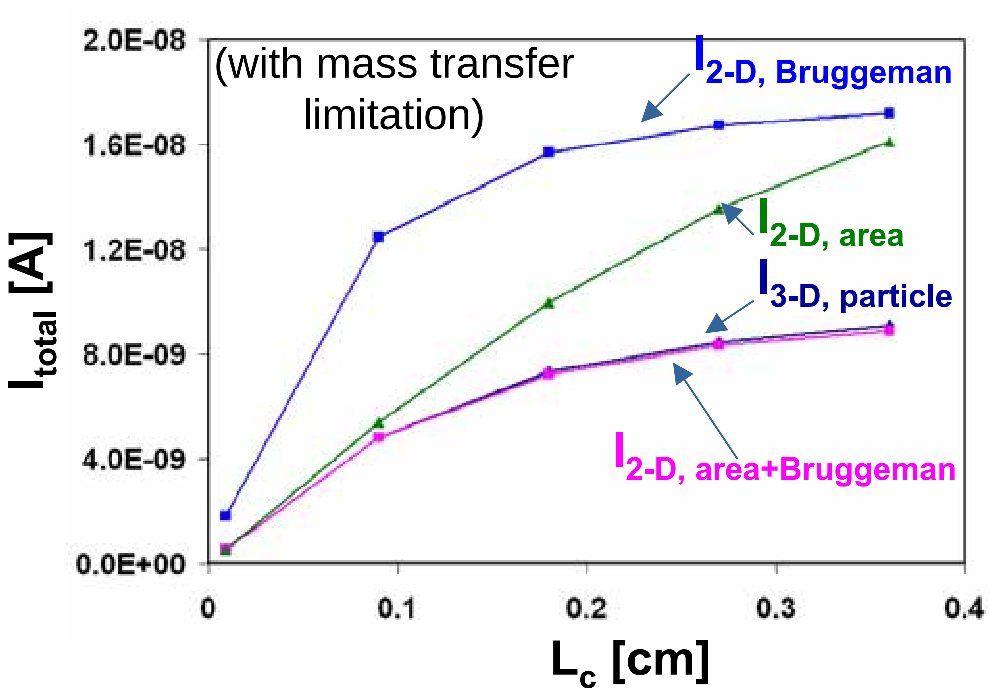
L_c = 0.18 cm

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



$$\frac{A_{active}}{A_{geometric}} = 0.306$$

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β_c = 0.1 V/dec,
E_{rp} = -0.31 V_{NHE},
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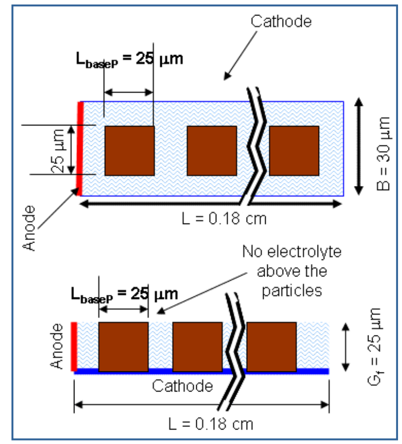
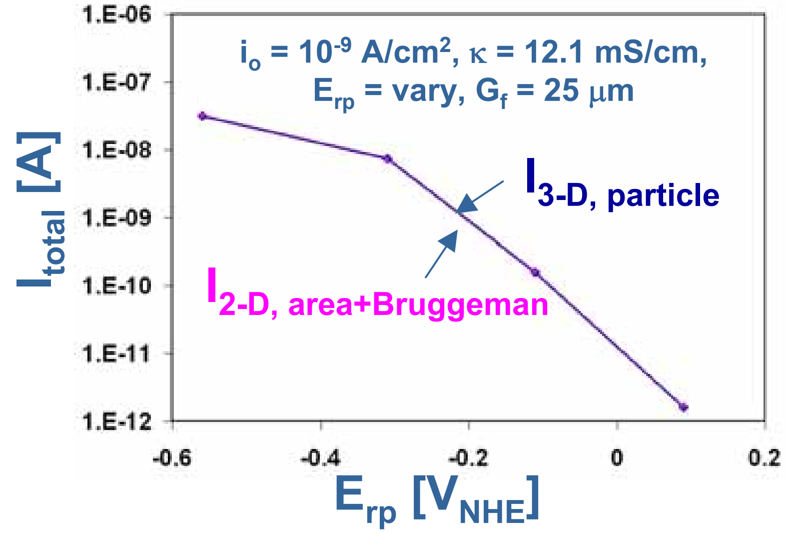
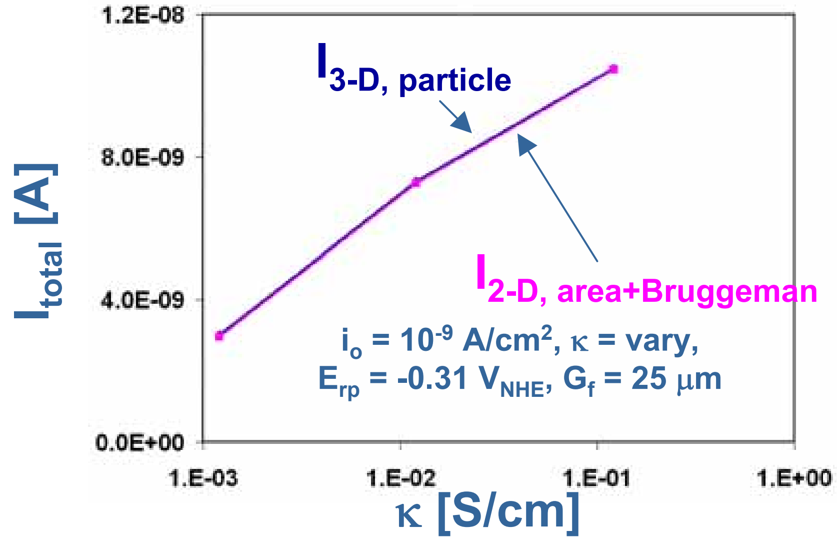
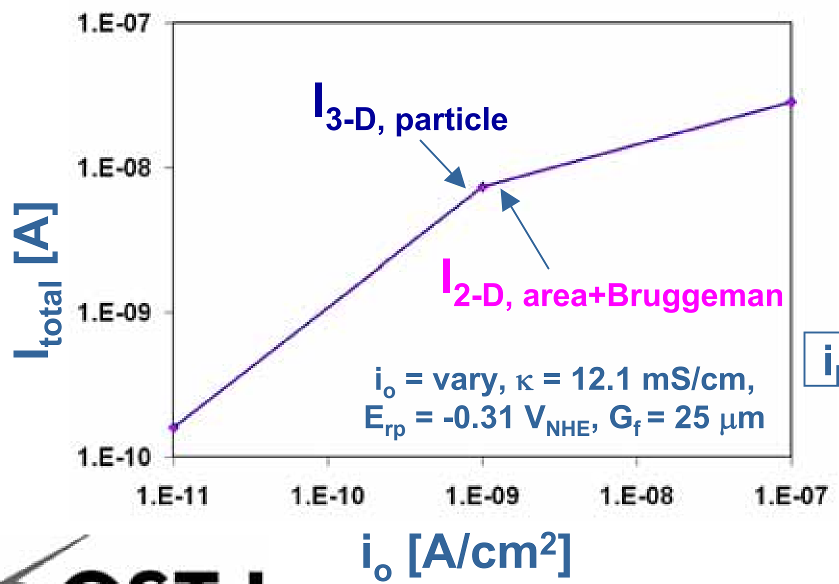


- Volume (Bruggeman) and surface coverage (area) corrections in 2-D simulations produce accurate 3-D results
- Independently, area or volume correction are insufficient
- Similar results obtained without mass transfer limitations

Effect of Process Parameters – (E_{rp}, i_o, κ)







$$\frac{A_{active}}{A_{geometric}} = 0.306$$

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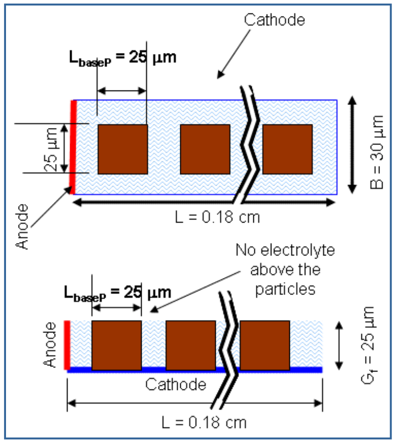
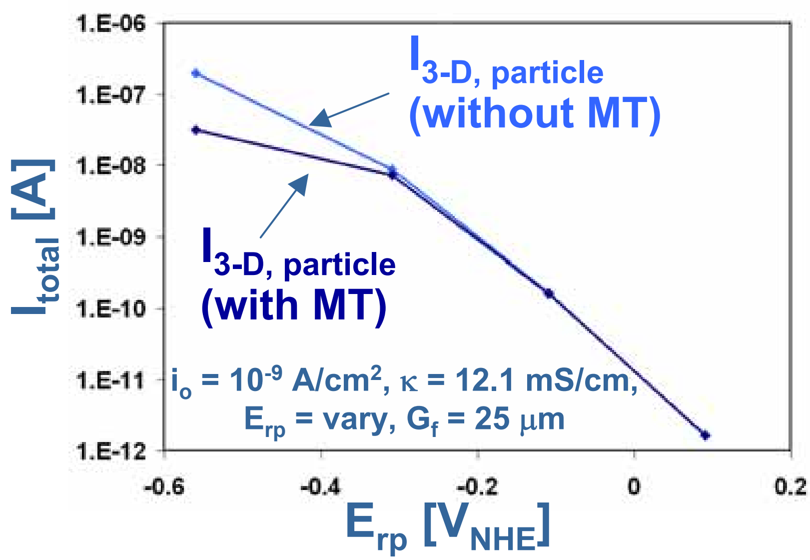
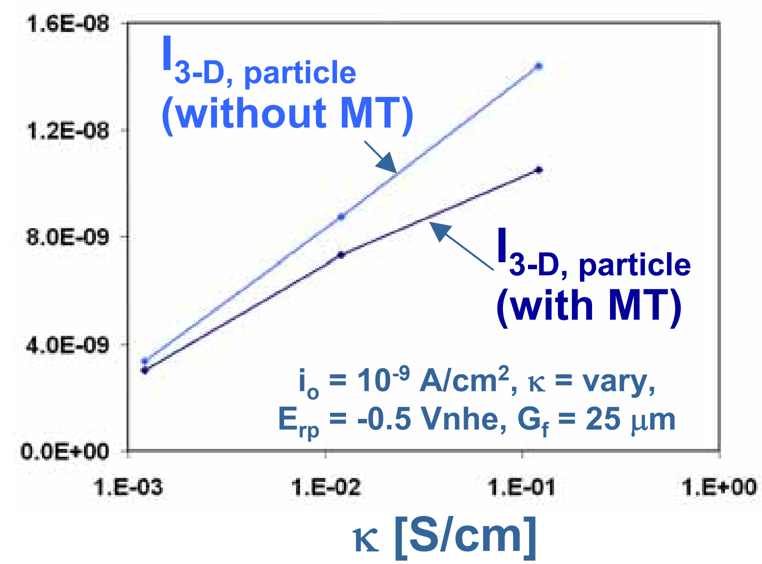
i_L = 2.2e-4 A/cm², L_c = 0.18 cm

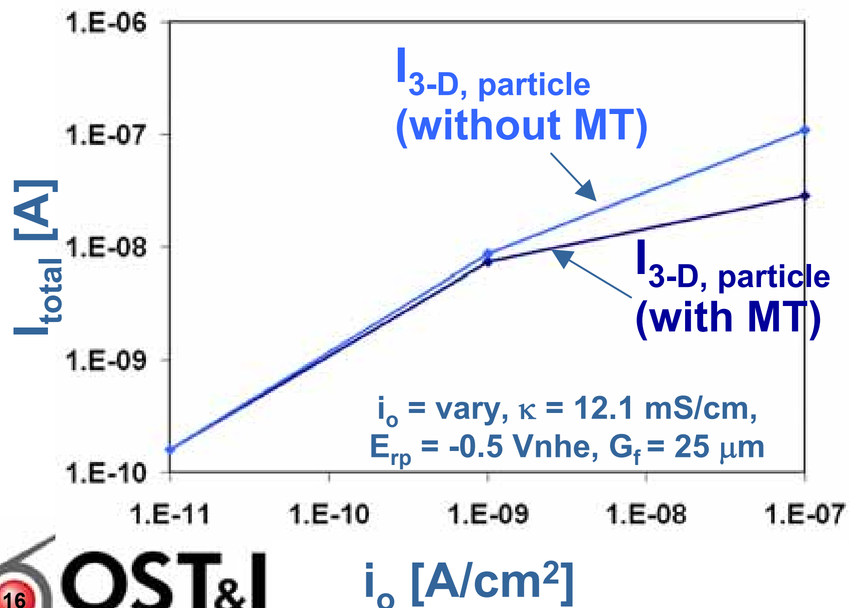


- **Volume (Bruggeman) and surface (area) coverage corrections in 2-D simulations produce accurate 3-D results**

Effect of Mass Transfer (MT) Limitation on I_{total} in Presence of Particles:



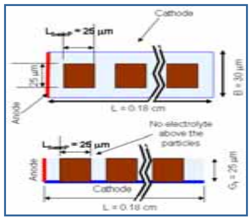




i_L = 2.2e-4 A/cm², L_c = 0.18 cm

$$\frac{A_{active}}{A_{geometric}} = 0.306$$

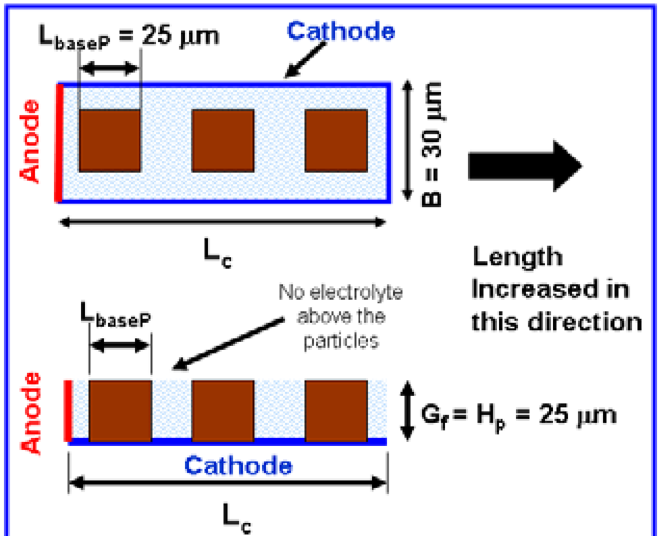
$$\frac{V_{solution}}{V_{geometric}} = 0.306$$



MT effects significant for

- **Large potential driving force (high E_{rp}),**
- **Fast kinetics (large i_o) and**
- **High solution conductivity (large κ).**

Effect of Particle Arrangement on Cathode Capacity (I_{total}):



$$\frac{A_{active}}{A_{geometric}} = 0.306$$

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κ= 1.21x10^{-2} S/cm,
i_o = 10^{-9} A/cm^2,
β_c = 0.1 V/dec,
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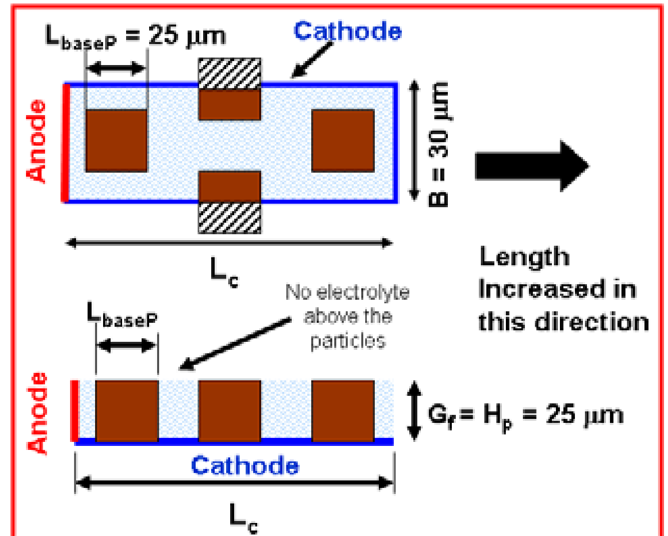
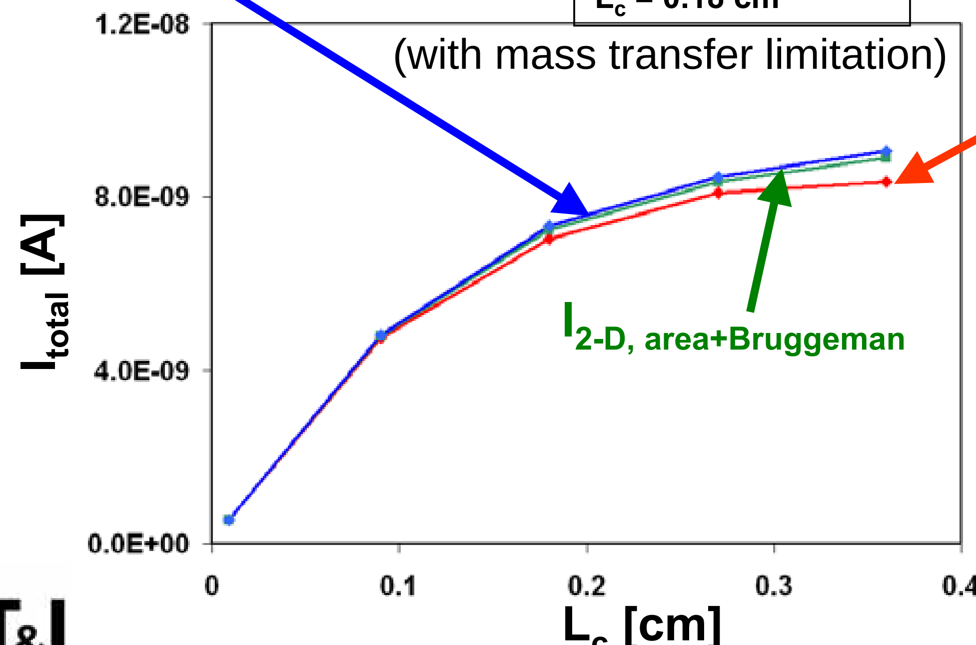
$E_{o,c}$ = 0.19 V_{NHE},
i_L = 2.2e-4 A/cm^2,
L_c = 0.18 cm

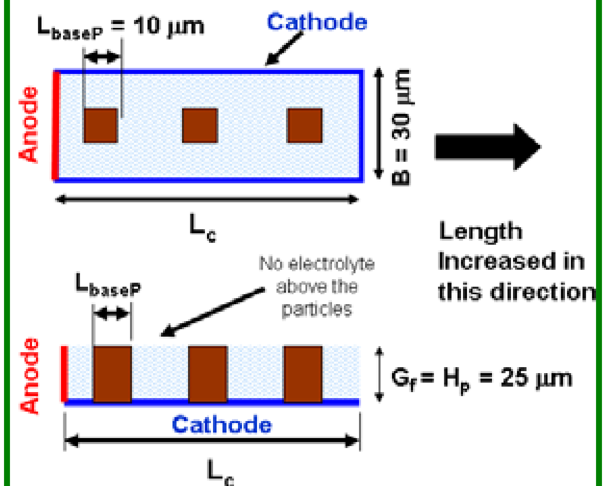




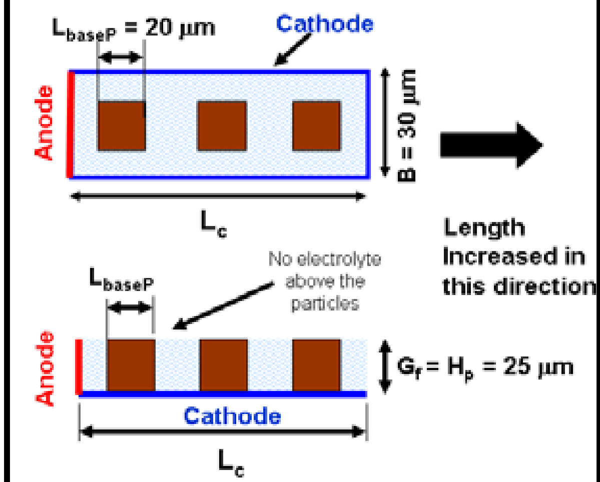
- Particles of same size and shape give almost identical I_{total}, irrespective of arrangement

Effect of Variation of Solution and Area Coverage of Particles on I_{total} :

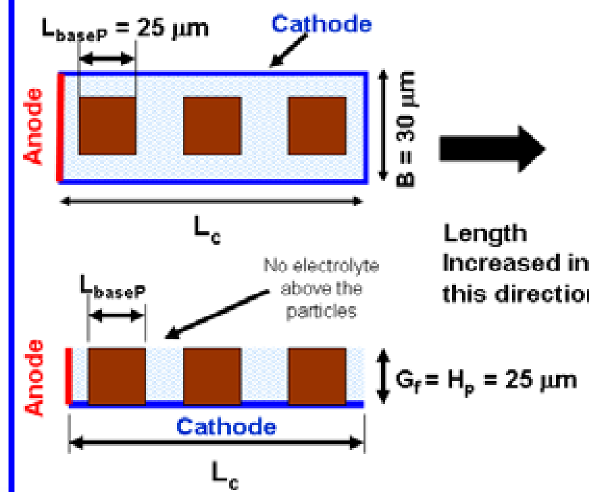
$$\frac{A_{active}}{A_{geometric}} = 0.889 \qquad \frac{V_{solution}}{V_{geometric}} = 0.889$$



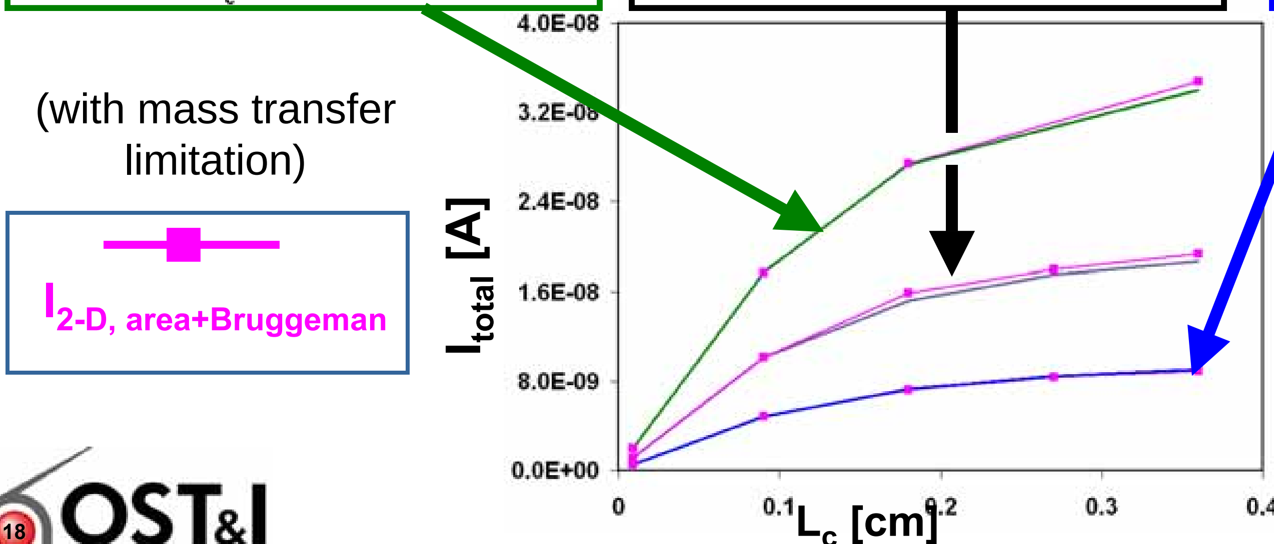
$$\frac{A_{active}}{A_{geometric}} = 0.556 \qquad \frac{V_{solution}}{V_{geometric}} = 0.556$$



$$\frac{A_{active}}{A_{geometric}} = 0.306 \qquad \frac{V_{solution}}{V_{geometric}} = 0.306$$



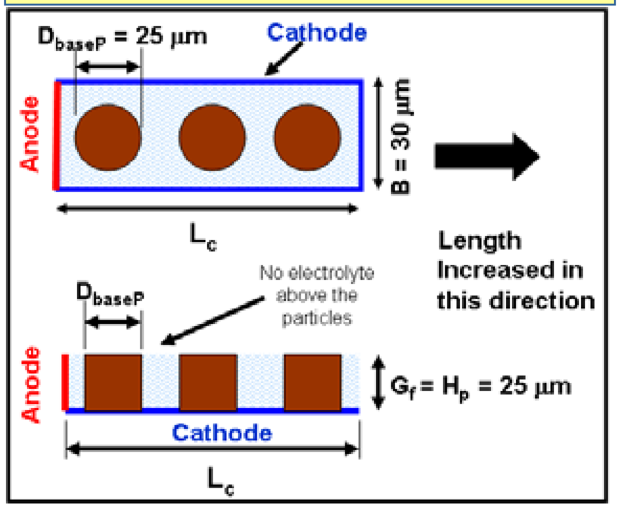
(with mass transfer limitation)



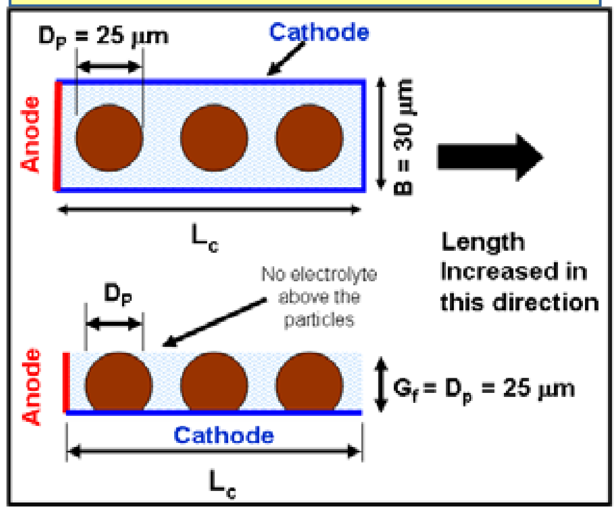
- **Volume and surface coverage significantly affects I_{total}**
- **2-D corrections are valid**

Other Particle Shapes Considered:

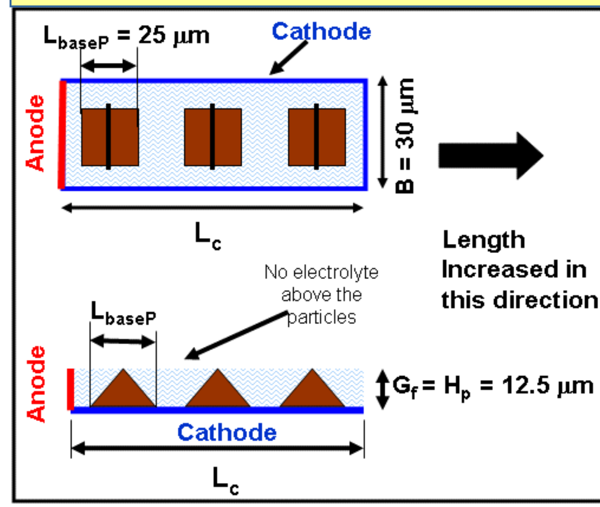
$$\frac{A_{active}}{A_{geometric}} = 0.454\,;\ \frac{V_{solution}}{V_{geometric}} = 0.454$$



$$\frac{A_{active}}{A_{geometric}} = 0.850\,;\ \frac{V_{solution}}{V_{geometric}} = 0.450$$



$$\frac{A_{active}}{A_{geometric}} = 0.390\,;\ \frac{V_{solution}}{V_{geometric}} = 0.706$$



- **Volume and surface coverage significantly affects I_{total}**
- **2-D corrections are valid**

CONCLUSIONS

I. 3-D Simulation of cathode with particulates

under the following conditions :

i. Uniform particle distribution

ii. $A_{active}/A_{geometric} \geq 0.3$

iii. $V_{solution}/V_{total} \geq 0.3$

indicate;

1. Particles in electrolyte exhibit both, volumetric (solution) and cathode area (interfacial kinetic) effects
2. Shape and arrangement of particles has negligible effect
3. Mass transport limitations become significant under conditions for high cathode capacities
4. Most of the contribution to the current is close to the anode

II. 2-D modeling for homogeneous electrolyte corrected for

- Volume effect (Bruggeman)
- Surface area effect

predicts the cathode capacity in the presence of particulates under above conditions.

QUESTIONS