Modelling the Electroplating of Hexavalent Chromium

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COMSOL CONFERENCE
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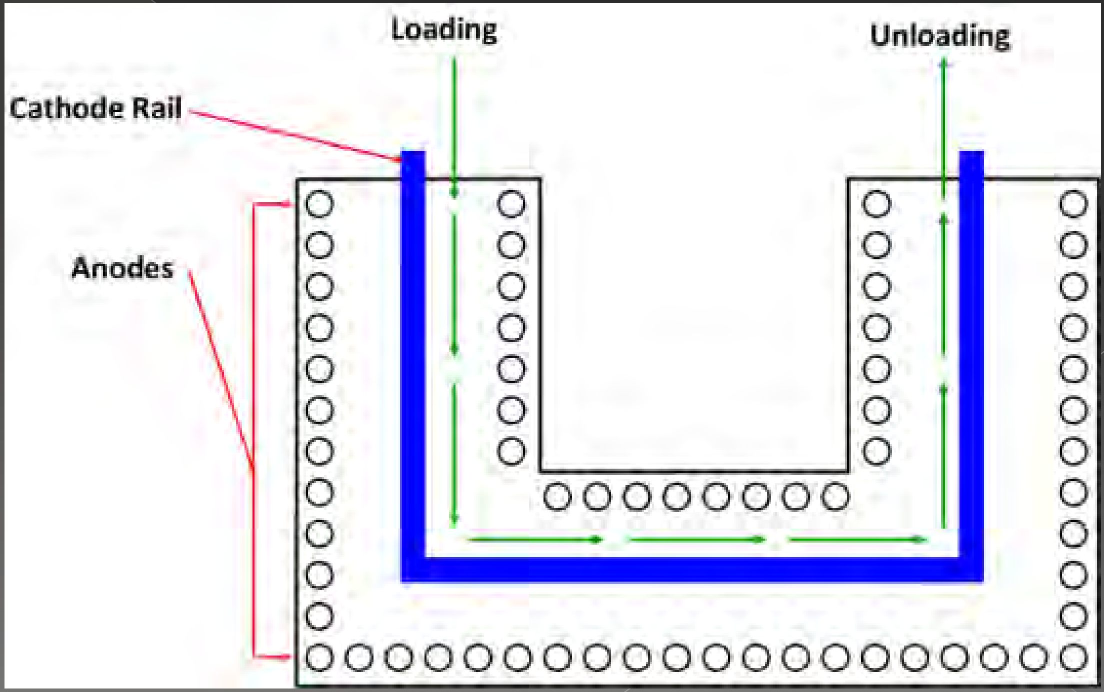
Topics

- Introduction & Problem Analysis
- Solution Design
- Results
- Conclusions
- Moving Forward

Motivation

Introduction: Process Description

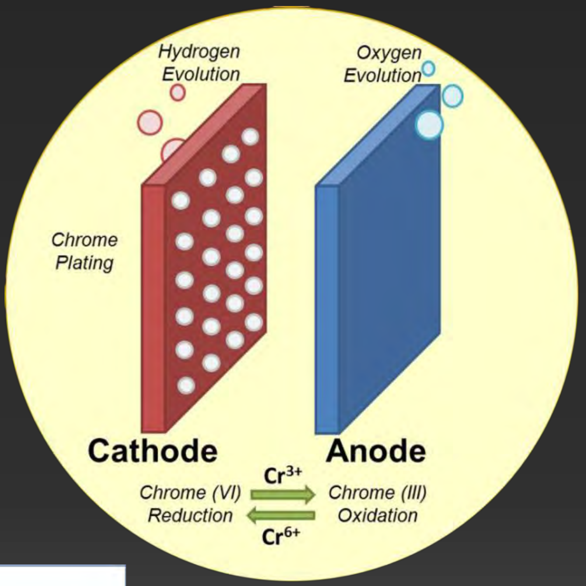
- Chrome plating on strut rods
  - Corrosion resistance
  - Mechanical properties



Areal view of plating tank

Introduction: Process Description

- Chrome Electrodeposition
  - Cathode: Carbon Steel (to be plated)
  - Anode: Lead (Inert)
  - Electrolyte: Chromic acid solution
  - Overall Current Efficiency: 22%



Electrode	Material	Reactions
Cathode	Carbon Steel	$Cr^{3+} + 3e^- \rightarrow Cr^0$ $2H^+ + 2e^- \rightarrow H_2$ $(Cr_2O_7)^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$
Anode	Lead (Inert)	$2Cr^{3+} + 7H_2O \rightarrow (Cr_2O_7)^{2-} + 6e^- + 14H^+$ $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Problem Definition

Limited knowledge of solution chemistry

Limited knowledge of process parameters

Deliberate Overplating

Lack of mathematical model

"This is how we've always done it" approach

Consequences

- Chrome consumption
- Energy
- Cost
- Strain on downstream units
  - Grinders
  - Scrubbers

Design

2D COMSOL Model Options

Electrodeposition Secondary

- Electric overpotential controlled
- Completely Mixed
- Stationary

☑

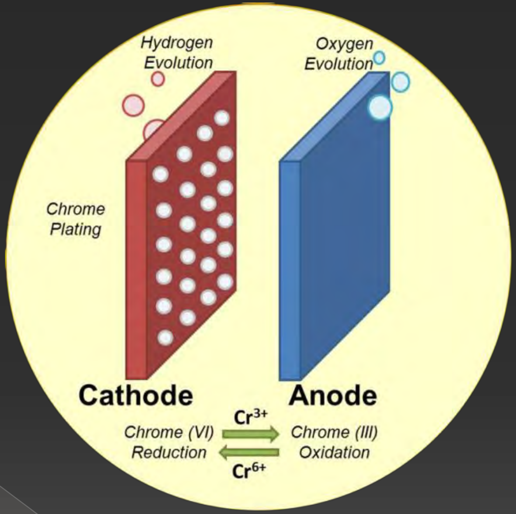
Electrodeposition Tertiary Nernst-Planck

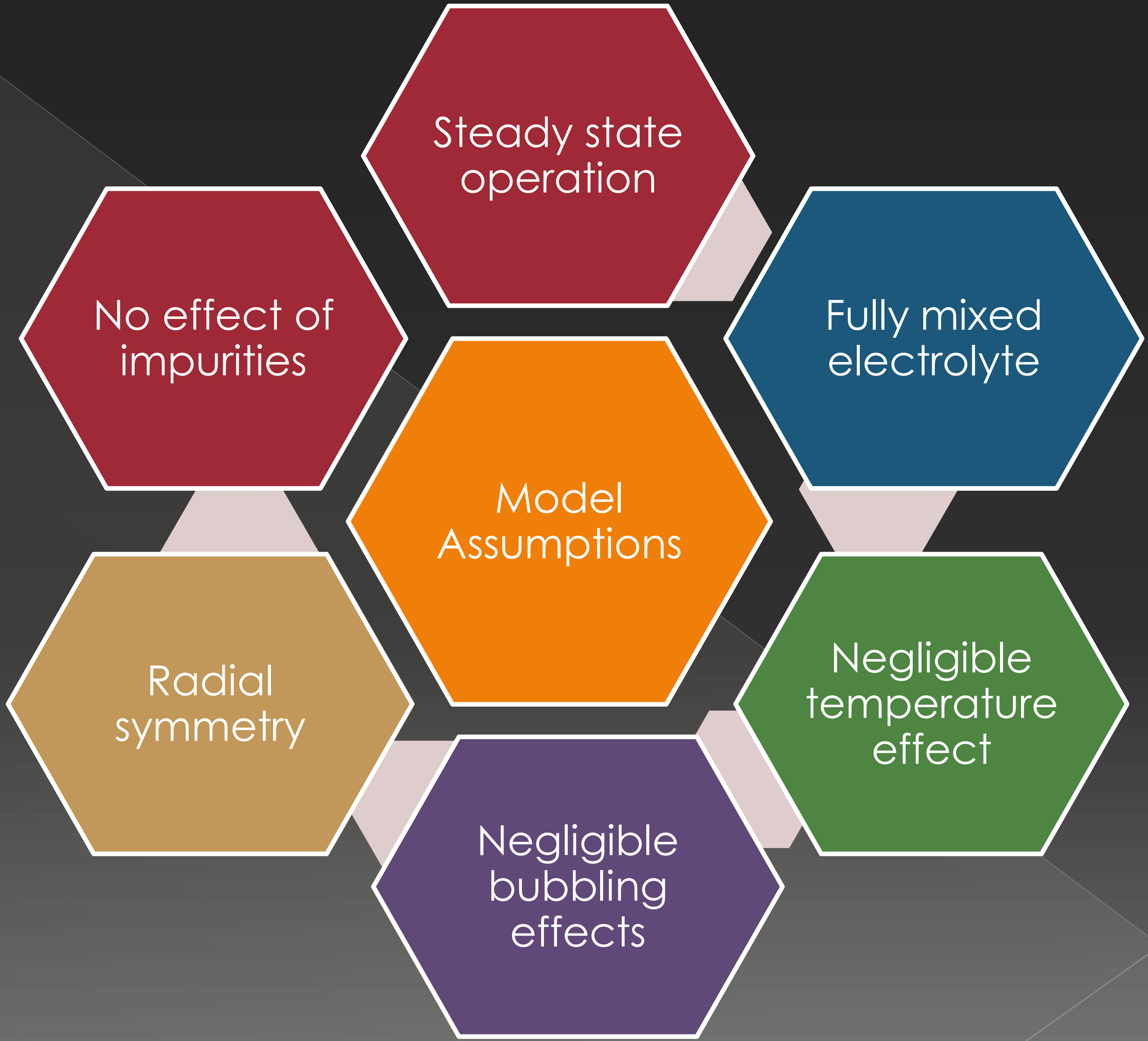
- Includes concentration overpotential
- Quiescent
- Stationary and Time Dependent

☒

Design

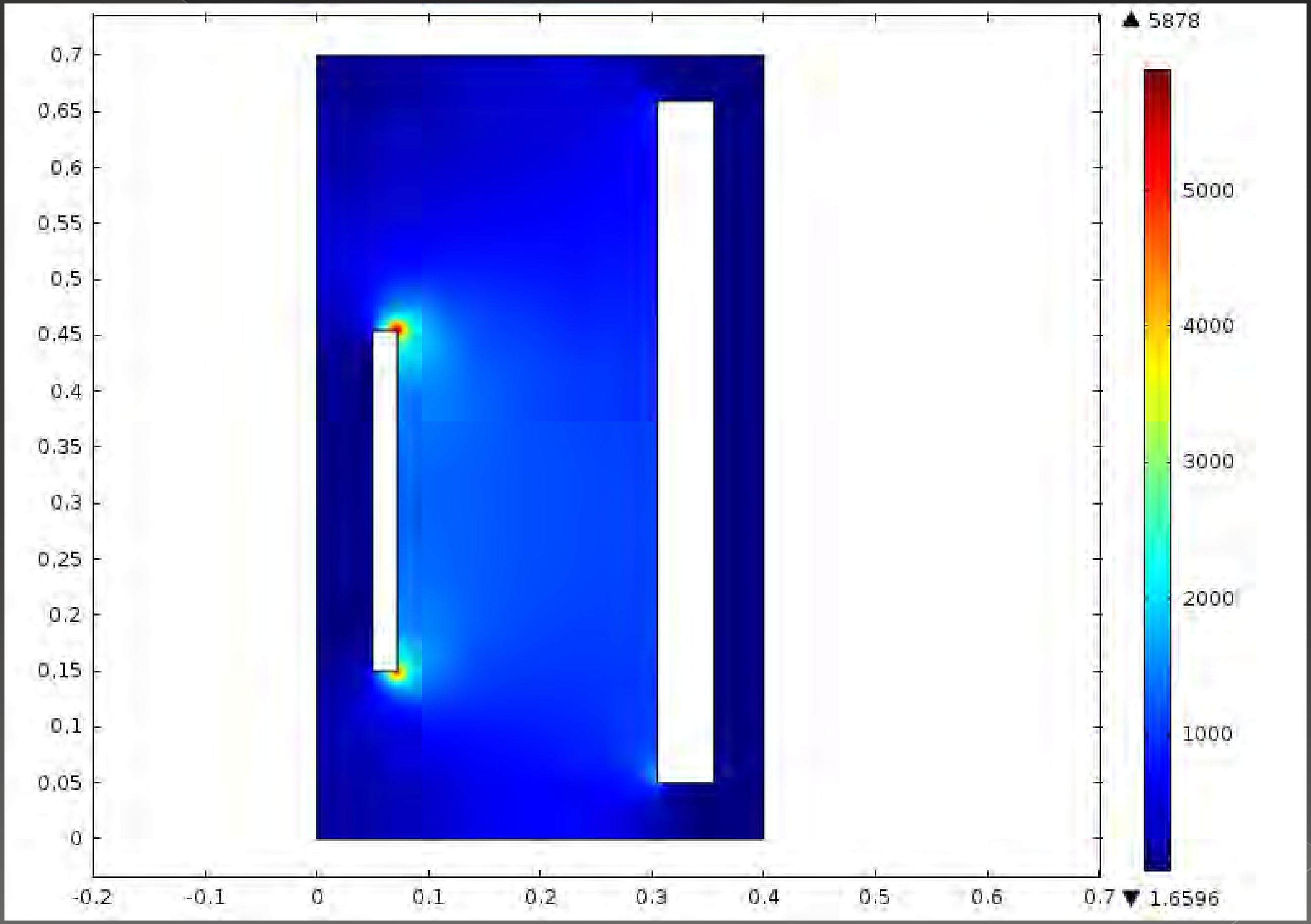
- Model
  - Accumulation of mass at the cathode surface
- Governing Equations
  - Butler-Volmer for kinetics:
    - $i = i_0\left[\exp\left(\frac{\alpha_a n_e F\eta}{RT}\right) - \exp\left(-\frac{\alpha_c n_e F\eta}{RT}\right)\right]$
- Current density data extracted to calculate corresponding thicknesses




Steady state operation
No effect of impurities
Fully mixed electrolyte
Model Assumptions
Radial symmetry
Negligible temperature effect
Negligible bubbling effects

Results

Current Density



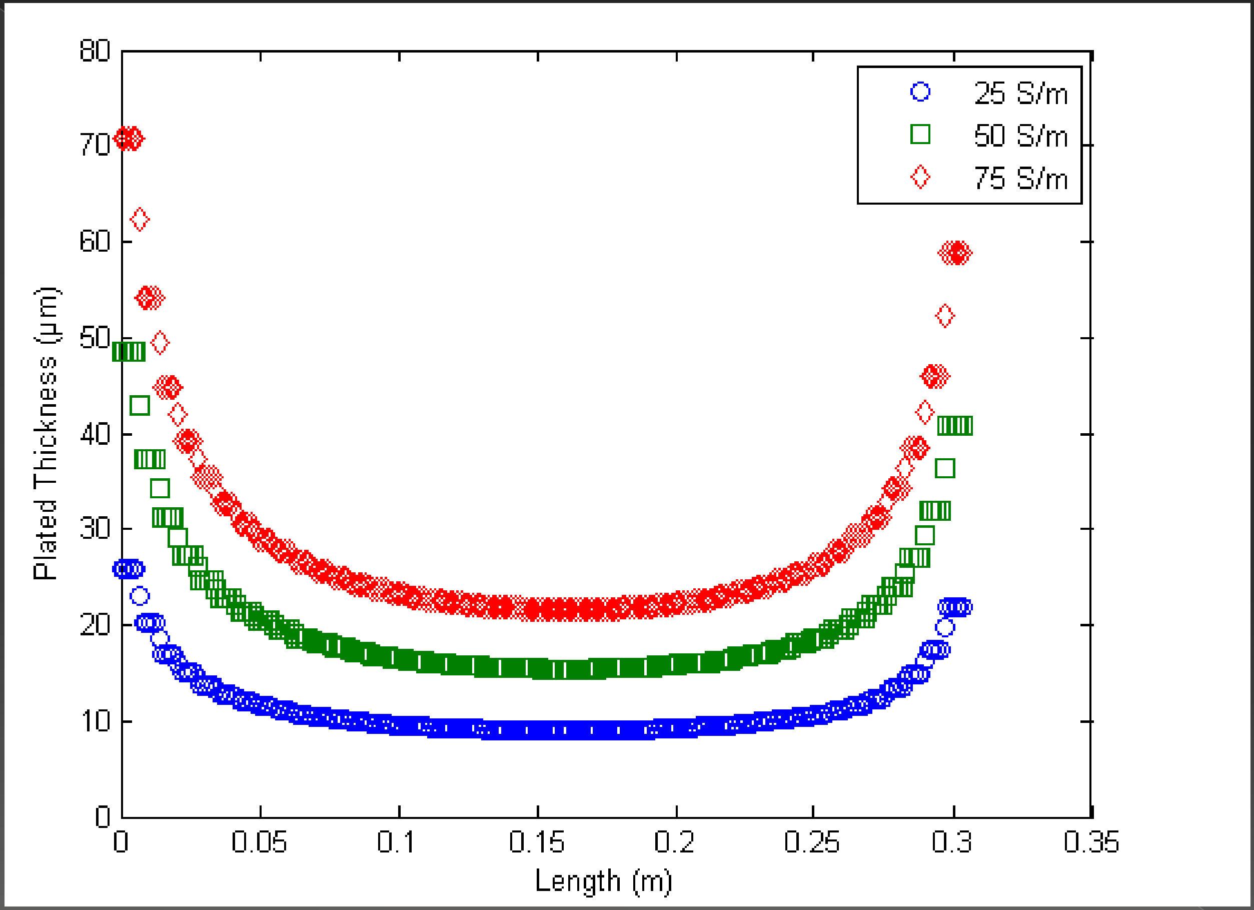
Excess current at the top and bottom

Excerpt from the Proceedings of the 2013 COMSOL Conference in Boston

Variables & Effects

Process Variables	Effects
Solution Conductivity	Midpoint Thickness
Anode-Cathode Spacing	Non-Uniformity
Anode Height	

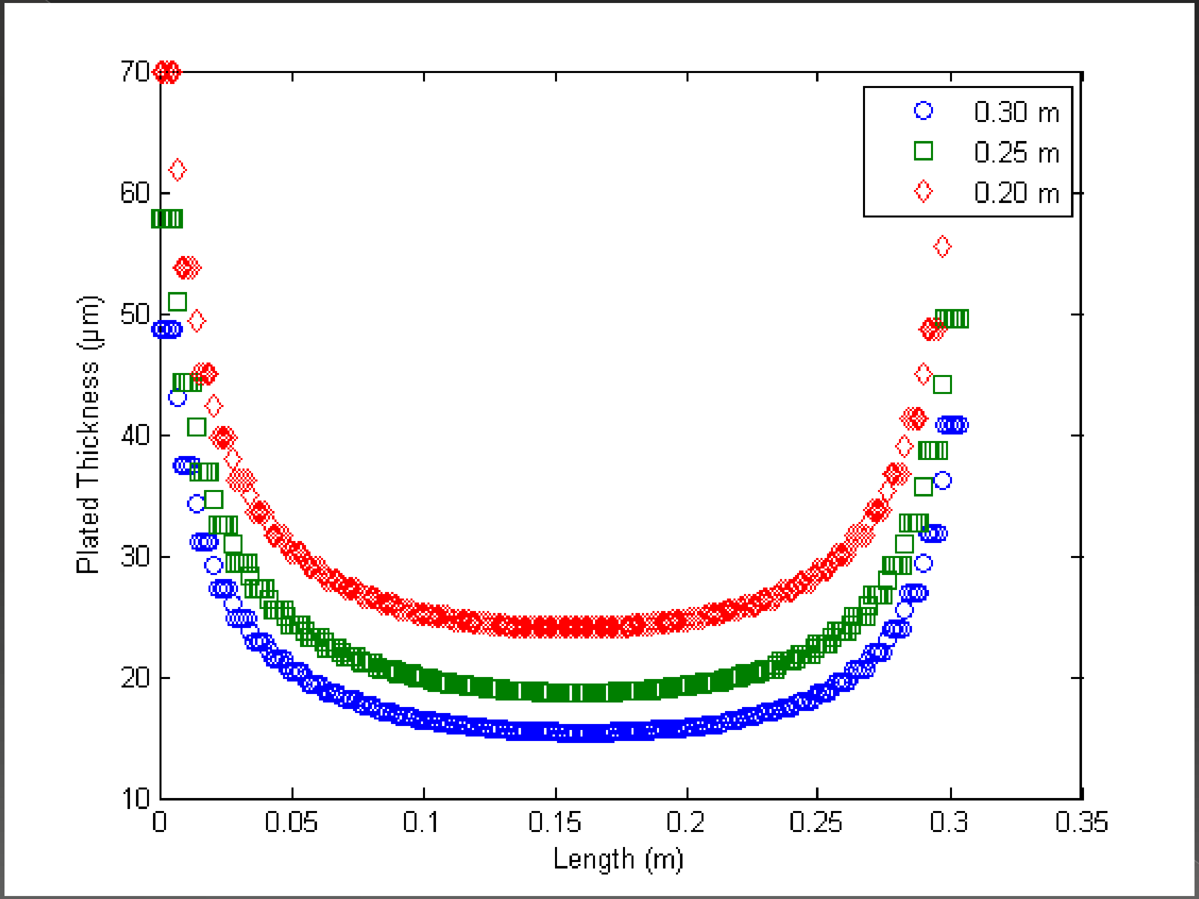
Conductivity



↑ Conductivity causes ↑ plating thickness

Excerpt from the Proceedings of the 2013 COMSOL Conference in Boston

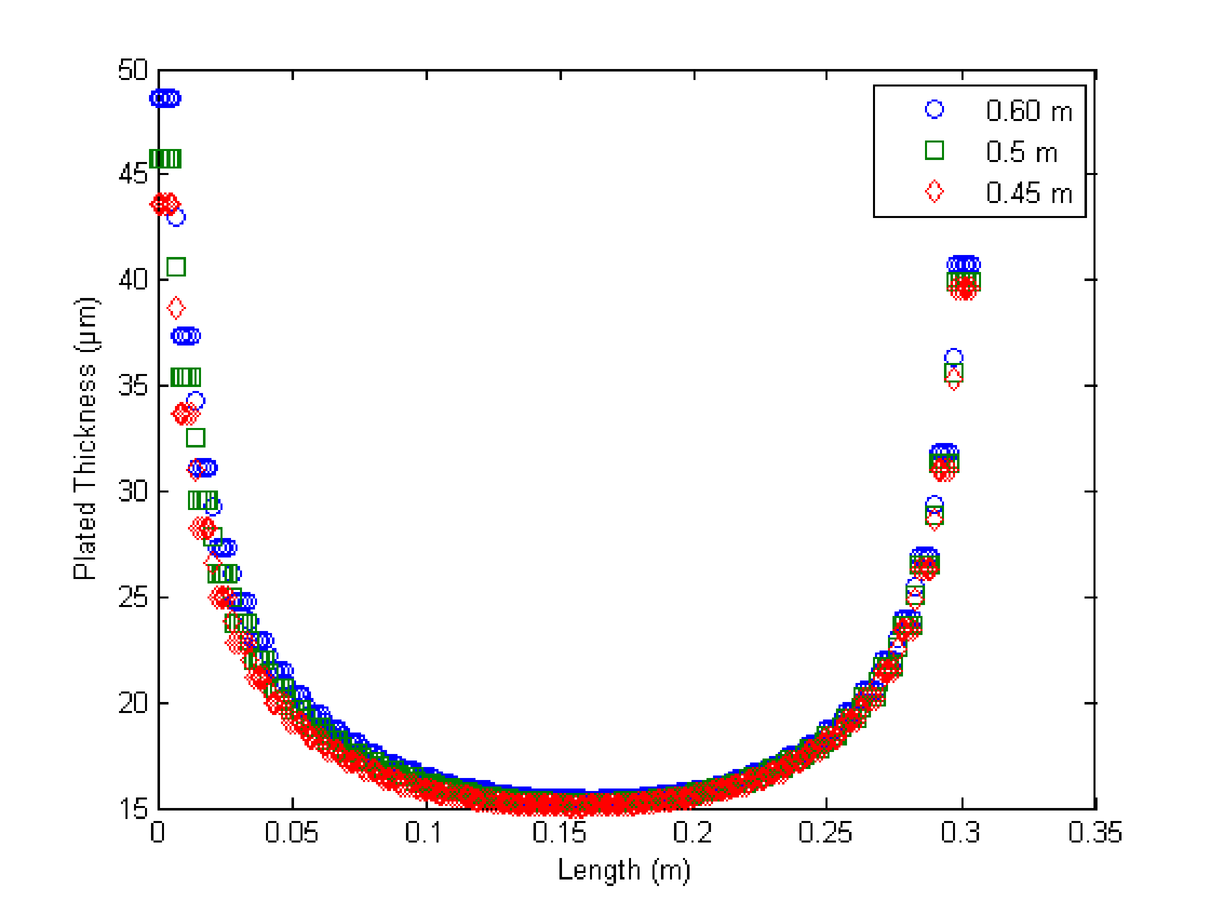
Anode - Cathode Spacing



↓ Spacing ↑ plating thickness

Excerpt from the Proceedings of the 2013 COMSOL Conference in Boston

Anode Height



Anode Height has negligible effect

Excerpt from the Proceedings of the 2013 COMSOL Conference in Boston

Mid-point Thickness

$$Y = 17.2228 + 14.3433X_1 - 11.3053X_2 + 0.4275X_3$$

Parameter	Effect
Conductivity (X_1)	Largest effect on mid-point thickness Increasing conductivity increases mid-point thickness
Anode-Cathode Spacing (X_2)	Increasing anode-cathode spacing decreases the mid-point thickness
Anode Height (X_3)	Negligible effect on mid-point thickness

Non-Uniformity

$$Y = 8.3610 + 8.3350X_1 - 4.2206X_2 + 1.6113X_3$$

Parameter	Effect
Conductivity (X_1)	Increasing conductivity decreases uniformity
Anode-Cathode Spacing (X_2)	Decreasing anode-cathode spacing decreases uniformity
Anode Height (X_3)	Small effect on uniformity Increasing anode height decreases the uniformity

Conclusions

Conclusions

- The model indicates uneven plating thickness across the height of the cathode
- The model must be modified to better incorporate effects of anode height
- Process parameters, such as solution conductivity and anode-cathode spacing, have significant effect on chrome plating

Next Steps

- Tertiary Nernst-Planck interface
  - Incorporate concentration overpotential
  - Removes the assumption of fully mixed solution

- Account for effects of bubbling on mass transfer

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Questions?