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A 2D Axisymmetric Electrodeposition Model

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- Widely Employed Technology

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- Nanotechnology
- etc.

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- Based on Fick's Law {3} plus Electrostatic Forces

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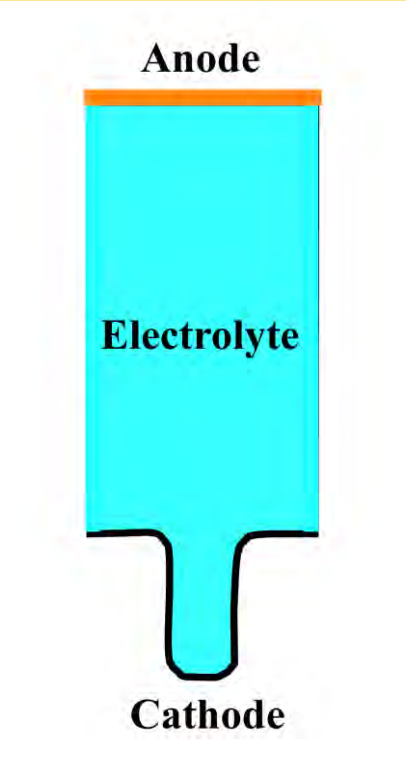

This 2D Axisymmetric Electrodeposition Model:

Governing Processes: Nernst-Planck Equation

$$N_i = \square D_i \square c_i \square z_i u_i F c_i \square V$$

Where: N_i = mass transport vector [mol/(m^2*s)]
D_i = Diffusivity of the i^{th} species in the electrolyte [m^2/s]
c_i = Concentration of the i^{th} species in the electrolyte [mol/m^3]
z_i = Charge of the i^{th} species in the electrolyte [1] (unitless)
u_i = Mobility of the i^{th} species in the electrolyte [(mol*m^2)/(J*s)]
F = Faraday's constant [A*s/mol]
V = Potential in the fluid [V]

This 2D Axisymmetric Electrodeposition Model:

Governing Processes: Nernst-Planck Equation

The mobility u_i of the i^{th} species can be expressed as:

$$u_i = \frac{D_i}{RT}$$

Where: D_i = Diffusivity of the i^{th} species in the electrolyte [m^2/s]
R = Universal gas constant 8.31447[J/mol*K]
T = Temperature [K]

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Governing Processes: Nernst-Planck Equation

The material balances for each species are expressed as:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i$$

Where: c_i = Concentration of the i^{th} species in the electrolyte [mol/m^3]
N$_i$ = mass transport vector [mol/(m^2*s)]
t = time [t]

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Governing Processes: Nernst-Planck Equation

The electroneutrality condition is given as follows:

$$\sum_i z_i c_i = 0$$

Where: z_i = Charge of the i[th] species in the electrolyte [1] (unitless)
c_i = Concentration of the i[th] species in the electrolyte [mol/m^3]

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Governing Processes: Butler-Volmer Equation {4}

The boundary conditions at the anode and the cathode are determined by the assumed electrochemical reaction and the Butler-Volmer equation.

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They are: $Cu^{2+} + e^{-} = Cu^{+}$ and $Cu^{+} + e^{-} = Cu$.

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(Typically, since not all things are equal and it is known that the Rate Determining Step (RDS) (slowest) is the $Cu^{2+}+e^{-} = Cu^{+}$, by about a factor of 1000 {5}.)

It is also herein assumed that the $Cu^{2+}+e^{-} = Cu^{+}$ step is in equilibrium.

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Governing Processes: Butler-Volmer Equation {4}

That being the case, then the cathode mass transport is:

$$N_{Cu^{2+}} \cdot n = \frac{i_0}{2F}\left(\exp\left(\frac{1.5F\eta_{cat}}{RT}\right) - \frac{c_{Cu^{2+}}}{c_{Cu^{2+},ref}}\exp\left(\frac{-0.5F\eta_{cat}}{RT}\right)\right)$$

Where: $\mathbf{N}_i$ = mass transport vector [mol/(m^2*s)]

n = normal vector

i_0 = Exchange current density [A/m^2]

R = Universal gas constant [J/(mol*K)]

$c_{Cu^{2+}}$ = Concentration of the Cu^{2+} species in the electrolyte [mol/m^3]

$c_{Cu^{2+},ref}$ = Reference concentration of the Cu^{2+} species in the electrolyte [mol/m^3]

η_{cat} = Cathode overpotential [V]

F = Faraday's constant [A*s/mol]

T = Temperature [K]

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It then follows that, the anode mass transport is:

$$N_{Cu^{2+}} \cdot n = \frac{i_0}{2F}\left(\exp\left(\frac{1.5F\eta_{an}}{RT}\right) - \frac{c_{Cu^{2+}}}{c_{Cu^{2+},ref}}\exp\left(\frac{-0.5F\eta_{an}}{RT}\right)\right)$$

Where: $\mathbf{N}_i$ = mass transport vector [mol/(m^2*s)]

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i_0 = Exchange current density [A/m^2]

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η_{an} = Anode overpotential [V]

F = Faraday’s constant [A*s/mol]

T = Temperature [K]

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Governing Processes: Butler-Volmer Equation {4}

For the insulating boundaries, where the mass transport is zero:

$$N_{Cu^{2+}} \cdot n = 0$$

Where: $\mathbf{N}_{Cu}{}^{2+}$ = mass transport vector [mol/(m^2*s)]
n = normal vector

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Governing Processes: Butler-Volmer Equation {4}

For sulfate ions, the insulating condition applies everywhere, thus:

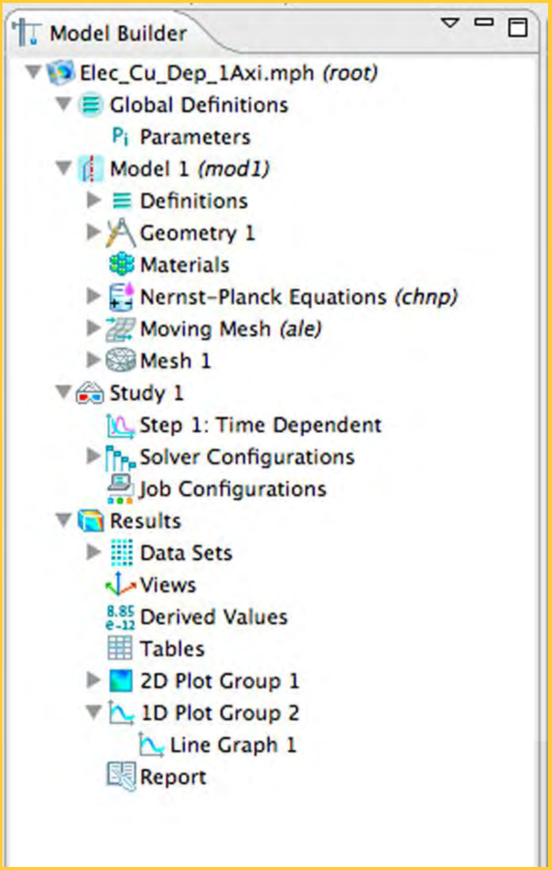
$$N_{SO_4^{2-}} \cdot n = 0$$

Where: $\mathbf{N}_{SO4}{}^{2+}$ = Mass Transport Vector [mol/(m^2*s)]
n = normal vector

This 2D Axisymmetric Electrodeposition Model:

Building the 2D Axisymmetric Electrodeposition Model

Model Builder Chart



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Global Parameters

Name	Expression	Description
Cinit	500 [mol/(m^3)]	Initial concentration
T0	298[K]	System temperature
i0	150[A/m^2]	Exchange current density
phi_eq	0[V]	Relative equilibrium potential
alpha	0.75[1]	Symmetry factor
phi_s_anode	0.0859[V]	Anode potential
phi_s_cathode	-0.0859[V]	Cathode potential
z_net	2[1]	Net species charge
z_c1	z_net[1]	Charge, species c1
z_c2	-z_net[1]	Charge, species c2
um_c1	D_c1/R_const/T0	Mobility, species c1
um_c2	um_c1	Mobility, species c2
MCu	63.546e-3[kg/mol]	Cu molar mass
rhoCu	7.7264e3[kg/m^3]	Cu density
D_c1	2e-9[m^2/s]	Diffusivity
alpha1	0.5[1]	Symmetry factor
alpha2	1.5[1]	Diffusivity
D_c2	D_c1	Symmetry factor

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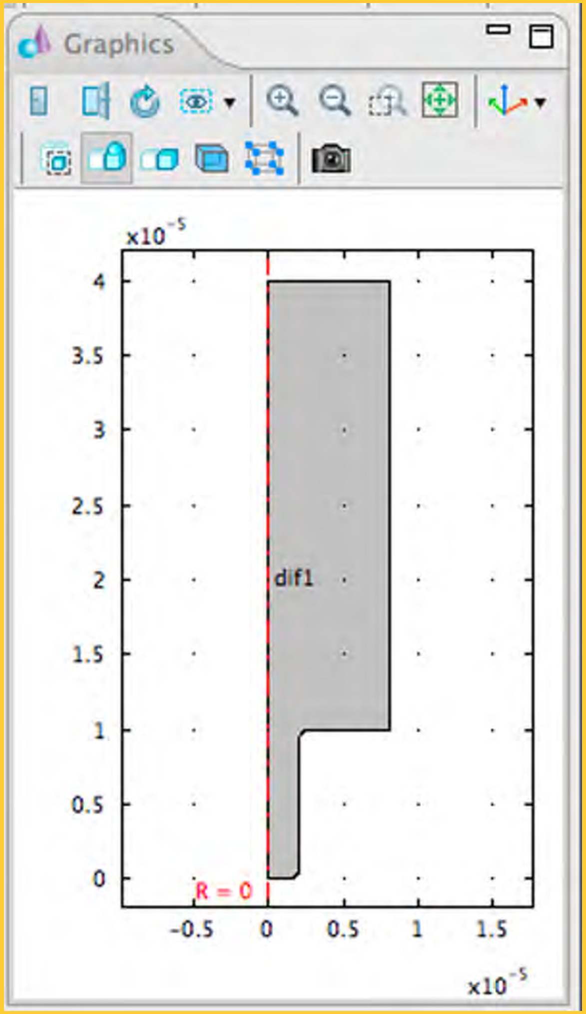
Model Geometry



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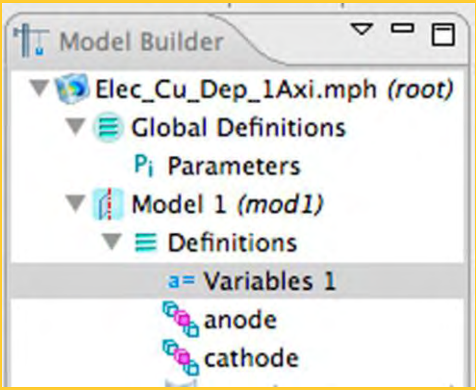
Local Variables



Name	Expression	Description
i_anode	i0*(exp(alpha*z_net*F_const/R_const/T0*(phi_s_anode-V-phi_eq))-c1/Cinit*exp(-alpha1*z_net*F_const/R_const/T0*(phi_s_anode-V-phi_eq)))	Anode current density
i_cathode	i0*(exp(alpha2*z_net*F_const/R_const/T0*(phi_s_cathode-V-phi_eq))-c1/Cinit*exp(-alpha1*z_net*F_const/R_const/T0*(phi_s_cathode-V-phi_eq)))	Cathode current density
growth	i_cathode*MCu/rhoCu/z_net/F_const	Deposition rate, cathode
n_growth	i_anode*MCu/rhoCu/z_net/F_const	Deposition rate, anode
displ_r	abs(r-R)	Absolute displacement in r direction

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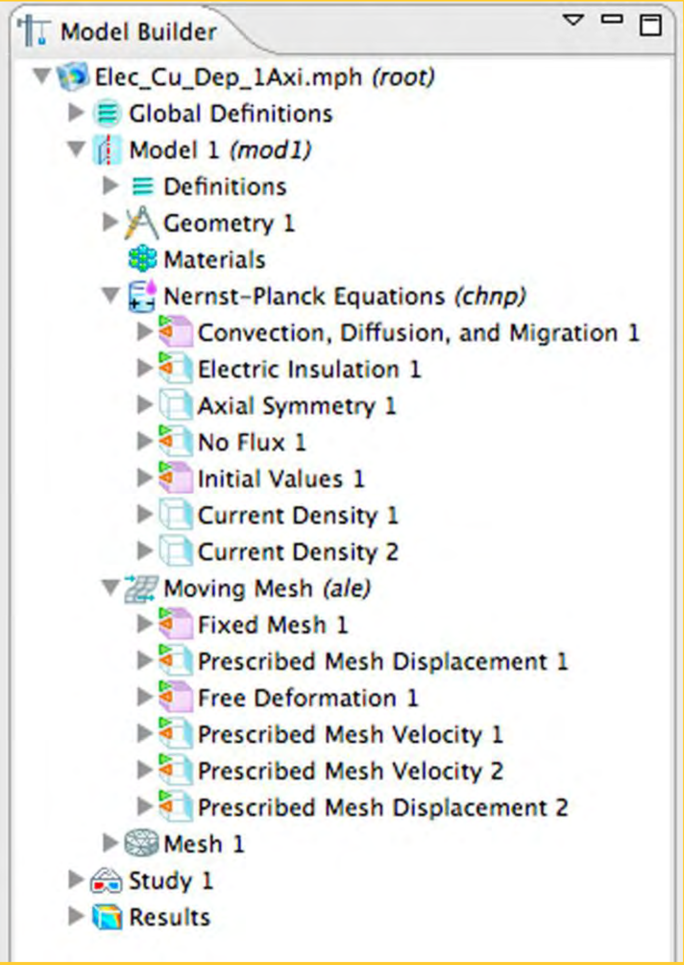
Domain and Boundary Specifications



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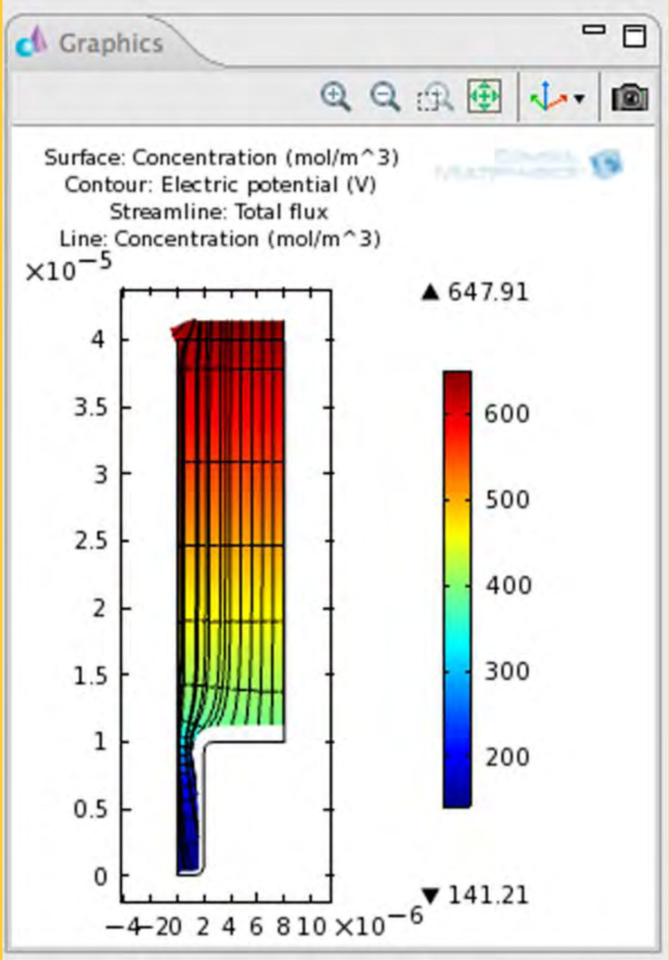
Results

Converged Model



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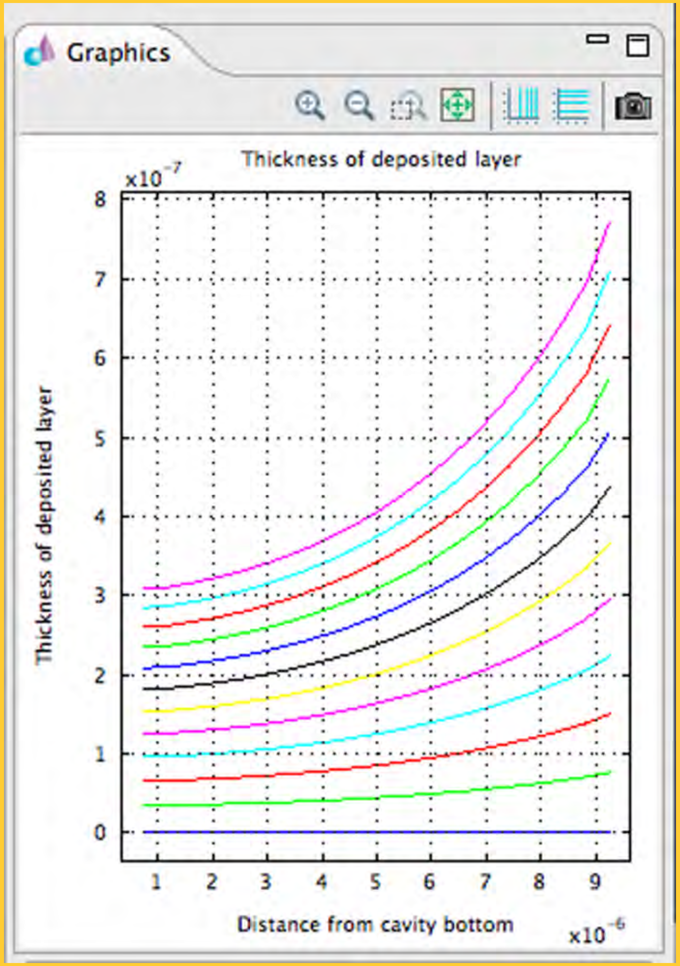
Electrodeposition Thickness



This 2D Axisymmetric Electrodeposition Model:

Conclusions

COMSOL Multiphysics 4.x works well for the modeling of electrodeposition problems.

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References

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Thank You!