A 2D Axisymmetric Electrodeposition Model

Roger W. Pryor, Ph.D.
Pryor Knowledge Systems, Inc.
4918 Malibu Drive Bloomfield Hills, MI 48302

Abstract: Electroplating is a vital technology widely employed for many technological applications ranging from decorative or anti-corrosion coatings to high precision nanotechnology passive electromagnetic cloaking devices. This 2D Axisymmetric Electroplating Model demonstrates one of the modeling methodologies that can be used to calculate the transient generation of a coating thickness of a deposited metal layer on the cathode electrode well in a copper-electroplating bath. This model computes the mass transport and deposition on the electrode of copper ions through the fluid medium, thus resulting in the transient calculation of the electrodeposition (electroplating) of a new copper layer.

Keywords: electroplating, nanotechnology, cloaking, electrodeposition, coating thickness.

1. Introduction

Electrodeposition is a critical technology that is widely employed for many diverse technological applications ranging from decorative or anti-corrosion coatings to high precision nanotechnology passive electromagnetic cloaking devices.

This 2D Axisymmetric Electroplating Model demonstrates one of the transient modeling methodologies that can be used to calculate the coating thickness of the deposited metal layer on the cathode electrode for a well structure immersed in a copper-electroplating bath (Figure 1).

This model computes the mass transport and deposition on the well structure electrode of copper ions through the fluid medium, thus resulting in the transient calculation of the electrodeposition (electroplating) of a new copper layer.

2. The COMSOL Multiphysics Model

There is a very large literature of specific, experimentally detailed electroplating processes just for copper and copper alloys [1]. Many of those highly detailed books have been written such that they include specific solution process chemistry and time/power process details.

The object of this 2D Axisymmetric model is to demonstrate specifically, on a first approximation basis, the modeling of an example of the copper sulfate electroplating process, where the bath acidity (pH 4) is in the moderate range. Many of the more common electroplating processes utilize consumable anodes (copper) as the source of copper ion replenishment for the electroplating bath.

Since in this case the model is for a first approximation to the copper electroplating process, trace additives that are typically included in the bath to improve the second order properties of the deposited copper (brightness, porosity, adhesion, etc.) are not included within this model.

The inclusion of additional trace additives and the related ions will significantly increase the difficulty of building and solving the model. That inclusion of process detail will not necessarily expand or clarify the desired fundamental understanding sought by building a model of the electroplating process.

This model is set up as a two-dimensional axisymmetric time-dependent model. It employs the Nernst-Planck Equation (chnp) found in the Chemical Species Transport physics interface in conjunction with the Moving Mesh (ale) technique found in the Mathematics Interface. The Nernst-Planck Equation governs the ionic mass transport process that occurs in the fluid electrol-
lyte. The Nernst-Planck Equation is a conservation of mass equation and is an extension of Fick's Law of diffusion to include electrostatic forces. The Moving Mesh tracks the growth of the copper layer.

3. Governing Process

The Nernst-Planck Equation (2) specifies the ionic mass transport process that occurs in the fluid electrolyte. The Nernst-Planck Equation is a conservation of mass equation and is an extension of Fick's Law of diffusion (3) to include electrostatic forces.

The flux of each of the ions in the electrolyte is given by the Nernst-Planck equation as follows:

\[ N_i = -D_i \nabla c_i - z_i u_i F c_i \nabla V \]  

(1)

Where:

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

And the mobility \( u_i \) can be expressed as:

\[ u_i = \frac{D_i}{RT} \]  

(2)

Where:

- \( D_i \) = Diffusivity of the \( i \)th species in the electrolyte \([\text{m}^2/\text{s}]\)
- \( R \) = Universal gas constant \([\text{J}/\text{mol} \cdot \text{K}]\)
- \( T \) = Temperature \([\text{K}]\)

The material balances for each species are expressed as:

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

(3)

Where:

- \( c_i \) = Concentration of the \( i \)th species in the electrolyte \([\text{mol}/\text{m}^3]\)
- \( N_i \) = mass transport vector \([\text{mol}/(\text{m}^2 \cdot \text{s})]\)
- \( t \) = time \([\text{t}]\)

The electroneutrality condition is given as follows:

\[ \sum_i z_i c_i = 0 \]  

(4)

Where:

- \( z_i \) = Charge of the \( i \)th species in the electrolyte \([\text{unitless}]\)
- \( c_i \) = Concentration of the \( i \)th species in the electrolyte \([\text{mol}/\text{m}^3]\)

The boundary conditions at the anode and the cathode are determined by the assumed electrochemical reaction and the Butler-Volmer equation (4).

In the case of building this model, the assumed electrochemical reaction by which copper is deposited on the cathode is as follows. There are two reactions that occur. They are: \( \text{Cu}^{2+} + e^- = \text{Cu}^+ \) and \( \text{Cu}^+ + e^- = \text{Cu} \). Typically, since not all things are equal and it is known that the Rate Determining Step (RDS) (slowest) is the \( \text{Cu}^{2+} + e^- = \text{Cu}^+ \) step is in equilibrium.

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

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

(5)

Where:

- \( N_i \) = mass transport vector \([\text{mol}/(\text{m}^2 \cdot \text{s})]\)
- \( n \) = normal vector
- \( i_0 \) = Exchange current density \([\text{A}/\text{m}^2]\)
- \( R \) = Universal gas constant \([\text{J}/\text{mol} \cdot \text{K}]\)
- \( T \) = Temperature \([\text{K}]\)
- \( c_{\text{Cu}^{2+}} \) = Concentration of the \( \text{Cu}^{2+} \) species in the electrolyte \([\text{mol}/\text{m}^3]\)
- \( c_{\text{Cu}^{2+}}^{\text{ref}} \) = Reference concentration of the \( \text{Cu}^{2+} \) species in the electrolyte \([\text{mol}/\text{m}^3]\)
- \( \eta_{\text{cat}} \) = Cathode overpotential \([\text{V}]\)
- \( F \) = Faraday’s constant \([\text{A} \cdot \text{s}/\text{mol}]\)
- \( T \) = Temperature \([\text{K}]\)
It also follows from the above then that, the anode mass transport is:

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

(6)

Where: \( N_i \) = mass transport vector \([\text{mol}/(\text{m}^2\cdot\text{s})]\)
\( n \) = normal vector
\( i_0 \) = Exchange current density \([\text{A}/\text{m}^2]\)
\( R \) = Universal gas constant \([\text{J}/(\text{mol} \cdot \text{K})]\)
\( c_{\text{Cu}^{2+}} \) = Concentration of the \( \text{Cu}^{2+} \) species in the electrolyte \([\text{mol}/\text{m}^3]\)
\( c_{\text{Cu}^{2+}}^{\text{ref}} \) = Reference concentration of the \( \text{Cu}^{2+} \) species in the electrolyte \([\text{mol}/\text{m}^3]\)
\( \eta_{an} \) = Anode overpotential \([\text{V}]\)
\( F \) = Faraday’s constant \([\text{A} \cdot \text{s}/\text{mol}]\)
\( T \) = Temperature \([\text{K}]\)

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

\[
N_{\text{Cu}^{2+}} \cdot n = 0
\]

(7)

Where: \( N_{\text{Cu}^{2+}} \) = mass transport vector \([\text{mol}/(\text{m}^2\cdot\text{s})]\)
\( n \) = normal vector

And for sulfate ions, the insulating applies everywhere, thus,

\[
N_{\text{SO}_4^{2-}} \cdot n = 0
\]

(8)

Where: \( N_{\text{SO}_4^{2-}} \) = Mass Transport Vector \([\text{mol}/(\text{m}^2\cdot\text{s})]\)
\( n \) = normal vector

4. Building the Model

Figure 2 shows the Model Builder flow chart from the completed 2D Axisymmetric Electrodeposition Model. The Model Builder flowchart shows that this model is set up as a two-dimensional axisymmetric time-dependent model. It employs the physics of the Nernst-Planck Equation (chnp) found in the Chemical Species Transport physics interface in conjunction with the Moving Mesh (ale) technique found in the Mathematics Interface.

![Model Builder flow chart](image)

**Table 1: Global Parameters**

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

Now that the Parameters have been entered, the model geometry can be built as shown in Figure 3.

![Figure 3](image)

**Figure 3.** 2D Axisymmetric Electrodeposition Model Geometry

Once the geometry has been completed, the local variables are added to the model by entry in the Variables 1 edit field, as indicated in Figure 4.

![Figure 4](image)

**Figure 4.** Local Variables, Variable 1.

The expressions are indicated in Table 2.

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

**Table 2: Local Variables**

5. Specifying the Modeling Conditions

One of the most important parts of any model is the definition and specification of the condition within the domains and at the boundaries of the model. Each physics interface requires a set of conditions that define the behavior of the media within and at each boundary.

As discussed in section 3 of this paper, the appropriate parameters and variable expressions need to be entered in subsections of the Nernst-Planck Equations Interface (chnp) and the Moving Mesh Interface (ale) as shown in Figure 5.
6. Results

The model, once configured, runs to convergence quickly. The converged result is shown in Figure 6.

Figure 6. 2D Axisymmetric Electrodeposition Model.

Figure 7 shows the thickness of the copper coating as a function of distance from the bottom of the cavity.

7. Conclusions

COMSOL Multiphysics 4.x works well for the solution of electrodeposition and many other types of multiphysics problems.

8. References