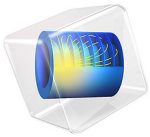

Copper Electroless Deposition

This model is licensed under the COMSOL Software License Agreement 6.1.
All trademarks are the property of their respective owners. See www.comsol.com/trademarks.

Introduction

In the electroless deposition, partial oxidation and reduction reactions occur simultaneously at the same position at the electrode surface. The difference between the equilibrium potentials for the two reactions is hence the driving force for the deposition process. The potential at the electrode surface is estimated from the mixed potential theory so that the total anode current density is equal and opposite to the total cathode current density (Ref. 1 and Ref. 2). Since the sum of all reaction current densities sum up to zero locally on the surface, the electroless deposition can be used for plating on objects with low electric conductivity (for instance, plastics).

This model simulates copper electroless deposition wherein copper reduction is a cathodic reaction and formaldehyde oxidation is an anodic reaction. The model accounts for mass transport by diffusion and electrochemical reactions at the electrode surface. The equilibrium potentials of partial electrochemical reactions are considered to be concentration dependent. The model estimates the change in current density, deposition thickness, and concentration of ionic species during the electroless deposition.

Model Definition

The model is solved over a 1D computational domain that consists of a diffusion layer with an electrode surface at one end and a bulk electrolyte at the other end, as shown in Figure 1. The diffusion layer thickness is set to 2 mm.

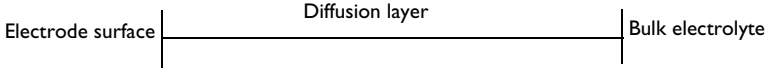

Figure 1: Description of the boundary layer adjacent to the steel surface.

Mass transport by diffusion for five ionic species is solved using the **Electroanalysis** physics interface:

$$\begin{aligned} \mathbf{N}_i &= -D_i \nabla c_i \\ \frac{\partial c_i}{\partial t} &+ \nabla \cdot \mathbf{N} = 0 \end{aligned} \tag{1}$$

where c_i (mol/m^3) is the concentration, $\mathbf{N}_i$ (mol/(m^2·s)) is the flux vector, D_i (m^2/s) is the diffusion coefficient, and subscript i indicates i^{th} species. All species are assumed to be

diluted in water. The species along with their diffusion coefficients and initial concentrations are tabulated in Table 1.

TABLE 1: MODELED SPECIES WITH THEIR RESPECTIVE DIFFUSION COEFFICIENTS (Ref. 1).

Species	D (m^2/s)·10^9	c_{ref} (mol/m^3)·10^{-3}
$Cu(OH)_2L_2^{-4}$	0.7	0.1
HCHO	1.2	0.05
$HCOO^-$	1.454	0
OH^-	5.273	0.0316
L^{-2}	0.794	0.075

Concentration at the bulk electrolyte boundary is set to the reference concentration as tabulated in Table 1.

$$c = c_{\text{ref}} \tag{2}$$

At the electrode surface boundary, an **Electrode Surface** boundary condition is used wherein the total current is set to 0. This boundary condition yields a constant potential, $\phi_{s,\text{ ext}}$, at the electrode surface boundary, which satisfies the condition:

$$\int (\mathbf{n} \cdot \mathbf{i}_l) dl = 0 \tag{3}$$

where

$$\mathbf{n} \cdot \mathbf{i}_l = \sum_m i_{\text{loc},m} \tag{4}$$

The initial value for the boundary electric potentials is set to –0.65 V.

ELECTROCHEMICAL REACTIONS

The following electrochemical reactions occur at the electrode surface:

Copper reduction

$$Cu(OH)_2L_2^{-4} + 2e^- \rightarrow Cu + 2OH^- + 2L^{-2} \qquad E^0_{\text{eq, Cu}} = -0.52\,V \tag{5}$$

Formaldehyde oxidation

$$2HCHO + 4OH^- \rightarrow 2HCOO^- + H_2 + 2H_2O + 2e^- \qquad E^0_{\text{eq, HCHO}} = -1.04\,V \tag{6}$$

Concentration dependent kinetics is used to model copper reduction and formaldehyde oxidation reactions, which will set the local current density according to

$$i_{\text{loc, m}} = i_{0,\text{m}}\left(C_{\text{R,m}}\exp\left(\frac{0.5F\eta_{\text{m}}}{RT}\right) - C_{\text{O,m}}\exp\left(-\frac{0.5F\eta_{\text{m}}}{RT}\right)\right) \tag{7}$$

where $i_{0,\text{m}}$ is the exchange current density, $C_{\text{R,m}}$ is the reduced species expression, $C_{\text{O,m}}$ is the oxidized species expression and $\eta_{,\text{m}}$ is the overpotential for species m (Cu and HCHO, respectively).

The overpotential $\eta_{,\text{m}}$ (V) is calculated from

$$\eta_{\text{m}} = \phi_{s,\text{ ext}} - \phi_l - E_{\text{eq, m}} \tag{8}$$

The equilibrium potentials for the copper reduction and formaldehyde oxidation reactions are calculated using the Nernst equation,

$$E_{\text{eq,Cu}} = E^0_{\text{eq, Cu}} + \frac{RT}{nF}\ln\frac{[\text{Cu(OH)}_2\text{L}_2^{-4}]}{[\text{OH}^-]^2[\text{L}^{-2}]^2} \tag{9}$$

$$E_{\text{eq,HCHO}} = E^0_{\text{eq, HCHO}} + \frac{RT}{nF}\ln\frac{[\text{HCOO}^-]^2}{[\text{OH}^-]^4[\text{HCHO}]^2} \tag{10}$$

At the electrode surface boundary, fluxes of ionic species are defined in terms of the electrochemical reactions as

$$\mathbf{n}\cdot\mathbf{N}_j = \frac{\nu_j i_j}{n_j F} \tag{11}$$

where ν_j is the stoichiometric coefficient, i_j is the local current density, n_j is the number of electrons and F is Faraday's constant (96485 C/mol). The subscript j signifies the j^{th} electrochemical reaction. This will set the flux to be proportional to the electrode current density according to Faraday's law. The electrode kinetics parameters: $i_{0,\text{Cu}}$=1 A/m^2 and $i_{0,\text{HCHO}}$=1 A/m^2 are taken from the current-potential curves reported in Ref. 2.

Results and Discussion

Figure 2 shows the change in the mixed potential at the electrode surface during electroless deposition. It can be seen that the change is significant during the initial stages of deposition, which is attributed to the equilibrium potentials of copper reduction and

formaldehyde oxidation reactions, and the constraint of equal and opposite anode and cathode current densities. At about 400 s the potential reaches a maximum.

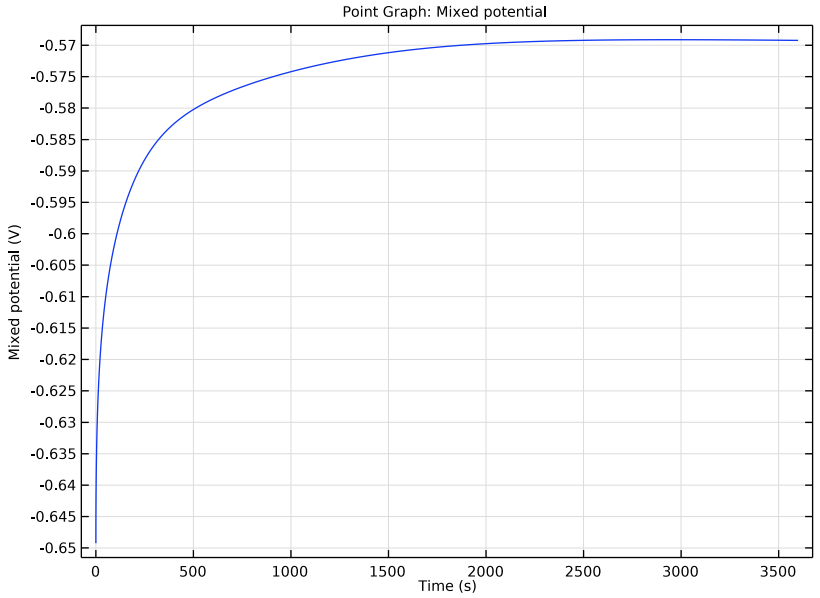

Figure 2: The change in the mixed potential at the electrode surface against time during electroless deposition.

Figure 3 shows the change in the local current density at the electrode surface during electroless deposition. It can be seen that the current density is considerably increased in the initial stages of electroless deposition, corresponding to the trend observed for the mixed potential in Figure 2.

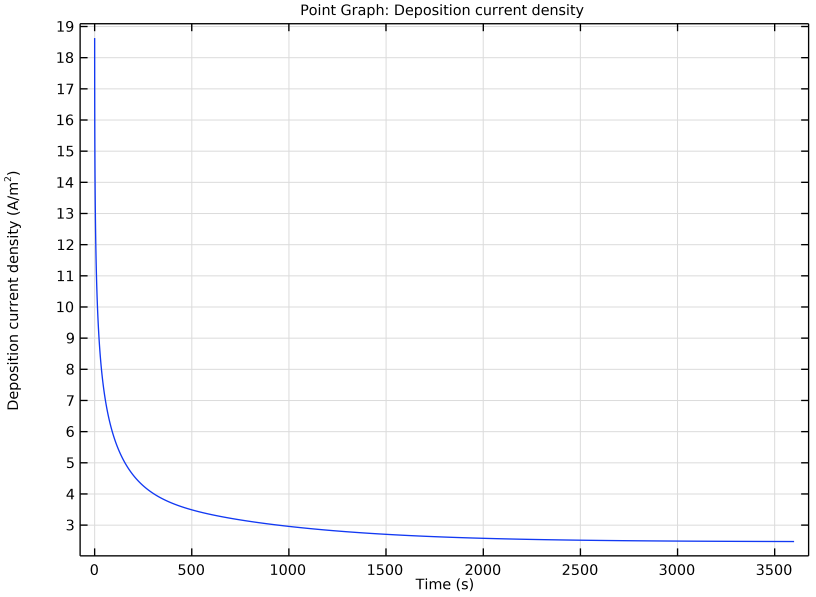

Figure 3: The change in the local current density at the electrode surface against time during electroless deposition.

Figure 4 shows the change in the deposition thickness at the electrode surface during electroless deposition. It can be seen that after approximately 400 s, the increase in electroless plating thickness is almost linear with time.

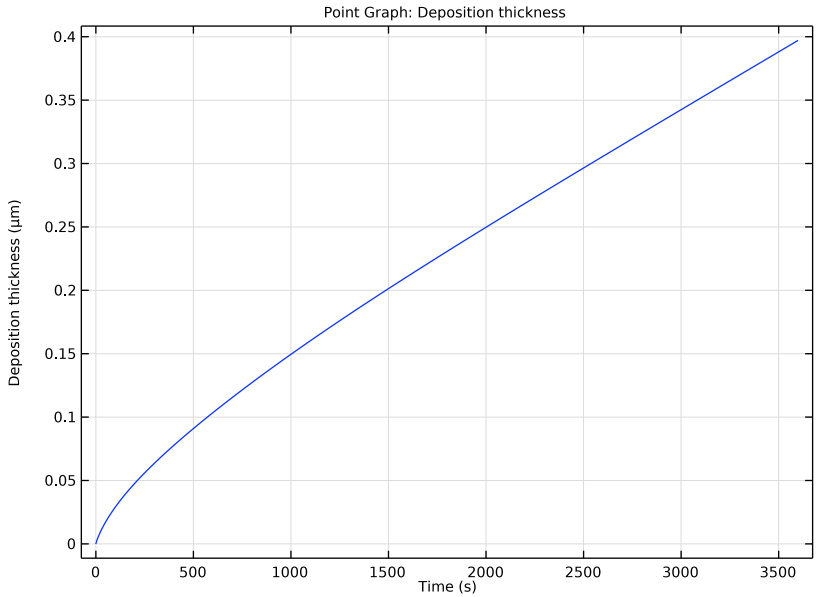

Figure 4: The change in the deposition thickness at the electrode surface against time during electroless deposition.

Figure 5 shows the change in the normalized concentration of various ionic species at the electrode surface during electroless deposition. It can be seen that the concentrations of the copper complex and formaldehyde species decrease with time, since they are consumed

during the deposition. The free tartrate ligand (L^{-2}) concentration increases with time since it is produced in the deposition process.

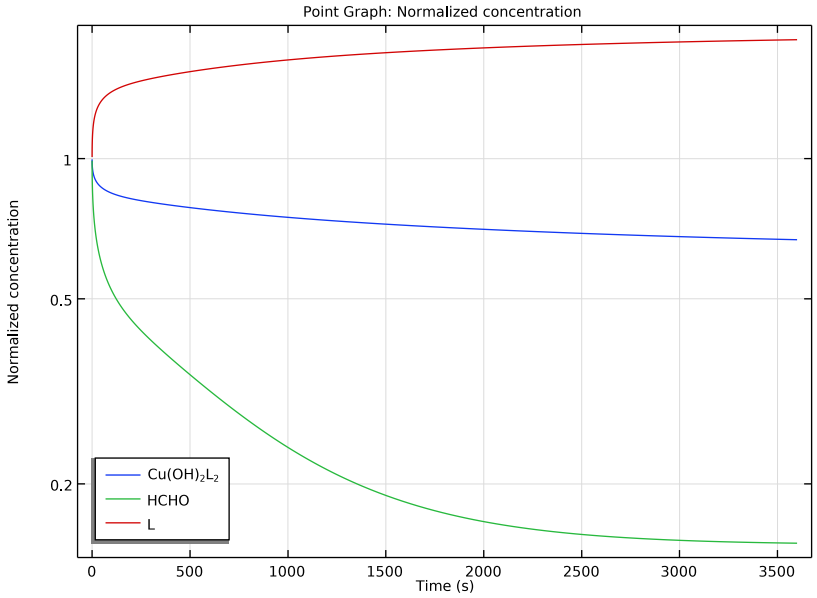

Figure 5: The change in the normalized concentration at the electrode surface against time during electroless deposition.

References

1. M. Ramasubramanian, B.N. Popov, R.E. White, and K.S. Chen, "A Mathematical Model for Electroless Copper Deposition on Planar Substrates", *Journal of The Electrochemical Society*, vol. 146, no. 1, pp. 111–116, 1999.

2. M. Paunovich and M. Schlesinger, *Fundamentals of electrochemical deposition, 2nd edition, Chapter 8*, Wiley-Interscience, a John Wiley & Sons, Inc. Publication, 2006.

Application Library path: `Electrodeposition_Module/Tutorials/cu_electroless_deposition`

From the **File** menu, choose **New**.

NEW

In the **New** window, click **Model Wizard**.

MODEL WIZARD

1 In the **Model Wizard** window, click **1D**.

2 In the **Select Physics** tree, select **Electrochemistry>Electroanalysis (tcd)**.

3 Click **Add**.

4 In the **Number of species** text field, type 4.

5 In the **Concentrations** table, enter the following settings:

cCuOH2L2
cHCHO
cOH
cL

6 Click **Study**.

7 In the **Select Study** tree, select **General Studies>Time Dependent**.

8 Click **Done**.

GLOBAL DEFINITIONS

Load the model parameters from a text file.

Parameters 1

1 In the **Model Builder** window, under **Global Definitions** click **Parameters 1**.

2 In the **Settings** window for **Parameters**, locate the **Parameters** section.

3 Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `cu_electroless_deposition_parameters.txt`.

GEOMETRY 1

The geometry consists of a single interval.

Interval 1 (i1)

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Geometry 1** and choose **Interval**.

2 In the **Model Builder** window, expand the **Geometry 1** node, then click **Interval 1 (i1)**.

3 In the **Settings** window for **Interval**, locate the **Interval** section.

4 In the table, enter the following settings:

Coordinates (m)
0
2 [mm]

5 Click **Build All Objects**.

ELECTROANALYSIS (TCD)

Start defining the physics.

Electrolyte 1

1 In the **Model Builder** window, under **Component 1 (comp1)>Electroanalysis (tcd)** click **Electrolyte 1**.

2 In the **Settings** window for **Electrolyte**, locate the **Diffusion** section.

3 In the D_{cCuOH2L2} text field, type `DCuOH2L2`.

4 In the D_{cHCHO} text field, type `DHCHO`.

5 In the D_{cOH} text field, type `DOH`.

6 In the D_{cL} text field, type `DL`.

Initial Values 1

Set the initial values to the bulk equilibrium concentration.

1 In the **Model Builder** window, click **Initial Values 1**.

2 In the **Settings** window for **Initial Values**, locate the **Initial Values** section.

3 In the $cCuOH2L2$ text field, type `cCuOH2L20`.

4 In the $cHCHO$ text field, type `cHCHO0`.

5 In the cOH text field, type `cOH0`.

6 In the cL text field, type `cL0`.

Concentration 1

Similarly, now set the concentrations at the bulk electrolyte boundary to the equilibrium concentrations.

1 In the **Physics** toolbar, click **Boundaries** and choose **Concentration**.

2 Select Boundary 2 only.

3 In the **Settings** window for **Concentration**, locate the **Concentration** section.

4 Select the **Species cCuOH2L2** check box.

5 In the $c_{0,\mathrm{cCuOH2L2}}$ text field, type `cCuOH2L20`.

6 Select the **Species cHCHO** check box.

7 In the $c_{0,\mathrm{cHCHO}}$ text field, type `cHCHO0`.

8 Select the **Species cOH** check box.

9 In the $c_{0,\mathrm{cOH}}$ text field, type `cOH0`.

10 Select the **Species cL** check box.

11 In the $c_{0,\mathrm{cL}}$ text field, type `cL0`.

Electrode Surface 1

Now define the electrode surface. Set the total current to zero at the Electrode Surface, define the depositing species properties, and the copper reduction and formaldehyde oxidation electrode reactions.

1 In the **Physics** toolbar, click **Boundaries** and choose **Electrode Surface**.

2 Select Boundary 1 only.

3 In the **Settings** window for **Electrode Surface**, click to expand the **Dissolving-Depositing Species** section.

4 Click **Add**.

5 In the table, enter the following settings:

Species	Density (kg/m^3)	Molar mass (kg/mol)
Cu	rho_Cu	MW_Cu

6 Locate the **Electrode Phase Potential Condition** section. From the **Electrode phase potential condition** list, choose **Total current**.

7 In the $I_{\mathrm{l,total}}$ text field, type `0`.

8 In the $\phi_{\mathrm{s,ext,init}}$ text field, type `-0.65[V]`.

Electrode Reaction 1

1 In the **Model Builder** window, click **Electrode Reaction 1**.

2 In the **Settings** window for **Electrode Reaction**, locate the **Stoichiometric Coefficients** section.

3 In the $\nu_{cCuOH2L2}$ text field, type `-1/2`.

4 In the ν_{cOH} text field, type `1`.

5 In the ν_{cL} text field, type `1`.

6 In the **Stoichiometric coefficients for dissolving-depositing species:** table, enter the following settings:

Species	Stoichiometric coefficient (1)
Cu	1/2

7 Locate the **Equilibrium Potential** section. In the $E_{eq,ref}(T)$ text field, type `Eeq0_Cu`.

8 Click to expand the **Reference Concentrations** section. In the table, enter the following settings:

Electrolyte species	Reference concentrations (mol/m^3)
cCuOH2L2	`cCu0H2L20`
cOH	`cOH0`
cL	`cL0`

9 Locate the **Electrode Kinetics** section. In the $i_{0,ref}(T)$ text field, type `i0_Cu`.

10 In the α_a text field, type `1-alphac_Cu`.

Electrode Surface 1

In the **Model Builder** window, click **Electrode Surface 1**.

Electrode Reaction 2

1 In the **Physics** toolbar, click **Attributes** and choose **Electrode Reaction**.

2 In the **Settings** window for **Electrode Reaction**, locate the **Stoichiometric Coefficients** section.

3 In the ν_{cHCHO} text field, type `1`.

4 In the ν_{cOH} text field, type `2`.

5 Locate the **Equilibrium Potential** section. From the E_{eq} list, choose **User defined**. In the associated text field, type `Eeq0_HCHO`.

6 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Anodic Tafel equation**.

7 In the i_0 text field, type `i0_HCHO*(cOH/cOH0)^2*(cHCHO/cHCHO0)`.

8 In the A_a text field, type `Aa_HCHO`.

GLOBAL DEFINITIONS

Default Model Inputs

Set up the temperature value used in the entire model.

1 In the **Model Builder** window, under **Global Definitions** click **Default Model Inputs**.

2 In the **Settings** window for **Default Model Inputs**, locate the **Browse Model Inputs** section.

3 In the tree, select **General>Temperature (K) - minput.T**.

4 Find the **Expression for remaining selection** subsection. In the **Temperature** text field, type `T`.

MESH 1

Build a mesh with a finer resolution at the electrode surface.

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Mesh 1**.

2 In the **Settings** window for **Mesh**, locate the **Physics-Controlled Mesh** section.

3 From the **Element size** list, choose **Extremely fine**.

Size 1

1 Right-click **Component 1 (comp1)>Mesh 1** and choose **Size**.

2 In the **Settings** window for **Size**, locate the **Geometric Entity Selection** section.

3 From the **Geometric entity level** list, choose **Boundary**.

4 Select Boundary 1 only.

5 Locate the **Element Size** section. Click the **Custom** button.

6 Locate the **Element Size Parameters** section.

7 Select the **Maximum element size** check box. In the associated text field, type `2E-7`.

Edge 1

1 In the **Mesh** toolbar, click  **Edge**.

2 In the **Settings** window for **Edge**, click  **Build All**.

STUDY 1

Finally, set the time dependent solver settings and then the model is ready to run.

1 In the **Model Builder** window, click **Study 1**.

2 In the **Settings** window for **Study**, locate the **Study Settings** section.

3 Clear the **Generate default plots** check box.

Step 1: Time Dependent

1 In the **Model Builder** window, under **Study 1** click **Step 1: Time Dependent**.

2 In the **Settings** window for **Time Dependent**, locate the **Study Settings** section.

3 In the **Output times** text field, type `range(0,10,3600)`.

4 From the **Tolerance** list, choose **User controlled**.

5 In the **Relative tolerance** text field, type `1e-5`.

6 In the **Home** toolbar, click **Compute**.

RESULTS

The following reproduces the plots from the Results and Discussion section. First, plot the change in the mixed potential with time.

Mixed Potential

1 In the **Home** toolbar, click **Add Plot Group** and choose **1D Plot Group**.

2 In the **Settings** window for **1D Plot Group**, type `Mixed Potential` in the **Label** text field.

Point Graph 1

1 Right-click **Mixed Potential** and choose **Point Graph**.

2 Select Boundary 1 only.

3 In the **Settings** window for **Point Graph**, locate the **y-Axis Data** section.

4 In the **Expression** text field, type `tcd.phisext`.

5 Select the **Description** check box. In the associated text field, type `Mixed potential`.

6 Click to expand the **Title** section. From the **Title type** list, choose **Manual**.

7 In the **Title** text area, type `Point Graph: Mixed potential`.

8 In the **Mixed Potential** toolbar, click **Plot**.

Mixed Potential

Now, plot change in the deposition current density and deposition thickness with time.

Deposition Current Density

1 In the **Model Builder** window, right-click **Mixed Potential** and choose **Duplicate**.

2 In the **Settings** window for **1D Plot Group**, type `Deposition Current Density` in the **Label** text field.

Point Graph 1

1 In the **Model Builder** window, expand the **Deposition Current Density** node, then click **Point Graph 1**.

2 In the **Settings** window for **Point Graph**, locate the **y-Axis Data** section.

3 In the **Expression** text field, type `abs(tcd.iloc_er1)`.

4 In the **Description** text field, type `Deposition current density`.

5 Locate the **Title** section. In the **Title** text area, type `Point Graph: Deposition current density`.

6 In the **Deposition Current Density** toolbar, click **Plot**.

Deposition Thickness

1 In the **Model Builder** window, right-click **Mixed Potential** and choose **Duplicate**.

2 In the **Model Builder** window, click **Mixed Potential 1**.

3 In the **Settings** window for **1D Plot Group**, type `Deposition Thickness` in the **Label** text field.

Point Graph 1

1 In the **Model Builder** window, click **Point Graph 1**.

2 In the **Settings** window for **Point Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)> Electroanalysis>Dissolving-depositing species>tcd.sbtot - Total electrode thickness change - m**.

3 Locate the **y-Axis Data** section. From the **Unit** list, choose **µm**.

4 In the **Description** text field, type `Deposition thickness`.

5 Locate the **Title** section. In the **Title** text area, type `Point Graph: Deposition thickness`.

6 In the **Deposition Thickness** toolbar, click **Plot**.

Mixed Potential

Finally, plot change in the normalized concentration of selected species with time.

Normalized concentration

1 In the **Model Builder** window, right-click **Mixed Potential** and choose **Duplicate**.

2 In the **Settings** window for **1D Plot Group**, type `Normalized concentration` in the **Label** text field.

3 Locate the **Plot Settings** section.

4 Select the **y-axis label** check box. In the associated text field, type `Normalized concentration`.

5 Locate the **Axis** section. Select the **y-axis log scale** check box.

Point Graph 1

1 In the **Model Builder** window, expand the **Normalized concentration** node, then click **Point Graph 1**.

2 In the **Settings** window for **Point Graph**, locate the **y-Axis Data** section.

3 In the **Expression** text field, type `cCuOH2L2/cCuOH2L2O`.

4 Click to expand the **Legends** section. Select the **Show legends** check box.

5 From the **Legends** list, choose **Manual**.

6 In the table, enter the following settings:

Legends
`Cu(OH)<sub>2</sub>L<sub>2</sub>`

7 Locate the **Title** section. In the **Title** text area, type `Point Graph: Normalized concentration`.

Point Graph 2

1 Right-click **Results>Normalized concentration>Point Graph 1** and choose **Duplicate**.

2 In the **Settings** window for **Point Graph**, locate the **y-Axis Data** section.

3 In the **Expression** text field, type `cHCHO/cHCHOO`.

4 Locate the **Legends** section. In the table, enter the following settings:

Legends
HCHO

5 Locate the **Title** section. From the **Title type** list, choose **None**.

Point Graph 3

1 Right-click **Point Graph 2** and choose **Duplicate**.

2 In the **Settings** window for **Point Graph**, locate the **y-Axis Data** section.

3 In the **Expression** text field, type `cL/cLO`.

4 Locate the **Legends** section. In the table, enter the following settings:

Legends
L

5 In the **Normalized concentration** toolbar, click **Plot**.

Normalized concentration

1 In the **Model Builder** window, click **Normalized concentration**.

2 In the **Settings** window for **1D Plot Group**, locate the **Legend** section.

3 From the **Position** list, choose **Lower left**.