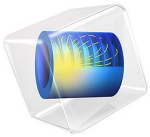

Electrode Growth Next to an Insulator

Introduction

This example models electrodeposition of copper with a deforming geometry where an electrode surface is placed next to an insulator, initially at an 180 degree angle. This situation is of interest from a benchmark perspective since non-right angles between insulators and growing electrodes may introduce singularities when modeling deforming geometries (Ref. 1).

No concentration gradients in the electrolytes are assumed, and a secondary current distribution is modeled.

The model qualitatively reproduces the results of J. Deconinck (Ref. 1).

Model Definition

GEOMETRY

The model is made in 2D and consists of a dissolving and a depositing electrode. Only the electrolyte domain is modeled in the geometry. See Figure 1.

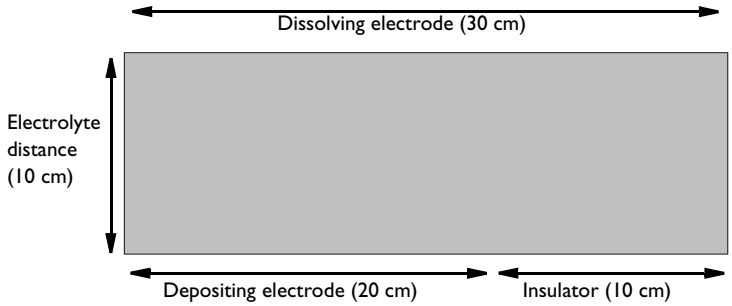

Figure 1: Initial modeled geometry.

ELECTROLYTE

The electrolyte is assumed to be a 0.8 M $CuSO_4$-0.8 M H_2SO_4 solution with a conductivity of $\sigma = 0.23\Omega^{-1}cm^{-1}$, where the H_2SO_4 is assumed to act as a supporting electrolyte (due to the high conductivity of the protons). Concentration gradients of Cu^{2+} are neglected in the model and thus a secondary current distribution is assumed.

ELECTRODES

The electrodes both consist of copper. On the dissolving electrode, copper dissolution occurs

$$\mathrm{Cu}(s) \Rightarrow \mathrm{Cu}^{2+} + 2e^{-}$$

whereas copper is deposited on the depositing electrode

$$\mathrm{Cu}^{2+} + 2e^{-} \Rightarrow \mathrm{Cu}(s)$$

A simplified electrode kinetic model is assumed for both electrodes, with a linear relation between the overpotential, η, and electrode reaction current density, i_{loc}, according to:

$$i_{\mathrm{loc}} = \eta \cdot 300 \ (\mathrm{mA}/(\mathrm{cm}^2\mathrm{V}))$$

By using the copper deposition red-ox reaction as reference potential, the equilibrium potential is set to zero for both electrodes.

The depositing electrode is grounded and a electric potential of 0.778 V is set to the dissolving electrode. All other boundaries are isolated.

DEFORMING GEOMETRY

Due to the dissolution and deposition of copper, the electrode boundaries move during the simulation. The molar flux of copper, N_{Cu} (mol/(m^2·s)), over the electrodes is described by Faraday's law according to

$$N_{\mathrm{Cu}} = -\frac{\nu_{\mathrm{Cu}} i_{\mathrm{loc}}}{nF}$$

where F is Faraday's constant (96485 C/mol). The stoichiometric coefficients for copper is $\nu_{Cu} = 1$ for both electrode reactions, and the number of electrons is $n = 2$.

The depositing velocity, v_{dep}, directed in the normal direction of the electrode into the electrode domain, can be deduced from the molar flux, the density and the molar mass of copper

$$v_{dep} = \frac{M_{\mathrm{Cu}} N_{\mathrm{Cu}}}{\rho_{\mathrm{Cu}}}$$

Figure 2 shows a surface plot of the electrolyte potential, and a streamline plot of the electrolyte current density, at 96 h, for the deformed geometry.

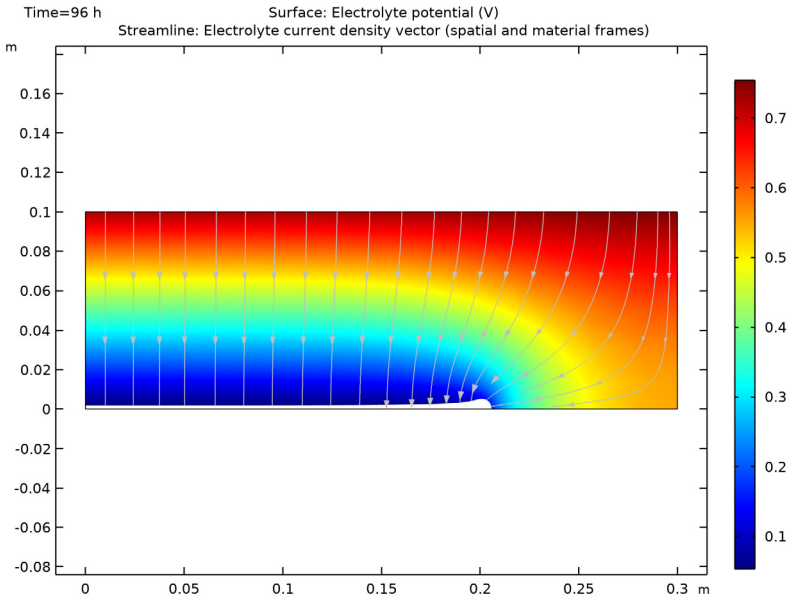

Figure 2: Electrolyte potential (surface) and electrolyte current direction (streamlines) at t=96 h.

The electrode growth reaches its maximum close to the insulator-electrode edge, due to the higher electrode currents in this area. Figure 3 shows the profile change of the depositing electrode during the simulation.

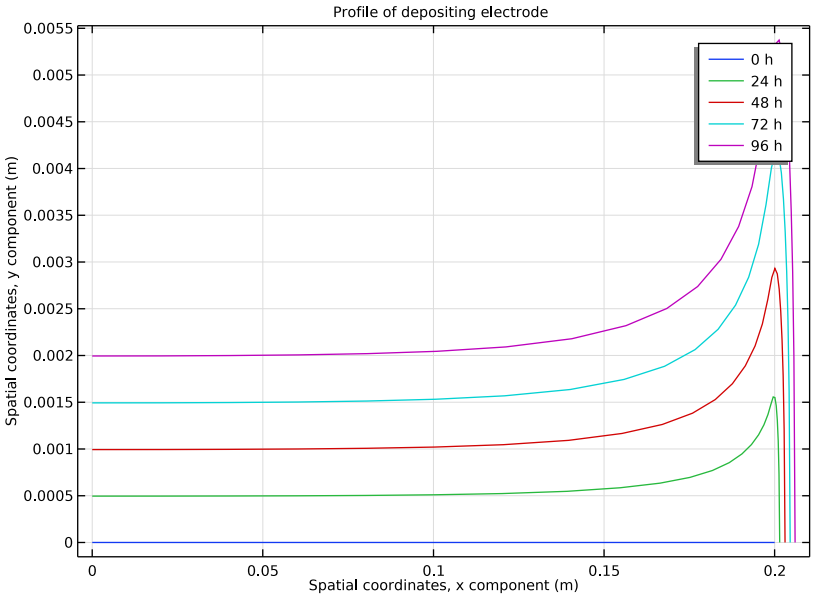

Figure 3: Profile of deposited electrode at various times during the simulation.

Notes About the COMSOL Implementation

The model is set up using the Electrodeposition, Secondary interface with a single Electrolyte domain. The depositing and dissolving electrodes are modeled with the External Depositing Electrode boundary nodes.

A time dependent study is used to simulate the electrode growth and dissolution during 96 h.

The default Nondepositing Boundary node is used for the geometry deformation at the insulated boundaries. The boundary condition setting of the feature is changed to Zero Normal Displacement, instead of using the default Zero Normal Velocity. This improves the numerical stability of the geometry deformation on these boundaries.

Reference

1. J. Deconinck, "Mathematical modelling of electrode growth," *J. Applied Electrochemistry*, vol. 24, pp. 212-218, 1994.

Application Library path: `Electrodeposition_Module/Verification_Examples/electrode_insulator_growth`

Modeling Instruction

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

NEW

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

MODEL WIZARD

1 In the **Model Wizard** window, click **2D**.

2 In the **Select Physics** tree, select **Electrochemistry>Electrodeposition, Deformed Geometry> Electrodeposition, Secondary**.

3 Click **Add**.

4 Click **Study**.

5 In the **Select Study** tree, select **Preset Studies for Selected Physics Interfaces> Secondary Current Distribution>Time Dependent with Initialization**.

6 Click **Done**.

GEOMETRY 1

Draw the geometry using a rectangle and a point.

Rectangle 1 (r1)

1 In the **Geometry** toolbar, click **Rectangle**.

2 In the **Settings** window for **Rectangle**, locate the **Size and Shape** section.

3 In the **Width** text field, type `30[cm]`.

4 In the **Height** text field, type `10[cm]`.

Point 1 (pt1)

1 In the **Geometry** toolbar, click **Point**.

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

3 In the **x** text field, type `20[cm]`.

4 In the **Geometry** toolbar, click **Build All**.

SECONDARY CURRENT DISTRIBUTION (CD)

Electrolyte 1

Now set up the electrochemical model. Start with the domain settings for the electrolyte.

1. In the **Model Builder** window, under **Component 1 (comp1)>** **Secondary Current Distribution (cd)** click **Electrolyte 1**.
2. In the **Settings** window for **Electrolyte**, locate the **Electrolyte** section.
3. From the σ_l list, choose **User defined**. In the associated text field, type `0.23[S/cm]`.

Electrode Surface 1

1. In the **Physics** toolbar, click **Boundaries** and choose **Electrode Surface**.
2. Select Boundary 2 only.
3. In the **Settings** window for **Electrode Surface**, click to expand the **Dissolving-Depositing Species** section.
4. Click **Add**.

Electrode Reaction 1

1. In the **Model Builder** window, expand the **Electrode Surface 1** node, then click **Electrode Reaction 1**.
2. In the **Settings** window for **Electrode Reaction**, locate the **Stoichiometric Coefficients** section.
3. In the n text field, type `2`.
4. In the **Stoichiometric coefficients for dissolving-depositing species:** table, enter the following settings:

Species	Stoichiometric coefficient (1)
sl	1

5. Locate the **Electrode Kinetics** section. From the $i_{\text{loc,expr}}$ list, choose **User defined**. In the associated text field, type `cd.eta_er1*300[mA/cm^2/V]`.

Electrode Surface 2

1. In the **Model Builder** window, under **Component 1 (comp1)>** **Secondary Current Distribution (cd)** right-click **Electrode Surface 1** and choose **Duplicate**.
2. Select Boundary 3 only.
3. In the **Settings** window for **Electrode Surface**, locate the **Electrode Phase Potential Condition** section.
4. In the $\phi_{s,ext}$ text field, type `0.778`.

MULTIPHYSICS

Nondeforming Boundary 1 (ndb1)

The following applies a stronger constraint (than the default condition) for the planar nondepositing walls, in order to enforce a zero boundary movement in the normal direction.

1 In the **Model Builder** window, under **Component 1 (comp1)>Multiphysics** click **Nondeforming Boundary 1 (ndb1)**.

2 In the **Settings** window for **Nondeforming Boundary**, locate the **Nondeforming Boundary** section.

3 From the **Boundary condition** list, choose **Zero normal displacement**.

MESH 1

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

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

3 From the **Sequence type** list, choose **User-controlled mesh**.

Size 1

1 In the **Model Builder** window, right-click **Free Triangular 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 **Point**.

4 Select Point 3 only.

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

6 Locate the **Element Size Parameters** section. Select the **Maximum element size** check box.

7 In the associated text field, type `0.1[mm]`.

8 Click **Build All**.

STUDY 1

Set the solver to simulate 96 hours of deposition, storing the solution every 3 hours.

Step 2: Time Dependent

1 In the **Model Builder** window, under **Study 1** click **Step 2: Time Dependent**.

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

3 From the **Time unit** list, choose **h**.

4 In the **Output times** text field, type `range(0,3,96)`.

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

RESULTS

Electrolyte Potential (cd)

A 2D plot of the electrolyte potential and the deformation is created by default. Change the frame of the dataset edges to Geometry in order to show the outline of the original (undeformed) geometry in the figure.

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

2 From the **Frame** list, choose **Geometry (Xg, Yg, Zg)**.

3 In the **Electrolyte Potential (cd)** toolbar, click **Plot**.

4 Click the **Zoom Extents** button in the **Graphics** toolbar.

1D Plot Group 6

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

Use the following steps to create Figure 3.

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

3 From the **Time selection** list, choose **From list**.

4 In the **Times (h)** list, choose **0**, **24**, **48**, **72**, and **96**.

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

6 In the **Title** text area, type `Profile of depositing electrode`.

Line Graph 1

1 Right-click **1D Plot Group 6** and choose **Line Graph**.

2 Select Boundary 2 only.

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

4 In the **Expression** text field, type `y`.

5 Locate the **x-Axis Data** section. From the **Parameter** list, choose **Expression**.

6 In the **Expression** text field, type `x`.

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

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

9 In the table, enter the following settings:

Legends
0 h
24 h
48 h

Legends
72 h
96 h

10 In the **1D Plot Group 6** toolbar, click  **Plot**.