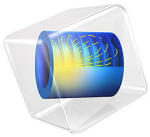


Fountain Flow Effects on Electrodeposition on a Rotating Wafer

Introduction

This example extends the analysis made in the model Electrodeposition on a Resistive Patterned Wafer by including the diffusion and convection of copper ions in the electrolyte.

The coupled mass transport convection-diffusion effects are of interest in this type of reactor since they are accentuated toward the rim of the wafer, limiting the current density. This counterbalances the activation overpotential, which is highest at the rim due to electric current conduction effects in the wafer. By the design of the reactor, the relation between mass transport and activation potential effects can be optimized to make the current distribution over the wafer more uniform.

Note: This application requires the CFD Module.

Model Definition

Due to symmetry the model geometry is made axisymmetric in two dimensions. The model geometry is shown in Figure 1. A wafer is mounted in a holder of isolating material at the top of the cell and rotates at a given rotational speed of 30 rpm. Electrolyte enters the reactor (which does not rotate) from the bottom at a given flow rate and exits through

the narrow gap at the top right in the figure. Copper is deposited on the rotating cathode wafer at a known average current density.

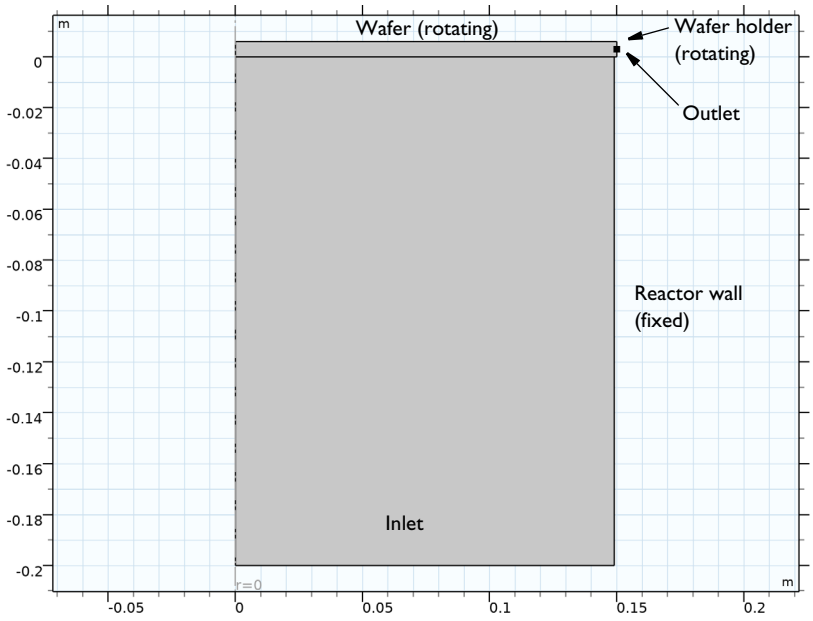


Figure 1: Model geometry, axisymmetric around r = 0. Two domains are used, with the copper concentration being solved for in the top domain only to save computational time.

CHOICE OF PHYSICS

Use the Electrode, Shell physics for solving for the potential on the wafer boundary, $\phi_{s,\,\mathrm{wafer}}$ (V).

In the cell, use a supporting electrolyte so that the electrolyte conductivity is not affected by local copper concentration changes. This implies that the Secondary Current Distribution physics can be used to model the electrolyte potential ϕ_l (V), and the Transport of Diluted Species physics to model the mass transfer, solving for the electrolyte concentration of copper ions, c (mol/m^3).

The relatively low rotational speed, in combination with the large wafer size, implies that the flow is not turbulent. This means that a Laminar Flow interface is suitable for solving for the velocity, $\mathbf{v}$ (m/s), and pressure p (Pa).

ELECTRODE, SHELL

Use a resistivity of $1.7{\cdot}10^{-6}$ ($\Omega{\cdot}$cm) and an electrode layer thickness of either 75 nm or 150 nm. The latter parameter will be varied by the Continuation settings in the solver.

Ground the right endpoint of the wafer. Use a Normal Current Density feature to create a current source, which becomes coupled to the Electrode Reaction current density set up by the Secondary Current Distribution physics.

SECONDARY CURRENT DISTRIBUTION

Use an electrolyte conductivity of 0.5 (S/m). Set the total current at the inlet boundary to correspond to an average wafer current density (0.5 or 2 A/dm^2), which is varied by the Continuation settings in the solver.

On the wafer boundary, use an Electrode Surface node to set up the electrode current density according to

$$i = i_0\left(\exp\left(\frac{1.5F\eta}{RT}\right) - \frac{c}{c_\mathrm{b}}\exp\left(-\frac{0.5F\eta}{RT}\right)\right) \quad (1)$$

where i_0 (10 A/m^2) is the exchange current density, F is Faraday's constant (96,485 C/mol), R is the molar gas constant (8.3145 J/(mol·K)), T is the temperature (298.15 K), and c_b (0.3 mol/l) is the bulk concentration of copper ions.

The overpotential, η (V), is defined as

$$\eta = \phi_{s,\,\mathrm{wafer}} - \phi_l$$

LAMINAR FLOW

Enable Swirl Flow to solve also for the velocity in the φ direction. Specify the inflow velocity to correspond to a total flow of 30 l/min, and set the outlet pressure to 0 Pa. Use a Wall boundary condition, with the Sliding Wall feature enabled, to define a rotational velocity for the rotating wafer and the holder boundaries.

TRANSPORT OF DILUTED SPECIES

Since concentration gradients are expected only in the vicinity of the electrode surface, the computational time can be reduced by modeling the copper ion transport in upper domain only.

Use a diffusion coefficient of $5\cdot10^{-6}$ (cm^2/s) and couple the convective flow to the velocity solved for by the Laminar Flow physics. Enable Migration and couple it to the electrolyte potential solved for by Secondary Current Distribution physics.

Set the concentration at the inlet boundary to c_b and set zero diffusional flux at the outlet using an Outlet condition.

Couple the flux of copper ions at the wafer to the electrode current density in the Secondary Current Distribution physics boundary using an Electrode-Electrolyte Interface Coupling. This sets up a flux condition using Faraday's law.

STUDY

Since the flow profile is not affected by any other physics, solve the model in two steps with Laminar Flow only in the first step, and the other physics in the second step. Use a Study Extension with Continuation in the second study step to solve for two different average wafer current densities (0.5 and 2 A/dm^2) and two different wafer seed layer thicknesses (75 and 150 nm).

Results and Discussion

Figure 2 shows the concentration in copper ions in the electrolyte. The concentration is lowest toward the rim of the rotating wafer.

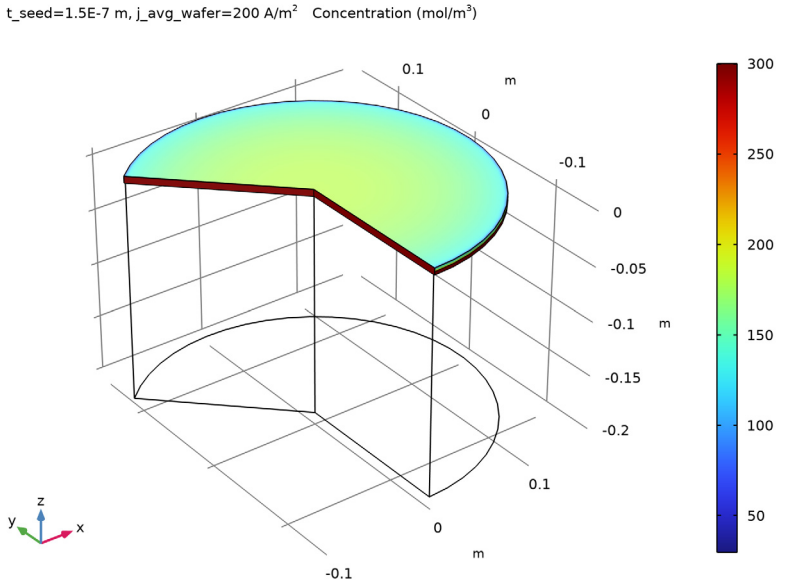


Figure 2: Copper concentration for an average wafer current of 200 A/m^2 and a seed layer thickness of 150 nm.

Figure 3 shows the velocity steam lines in the reactor. The velocity magnitude is highest close to the rotating surfaces, as indicated by the higher density of streamlines.

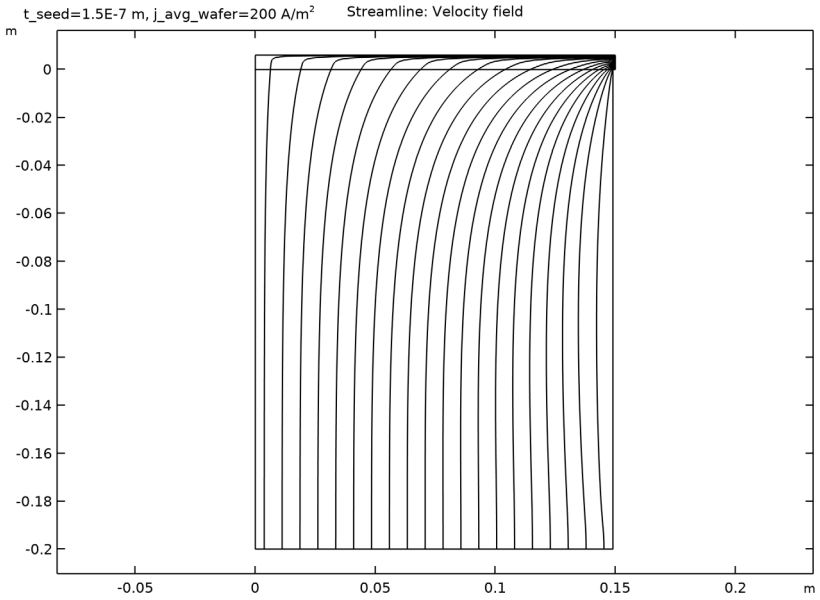


Figure 3: Velocity streamlines.

Figure 4 shows the electrode current density as described by Equation 1. The cathodic current density increases toward the rim of the wafer until concentration effects start to dominate, at the end of the wafer the current density drops significantly.

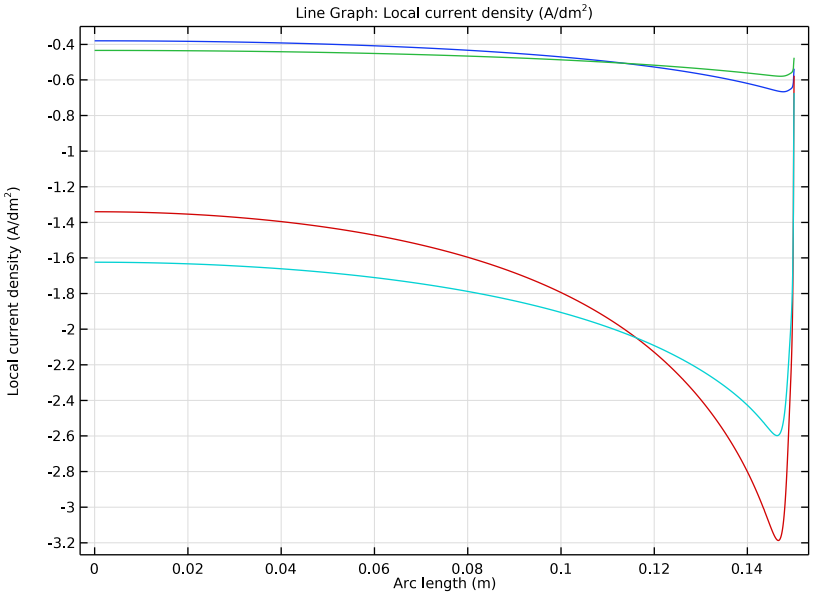


Figure 4: Cathode current density versus radial coordinate.

Notes About the COMSOL Implementation

Use second-order elements in all physics interfaces.

Application Library path: `Electrodeposition_Module/Tutorials/fountain_flow`

Modeling Instructions

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

NEW

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

MODEL WIZARD

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

Add the four different physics that are used in this model.

2 In the **Select Physics** tree, select **Chemical Species Transport>Transport of Diluted Species (tds)**.

3 Click **Add**.

4 In the **Select Physics** tree, select **Electrochemistry>Primary and Secondary Current Distribution>Secondary Current Distribution (cd)**.

5 Click **Add**.

6 In the **Select Physics** tree, select **Electrochemistry>Electrode, Shell (els)**.

7 Click **Add**.

8 In the **Electric potential** text field, type `phis_wafer`.

9 In the **Select Physics** tree, select **Fluid Flow>Single-Phase Flow>Laminar Flow (spf)**.

10 Click **Add**.

11 Click **Study**.

12 In the **Select Study** tree, select **General Studies>Stationary**.

13 Click **Done**.

GLOBAL DEFINITIONS

Parameters 1

Load the model parameters from a text file.

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 `fountain_flow_parameters.txt`.

GEOMETRY 1

Draw the geometry as the union of two rectangles, split one boundary by adding a point. The lower part of the split boundary will become the outlet.

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 `d_cell/2`.

4 In the **Height** text field, type `h_cell`.

5 Locate the **Position** section. In the **z** text field, type `-h_cell`.

Rectangle 2 (r2)

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 `d_wafer/2`.

4 In the **Height** text field, type `h_gap`.

Point 1 (pt1)

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

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

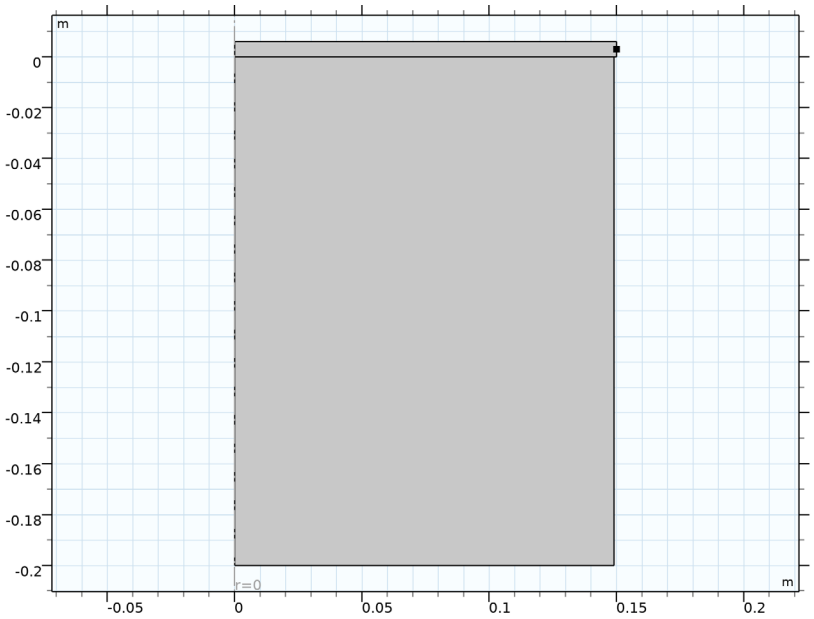
3 In the **r** text field, type `d_wafer/2`.

4 In the **z** text field, type `h_outlet`.

5 Click **Build All Objects**.

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

The finalized geometry should now look like the figure below:



DEFINITIONS

Add some explicit selections to facilitate boundary selection when setting up the physics.

Cathode

1 In the **Definitions** toolbar, click **Explicit**.

2 In the **Settings** window for **Explicit**, locate the **Input Entities** section.

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

4 Select Boundary 5 only.

5 In the **Label** text field, type `Cathode`.

Inlet

1 In the **Definitions** toolbar, click **Explicit**.

2 In the **Settings** window for **Explicit**, locate the **Input Entities** section.

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

4 Select Boundary 2 only.

5 In the **Label** text field, type `Inlet`.

Outlet

1 In the **Definitions** toolbar, click **Explicit**.

2 In the **Settings** window for **Explicit**, locate the **Input Entities** section.

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

4 Select Boundary 8 only.

5 In the **Label** text field, type `Outlet`.

Rotating wall

1 In the **Definitions** toolbar, click **Explicit**.

2 In the **Settings** window for **Explicit**, locate the **Input Entities** section.

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

4 Select Boundaries 5 and 9 only.

5 In the **Label** text field, type `Rotating wall`.

LAMINAR FLOW (SPF)

Now start defining the Laminar flow settings of the physics. Enable Swirl Flow to also solve for the velocity in the φ direction.

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Laminar Flow (spf)**.

2 In the **Settings** window for **Laminar Flow**, locate the **Physical Model** section.

3 Select the **Swirl flow** check box.

Fluid Properties 1

1 In the **Model Builder** window, under **Component 1 (comp1)>Laminar Flow (spf)** click **Fluid Properties 1**.

2 In the **Settings** window for **Fluid Properties**, locate the **Fluid Properties** section.

3 From the ρ list, choose **User defined**. In the associated text field, type `rho`.

4 From the μ list, choose **User defined**. In the associated text field, type `mu`.

Inlet 1

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

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

3 From the **Selection** list, choose **Inlet**.

4 Locate the **Velocity** section. In the U_0 text field, type `v_in`.

Outlet 1

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

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

3 From the **Selection** list, choose **Outlet**.

Wall 2

Use a sliding wall to define the rotating surfaces. The velocity is zero in the rz-plane and ωr in the φ direction.

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

2 Select Boundaries 5 and 9 only.

3 In the **Settings** window for **Wall**, click to expand the **Wall Movement** section.

4 Select the **Sliding wall** check box.

5 In the v_w text field, type `omega*r`.

Initial Values 1

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

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

3 Specify the **u** vector as

0	r
0	phi
v_in	z

4 In the p text field, type `1`.

SECONDARY CURRENT DISTRIBUTION (CD)

Electrolyte 1

Now set up the model for the electrolyte currents. Start with the electrolyte conductivity.

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 `sigma`.

Electrode Surface 1

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

   Set the electric potential of the electrode surface to the potential solved for by the Electrode, Shell physics.
2. In the **Settings** window for **Electrode Surface**, locate the **Boundary Selection** section.
3. From the **Selection** list, choose **Cathode**.
4. Locate the **Electrode Phase Potential Condition** section. In the $\phi_{s,ext}$ text field, type `phis_wafer`.

Electrode Reaction 1

Set the electrode kinetics to be dependent on the local concentration of copper ions.

1. In the **Model Builder** window, click **Electrode Reaction 1**.
2. In the **Settings** window for **Electrode Reaction**, locate the **Equilibrium Potential** section.
3. From the E_{eq} list, choose **Nernst equation**.
4. In the C_O text field, type `c/c_bulk`.
5. Locate the **Stoichiometric Coefficients** section. In the n text field, type `2`.
6. Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Butler-Volmer**.
7. From the **Exchange current density type** list, choose **From Nernst Equation**.
8. In the $i_{0,ref}(T)$ text field, type `i0`.
9. In the α_a text field, type `1.5`.

Electrolyte Current 1

Define the total current of the cell on the bottom electrolyte boundary.

1. In the **Physics** toolbar, click **Boundaries** and choose **Electrolyte Current**.
2. In the **Settings** window for **Electrolyte Current**, locate the **Boundary Selection** section.

3 From the **Selection** list, choose **Inlet**.

4 Locate the **Electrolyte Current** section. In the $I_{l,total}$ text field, type `I_tot`.

TRANSPORT OF DILUTED SPECIES (TDS)

Now define the physics for the transport of copper ions. To save computational time, model only the domain in direct vicinity to the electrode surface.

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Transport of Diluted Species (tds)**.

2 In the **Settings** window for **Transport of Diluted Species**, locate the **Domain Selection** section.

3 Click  **Clear Selection**.

4 Select Domain 2 only.

5 Locate the **Transport Mechanisms** section. Select the **Migration in electric field** check box.

Species Charges

1 In the **Model Builder** window, under **Component 1 (comp1)> Transport of Diluted Species (tds)** click **Species Charges**.

2 In the **Settings** window for **Species Properties**, locate the **Charge** section.

3 In the z_c text field, type `2`.

Transport Properties 1

1 In the **Model Builder** window, click **Transport Properties 1**.

2 In the **Settings** window for **Transport Properties**, locate the **Migration in Electric Field** section.

3 In the V text field, type `phil`.

4 Locate the **Diffusion** section. In the D_c text field, type `D_Cu`.

The velocity field will be coupled to Laminar Flow later using the Reacting Flow multiphysics feature.

Initial Values 1

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 c text field, type `c_bulk`.

Inflow 1

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

2 Select Boundary 4 only.

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

4 In the $c_{0,c}$ text field, type `c_bulk`.

Outflow 1

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

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

3 From the **Selection** list, choose **Outlet**.

Electrode Surface Coupling 1

Define the flux of copper ions on the electrode surface by coupling it to the electrode currents.

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

2 In the **Settings** window for **Electrode Surface Coupling**, locate the **Boundary Selection** section.

3 From the **Selection** list, choose **Cathode**.

Reaction Coefficients 1

1 In the **Model Builder** window, expand the **Electrode Surface Coupling 1** node, then click **Reaction Coefficients 1**.

2 In the **Settings** window for **Reaction Coefficients**, locate the **Model Inputs** section.

3 From the i_{loc} list, choose **Local current density, Electrode Reaction 1 (cd/es1/er1)**.

4 Locate the **Stoichiometric Coefficients** section. In the n text field, type `2`.

5 In the ν_c text field, type `-1`.

ELECTRODE, SHELL (ELS)

Now set up the model for the electric potential in the wafer.

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Electrode, Shell (els)**.

2 In the **Settings** window for **Electrode, Shell**, locate the **Boundary Selection** section.

3 From the **Selection** list, choose **Cathode**.

Electrode 1

1 In the **Model Builder** window, under **Component 1 (comp1)>Electrode, Shell (els)** click **Electrode 1**.

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

3 In the s text field, type `t_seed`.

4 From the σ list, choose **User defined**. In the associated text field, type `1/r_seed`.

Ground 1

1 In the **Physics** toolbar, click **Points** and choose **Ground**.

2 Select Point 8 only.

Normal Current Density 1

Couple the wafer potential model to the electrode reaction by adding a current source corresponding to the electrode reaction.

1 In the **Physics** toolbar, click **Boundaries** and choose **Normal Current Density**.

2 In the **Settings** window for **Normal Current Density**, locate the **Boundary Selection** section.

3 From the **Selection** list, choose **Cathode**.

4 Locate the **Normal Current Density** section. From the i_n list, choose **Local current density, Electrode Reaction 1 (cd/es1/er1)**.

MULTIPHYSICS

Finally, set up the Reactive Flow multiphysics feature.

Reacting Flow, Diluted Species 1 (rfd1)

In the **Physics** toolbar, click **Multiphysics Couplings** and choose **Domain>Reacting Flow, Diluted Species**.

MESH 1

Create a triangular mesh with higher resolution close to the electrode surface. Add boundary layers to further improve the accuracy where needed.

Size 1

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

Size

1 In the **Settings** window for **Size**, locate the **Element Size** section.

2 From the **Calibrate for** list, choose **Fluid dynamics**.

3 From the **Predefined** list, choose **Coarse**.

Size 1

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

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

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

4 From the **Selection** list, choose **Rotating wall**.

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 `1.5e-4`.

Free Triangular 1

In the **Mesh** toolbar, click **Free Triangular**.

Boundary Layers 1

In the **Mesh** toolbar, click **Boundary Layers**.

Boundary Layer Properties

1 In the **Model Builder** window, click **Boundary Layer Properties**.

2 Select Boundaries 5–7 and 9 only.

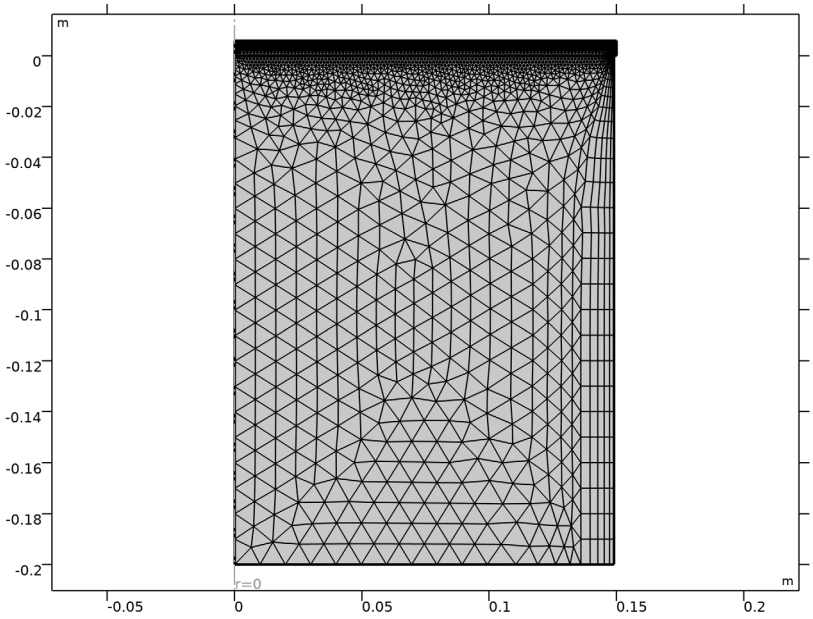
3 In the **Settings** window for **Boundary Layer Properties**, locate the **Layers** section.

4 In the **Number of layers** text field, type `5`.

5 In the **Thickness adjustment factor** text field, type `5`.

6 In the **Model Builder** window, right-click **Mesh 1** and choose **Build All**.

The finalized mesh should look like this:



TRANSPORT OF DILUTED SPECIES (TDS)

Use 2nd-order elements in all interfaces (Electrode, Shell uses 2nd-order elements by default).

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Transport of Diluted Species (tds)**.

2 In the **Settings** window for **Transport of Diluted Species**, click to expand the **Discretization** section.

3 From the **Concentration** list, choose **Quadratic**.

SECONDARY CURRENT DISTRIBUTION (CD)

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Secondary Current Distribution (cd)**.

2 In the **Settings** window for **Secondary Current Distribution**, click to expand the **Discretization** section.

3 From the **Electrolyte potential** list, choose **Quadratic**.

LAMINAR FLOW (SPF)

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Laminar Flow (spf)**.

2 In the **Settings** window for **Laminar Flow**, click to expand the **Discretization** section.

3 From the **Discretization of fluids** list, choose **P2+P1**.

STUDY 1

Step 1: Stationary

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

2 In the **Settings** window for **Stationary**, locate the **Physics and Variables Selection** section.

3 In the table, clear the **Solve for** check boxes for **Transport of Diluted Species (tds)**, **Secondary Current Distribution (cd)**, and **Electrode, Shell (els)**.

Stationary 2

1 In the **Study** toolbar, click **Study Steps** and choose **Stationary>Stationary**.

2 In the **Settings** window for **Stationary**, locate the **Physics and Variables Selection** section.

3 In the table, clear the **Solve for** check box for **Laminar Flow (spf)**.

4 Click to expand the **Study Extensions** section. Select the **Auxiliary sweep** check box.

5 From the **Sweep type** list, choose **All combinations**.

6 Click **Add**.

7 Click + **Add**.

8 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
j_avg_wafer (Average current density on wafer)	`0.5[A/dm^2] 2[A/dm^2]`	`A/m^2`
t_seed (Seed layer thickness)	`75[nm] 150[nm]`	`m`

9 In the **Study** toolbar, click = **Compute**.

RESULTS

Velocity Streamline

Create a streamline plot of the velocity field in the following way.

1 In the **Home** toolbar, click **Add Plot Group** and choose **2D Plot Group**.

2 In the **Settings** window for **2D Plot Group**, type `Velocity Streamline` in the **Label** text field.

Streamline 1

1 Right-click **Velocity Streamline** and choose **Streamline**.

2 In the **Settings** window for **Streamline**, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Component 1 (comp1)>Laminar Flow> Velocity and pressure>u,w - Velocity field**.

3 Select Boundary 2 only.

4 In the **Velocity Streamline** toolbar, click **Plot**.

Local Current Density

Create a line plot of the local electrode current density in the following way.

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

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

Line Graph 1

1 Right-click **Local Current Density** and choose **Line Graph**.

2 In the **Settings** window for **Line Graph**, locate the **Selection** section.

3 From the **Selection** list, choose **Cathode**.

4 Click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)>Secondary Current Distribution>Electrode kinetics> cd.iloc_er1 - Local current density - A/m²**.

5 Locate the **y-Axis Data** section. In the **Unit** field, type `A/dm^2`.

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