

Corrosion Under an Evans Droplet

Introduction

An Evans droplet experiment is a century-old corrosion experiment for demonstrating oxygen transport-limited corrosion. A droplet of water is placed on a metal surface, and over time the surface features differences in the radial direction of the surface in terms of amount of corroded material and deposited corrosion products.

This tutorial model defines corrosion of an iron surface in contact with a water droplet in a surrounding atmosphere containing both carbon dioxide and oxygen. The model accounts for charge and mass transport of a multitude of species as well as iron dissolution, oxygen reduction, carbonic acid equilibria and iron hydroxide formation.

The model computes the transient and spatial distributions of the various species within the droplet. A spatial gradient in pH is demonstrated and is attributed to the complex interplay between the dissolved iron and the carbonic acid.

The model is based on several journal papers (Ref. 1–Ref. 3).

Figure 1 shows the model geometry, defining an elliptical electrolyte droplet (with a 90° wetting angle) covering an iron metal surface. The geometry is defined in 2D with axial symmetry.

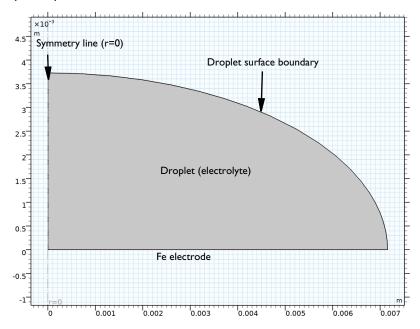


Figure 1: Model geometry.

The model is defined using the **Tertiary Current Distribution, Nernst-Planck** interface, solving for the electrolyte phase potential and the concentrations of the electrolyte species H^+ , OH^- , Fe^{2+} , O_2 , CO_2 , H_2CO_3 , HCO_3^- , and CO_3^{2-} .

Oxygen reduction occurs on the metal surface, which, due to limited oxygen diffusion, is more dominant toward the periphery of the droplet:

$$4H^{+} + 4e^{-} + O_{2} \rightarrow 2H_{2}O$$
 (1)

Iron is oxidized to counterbalance the oxygen reduction reaction:

$$Fe(s) \to Fe^{2+} + 2e^{-} \tag{2}$$

Concentration-dependent Butler–Volmer electrode kinetics expressions are used for both the oxygen-reduction and iron-dissolution reactions. The combination of these two reactions gives rise to a mixed electrode potential of the metal surface.

Dissolved iron forms iron hydroxide due to a precipitation reaction at the electrode surface:

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_{2}(s)$$
 (3)

The hydroxide precipitation reaction depends on the concentration of the iron and hydroxide ions, and is defined to occur irreversibly when the solubility product of the hydroxide is exceeded.

EOUILIBRIUM REACTIONS

The following equilibrium reactions are present in the electrolyte:

$$\begin{split} & \text{H}_2\text{O}(\text{I}) \Leftrightarrow \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) & K_1 = 6.418 \cdot 10^{-15} \\ & \text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \Leftrightarrow \text{H}_2\text{CO}_3(\text{aq}) & K_2 = 2.580 \cdot 10^{-3} \\ & \text{H}_2\text{CO}_3(\text{aq}) \Leftrightarrow \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq}) & K_3 = 1.251 \cdot 10^{-4} \\ & \text{HCO}_3^-(\text{aq}) \Leftrightarrow \text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) & K_4 = 1.382 \cdot 10^{-10} \end{split}$$

Here, K_1 through K_4 are the equilibrium constants at 293.15 K (Ref. 2).

The water dissociation equilibrium reaction is built-in for the Tertiary Current Distribution, Nernst–Planck interface when using a water-based with electroneutrality charge conservation model. The other three carbonic acid reactions are modeled using Equilibrium Reaction domain nodes, one for each reaction. Each Equilibrium Reaction node solves for one additional degree of freedom each, representing the local reaction rate required to fulfill the equilibrium expression. These equilibrium expressions are based on the reaction stoichiometry and the equilibrium constant K_k according to

$$K_k = \prod_i a(c_i)^{v_{ik}} \tag{5}$$

where c_i (SI unit: mol/m³) is the concentration of species i and v_{ik} is the stoichiometric coefficient of species i in reaction k. The activity of a species, $a(c_i)$ is obtained by dividing the concentration with reference concentration of 1 M, except for O_2 .

As a result of the above equilibrium reactions, the gaseous CO₂ dissolved at the droplet surface forms carbonic acid, generally lowering the pH.

The model is solved using a time-dependent solver, simulating the transient and spatial evolution of the species considered for 600 seconds. Fixed concentrations of O2 and CO2 are set at the upper droplet boundary facing the surrounding atmosphere.

Results and Discussion

Figure 2 shows the iron ion concentration distribution within the Evans droplet at 30 s (left) and 300 s (right). It can be seen that the iron ion concentration is higher toward the periphery of the droplet closer to the metal surface when compared to the center of the droplet. This an effect of the oxygen reduction currents being larger toward the rim of the electrode surface due to the limited oxygen transport, in combination with the limited electrolyte conductivity, thus favoring iron oxidation toward the rim.

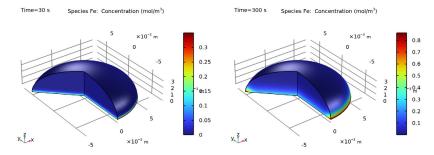


Figure 2: Iron ion concentration distribution within the droplet at time t = 30 s (left) and t = 300 s (right).

Figure 3 shows the anodic current density distribution along the electrode surface underneath the droplet at 600 s. It is found to be higher toward the periphery of the droplet, indicating that the corrosion rate is higher toward the periphery than at the core of the droplet. This explains the higher iron ion concentration toward the periphery of the droplet than that at the center of droplet, as seen in Figure 2.

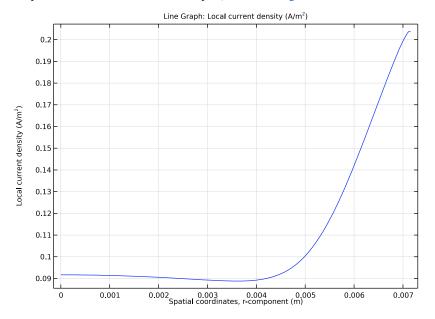


Figure 3: Anodic current density distribution along the iron electrode surface at time $t = 600 \, s.$

Figure 4 shows the CO₂ concentration distribution within the droplet at 30 s (left) and 300 s (right). It can be seen that the CO_2 concentration is reduced close to the electrode surface. This is related to the carbonic acid equilibria in combination with the increased pH.

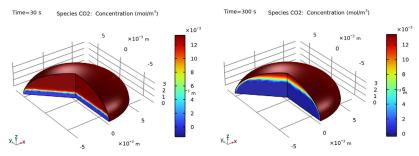


Figure 4: CO_2 concentration distribution within the droplet at time t = 30 s (left) and t = 300 s (right).

Figure 5 shows the pH distribution within the droplet at 30 s (left) and 300 s (right). The pH changes over time are substantial. It can also be seen that the pH is increased in the vicinity of the metal surface, when compared to the pH closer to the droplet surface. The pH changes are generally attributed to the dissolution of iron atoms which need to be counter-balanced by hydroxide ions from water autoprotolysis.

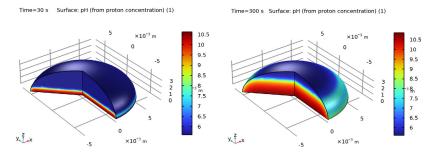
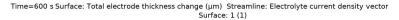


Figure 5: pH distribution within the droplet at time t = 30 s (left) and t = 300 s (right).

Figure 6 shows surface plot of the ferrous hydroxide precipitation thickness along the electrode surface underneath the droplet and streamline plot of the electrolyte current density over the droplet domain at 600 s. The precipitation thickness is found to be higher toward the core of the droplet than along the periphery of the droplet. This is a result of the pH being slightly higher toward the rim due to the higher CO₂ (and carbonic acid)

concentration at the atmospheric boundary. Streamline plot shows the ionic current flow from the rim toward the core of the droplet.



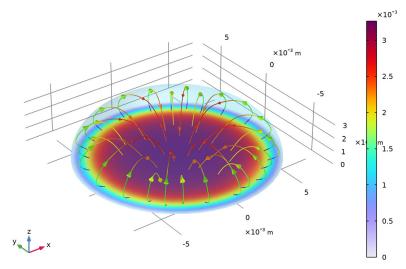


Figure 6: Ferrous hydroxide precipitation thickness along the iron electrode surface and streamline plot of the electrolyte current density at time t = 600 s.

References

- 1. A. Sainz-Rosales, X. Ocampo-Lazcarro, A. Hernández-Pérez, A.G. González-Gutiérrez, E.R. Larios-Durán, C.P. de León, F.C. Walsh, M. Bárcena-Soto and N. Casillas, "Classic Evans's Drop Corrosion Experiment Investigated in Terms of a Tertiary Current and Potential Distribution," Corrosion and Materials Degradation, vol. 3, no. 2, pp. 270-280, 2022.
- 2. M. Nordsveen, S. Nesic, R. Nyborg, and A. Stangeland, "A Mechanistic Model for Carbon Dioxide Corrosion of Mild Steel in the Presence of Protective Iron Carbonate Films-Part 1: Theory and Verification," Corrosion, vol. 59, no. 5, pp. 443-456, 2003.
- 3. A. Kahyarian and S. Nesic, "On the mechanism of carbon dioxide corrosion of mild steel: Experimental investigation and mathematical modeling at elevated pressures and non-ideal solutions," Corrosion Science, vol. 173, no. 108719, pp. 1-27, 2020.

Application Library path: Corrosion Module/Atmospheric Corrosion/ evans_droplet

Modeling Instructions

From the File menu, choose New.

NEW

In the New window, click Model Wizard.

MODEL WIZARD

- I In the Model Wizard window, click 2D Axisymmetric.
- 2 In the Select Physics tree, select Electrochemistry>Tertiary Current Distribution, Nernst-Planck>Tertiary, Water-Based with Electroneutrality (tcd).
- 3 Click Add.
- 4 In the Number of species text field, type 6.
- 5 In the Concentrations (mol/m³) table, enter the following settings:

cFe c02 cC02 cH2C03 cHC03 cC03

- 6 Click Study.
- 7 In the Select Study tree, select Preset Studies for Selected Physics Interfaces> Time Dependent with Initialization.
- 8 Click **Done**.

GLOBAL DEFINITIONS

Load the model parameters from a text file.

Parameters 1

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

- 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 evans_droplet_parameters.txt.

GEOMETRY I

The geometry consists of a sector of an eclipse.

Ellipse I (el)

- I In the **Geometry** toolbar, click Ellipse.
- 2 In the Settings window for Ellipse, locate the Size and Shape section.
- 3 In the a-semiaxis text field, type a.
- 4 In the **b-semiaxis** text field, type b.
- 5 In the Sector angle text field, type 90.
- 6 Click **Build All Objects**.

DEFINITIONS

Variables 1

Load the model variables from a text file.

- I In the Home toolbar, click ∂ = Variables and choose Local Variables.
- 2 In the Settings window for Variables, locate the Variables section.
- 3 Click Load from File.
- 4 Browse to the model's Application Libraries folder and double-click the file evans_droplet_variables.txt.

TERTIARY CURRENT DISTRIBUTION, NERNST-PLANCK (TCD)

Start by defining the physics.

Species Charges 1

- I In the Model Builder window, under Component I (compl)>Tertiary Current Distribution, Nernst-Planck (tcd) click Species Charges I.
- 2 In the Settings window for Species Charges, locate the Charge section.
- **3** In the z_{cFe} text field, type zFe.
- **4** In the $z_{\rm cHCO3}$ text field, type zHCO3.
- **5** In the z_{cCO3} text field, type zCO3.

Electrolyte I

- I In the Model Builder window, click Electrolyte I.
- 2 In the Settings window for Electrolyte, locate the Diffusion section.
- **3** In the D_{cFe} text field, type DFe.
- **4** In the $D_{\rm cO2}$ text field, type DO2.
- **5** In the $D_{\rm cCO2}$ text field, type DCO2.
- **6** In the $D_{\rm cH2CO3}$ text field, type DH2CO3.
- 7 In the $D_{\rm cHCO3}$ text field, type DHCO3.
- **8** In the $D_{\rm cCO3}$ text field, type DCO3.
- **9** In the $D_{\rm cH}$ text field, type DH.
- **IO** In the $D_{\rm cOH}$ text field, type DOH.

Initial Values 1

Set the initial values to the concentration of the species in the bulk.

- I In the Model Builder window, click Initial Values I.
- 2 In the Settings window for Initial Values, locate the Initial Values section.
- 3 In the cO2 text field, type c020.
- 4 In the cCO2 text field, type cCO20.
- **5** In the cH2CO3 text field, type cH2CO30.
- **6** In the *cHCO*3 text field, type cHC030.
- **7** In the *phil* text field, type philo.

Electrode Surface 1

Use the Dissolving-Depositing Species section to include precipitation of ferrous hydroxide at the surface.

- I 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.
- **5** In the table, enter the following settings:

Species	Density (kg/m^3)	Molar mass (kg/mol)
Fe0H2	rho_FeOH2	M_Fe0H2

Electrode Reaction: Iron Dissolution

- I In the Model Builder window, under Component I (compl)>Tertiary Current Distribution, Nernst-Planck (tcd)>Electrode Surface | click Electrode Reaction | 1.
- 2 In the Settings window for Electrode Reaction, type Electrode Reaction: Iron Dissolution in the Label text field.
- **3** Locate the **Stoichiometric Coefficients** section. In the n text field, type 2.
- 4 In the v_{cFe} text field, type -1.
- **5** Locate the **Equilibrium Potential** section. In the $E_{\text{eq.ref}}(T)$ text field, type Eeq_ref_Fe.
- **6** Locate the **Electrode Kinetics** section. In the $i_{0,ref}(T)$ text field, type i0_ref_Fe.
- 7 In the α_a text field, type alphaa_Fe.

Electrode Surface I

In the Model Builder window, click Electrode Surface 1.

Electrode Reaction: Oxygen Reduction

- I In the Physics toolbar, click Attributes and choose Electrode Reaction.
- 2 In the Settings window for Electrode Reaction, type Electrode Reaction: Oxygen Reduction in the Label text field.
- **3** Locate the **Stoichiometric Coefficients** section. In the n text field, type 4.
- 4 In the v_{cO2} text field, type -1.
- **5** Locate the **Equilibrium Potential** section. In the $E_{\text{eq,ref}}(T)$ text field, type Eeq_ref_02.
- 6 From the Balance reaction charges and define reference state using list, choose OH.
- 7 Click to expand the **Reference Concentrations** section. In the table, enter the following settings:

Electrolyte species	Reference concentrations (mol/m^3)
cO2	c02_sol

- **8** Locate the **Electrode Kinetics** section. In the $i_{0,ref}(T)$ text field, type i0_ref_02* (tcd.eta_er2<0).
- **9** In the α_a text field, type alphaa_02.

Electrode Surface I

In the Model Builder window, click Electrode Surface 1.

Nonfaradaic Reactions: Ferrous Hydroxide Precipitation

I In the Physics toolbar, click Attributes and choose Nonfaradaic Reactions.

- 2 In the **Settings** window for **Nonfaradaic Reactions**, type Nonfaradaic Reactions: Ferrous Hydroxide Precipitation in the **Label** text field.
- **3** Locate the **Reaction Rate** section. Select the **Species cFe** check box.
- **4** In the $R_{0 \text{ cFe}}$ text field, type rFe0H2.
- 5 In the Reaction rate for dissolving-depositing species table, enter the following settings:

Species	Reaction rate (mol/(m^2*s))
FeOH2	rFeOH2

Concentration I

Set concentrations for the gaseous species at the droplet surface boundary facing the atmosphere.

- I In the Physics toolbar, click Boundaries and choose Concentration.
- 2 Select Boundary 3 only.
- 3 In the Settings window for Concentration, locate the Concentration section.
- 4 Select the **Species cO2** check box.
- **5** Select the **Species cCO2** check box.
- **6** In the $c_{0,\text{cO}2}$ text field, type co2s.
- **7** In the $c_{0,\text{cCO}2}$ text field, type cCO20.

Equilibrium Reaction I

Now add three equilibrium reactions as follows:

- I In the Physics toolbar, click **Domains** and choose **Equilibrium Reaction**.
- 2 In the Settings window for Equilibrium Reaction, locate the Domain Selection section.
- 3 From the Selection list, choose All domains.
- **4** Locate the **Equilibrium Condition** section. In the K_{eq} text field, type KCO2H.
- **5** Locate the **Stoichiometric Coefficients** section. In the v_{cCO2} text field, type -1.
- **6** In the v_{cH2CO3} text field, type 1.

Equilibrium Reaction 2

- I In the Physics toolbar, click **Domains** and choose **Equilibrium Reaction**.
- 2 In the Settings window for Equilibrium Reaction, locate the Domain Selection section.
- **3** From the **Selection** list, choose **All domains**.
- **4** Locate the **Equilibrium Condition** section. In the $K_{\rm eq}$ text field, type KH2C03.
- **5** Locate the **Stoichiometric Coefficients** section. In the v_{cH2CO3} text field, type -1.

- 6 In the v_{cHCO3} text field, type 1.
- 7 In the v_{cH} text field, type 1.

Equilibrium Reaction 3

- I In the Physics toolbar, click **Domains** and choose **Equilibrium Reaction**.
- 2 In the Settings window for Equilibrium Reaction, locate the Domain Selection section.
- 3 From the Selection list, choose All domains.
- **4** Locate the **Equilibrium Condition** section. In the K_{eq} text field, type KHC03.
- **5** Locate the **Stoichiometric Coefficients** section. In the v_{cHCO3} text field, type -1.
- **6** In the v_{cCO3} text field, type 1.
- 7 In the v_{cH} text field, type 1.

MESH I

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

- I In the Model Builder window, under Component I (compl) click Mesh I.
- 2 In the Settings window for Mesh, locate the Sequence Type section.
- 3 From the list, choose User-controlled mesh.

Size 1

- I In the Model Builder window, right-click Free Triangular I 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 2 only.
- 5 Locate the Element Size section. From the Predefined list, choose Extremely fine.
- 6 Click **Build All**.

STUDY I

Steb 2: Time Dependent

- I In the Model Builder window, under Study I click Step 2: Time Dependent.
- 2 In the Settings window for Time Dependent, locate the Study Settings section.
- 3 In the Output times text field, type range (0,30,600).
- 4 In the Home toolbar, click **Compute**.

RESULTS

Several plots are added by default. The following steps reproduce the plots from the Results and Discussion section:

Concentration, Fe. 3D (tcd)

- I In the Model Builder window, under Results click Concentration, Fe, 3D (tcd).
- 2 In the Settings window for 3D Plot Group, locate the Data section.
- 3 From the Time (s) list, choose 30.
- 4 In the Concentration, Fe, 3D (tcd) toolbar, click Plot.
- 5 From the Time (s) list, choose 300.
- 6 In the Concentration, Fe, 3D (tcd) toolbar, click **1** Plot. The Fe concentration plots should look like Figure 2.

Fe Oxidation Current Density

Next, plot anodic current density variation at the electrode surface.

- I In the Home toolbar, click **Add Plot Group** and choose ID Plot Group.
- 2 In the Settings window for ID Plot Group, type Fe Oxidation Current Density in the Label text field.
- 3 Locate the Data section. From the Time selection list, choose Last.

- I In the Fe Oxidation Current Density toolbar, click Line Graph.
- 2 Select Boundary 2 only.
- 3 In the Settings window for Line Graph, click Replace Expression in the upper-right corner of the y-Axis Data section. From the menu, choose Component I (compl)> Tertiary Current Distribution, Nernst-Planck>Electrode kinetics>tcd.iloc_erl -Local current density - A/m2.
- 4 Select Boundary 2 only.
- 5 In the Fe Oxidation Current Density toolbar, click Plot.
- 6 Locate the x-Axis Data section. From the Parameter list, choose Expression.
- 7 In the **Expression** text field, type r.
- 8 In the Fe Oxidation Current Density toolbar, click **Plot**.

The plot should look like Figure 3.

Concentration, CO2, 3D (tcd)

I In the Model Builder window, under Results click Concentration, CO2, 3D (tcd).

- 2 In the Settings window for 3D Plot Group, locate the Data section.
- **3** From the **Time (s)** list, choose **30**.
- 4 In the Concentration, CO2, 3D (tcd) toolbar, click Plot.
- 5 From the Time (s) list, choose 300.
- 6 In the Concentration, CO2, 3D (tcd) toolbar, click Plot.

The CO2 concentration plots should look like Figure 4.

рН, 3D (tcd)

Next plot the pH variation.

- I In the Home toolbar, click **Add Plot Group** and choose **3D Plot Group**.
- 2 In the Settings window for 3D Plot Group, type pH, 3D (tcd) in the Label text field.

Surface I

- I Right-click pH, 3D (tcd) and choose Surface.
- 2 In the Settings window for Surface, locate the Expression section.
- 3 In the Expression text field, type tcd.pH.

pH, 3D (tcd)

- I In the Model Builder window, click pH, 3D (tcd).
- 2 In the Settings window for 3D Plot Group, locate the Data section.
- **3** From the **Time (s)** list, choose **30**.
- 4 In the pH, 3D (tcd) toolbar, click Plot.
- 5 From the Time (s) list, choose 300.
- 6 In the pH, 3D (tcd) toolbar, click Plot.

The pH plots should look like Figure 5.

Revolution 2D 3

Finally, create a new revolution dataset to plot the precipitation thickness change under the entire droplet.

- I In the Model Builder window, expand the Results>Datasets node.
- 2 Right-click Results>Datasets and choose Revolution 2D.
- 3 In the Settings window for Revolution 2D, click to expand the Revolution Layers section.

Total Electrode Thickness Change, 3D (tcd)

I In the Model Builder window, under Results click Total Electrode Thickness Change, 3D (tcd).

- 2 In the Settings window for 3D Plot Group, locate the Data section.
- 3 From the Dataset list, choose Revolution 2D 3.
- 4 Locate the Plot Settings section. Clear the Plot dataset edges check box.

Surface I

- I In the Model Builder window, expand the Total Electrode Thickness Change, 3D (tcd) node, then click Surface I.
- 2 In the Settings window for Surface, locate the Coloring and Style section.
- 3 Click Change Color Table.
- 4 In the Color Table dialog box, select Rainbow>Prism in the tree.
- 5 Click OK.

Total Electrode Thickness Change, 3D (tcd)

In the Model Builder window, click Total Electrode Thickness Change, 3D (tcd).

Streamline 1

- I In the Total Electrode Thickness Change, 3D (tcd) toolbar, click Streamline.
- 2 In the Settings window for Streamline, locate the Streamline Positioning section.
- 3 From the Positioning list, choose Uniform density.
- 4 In the Separating distance text field, type 0.1.
- 5 Locate the Coloring and Style section. Find the Line style subsection. From the Type list, choose Tube.
- 6 Select the Radius scale factor check box. In the associated text field, type 2.5e-5.
- 7 Find the Point style subsection. From the Type list, choose Arrow.
- 8 From the Arrow length list, choose Logarithmic.

Color Expression I

- I In the Total Electrode Thickness Change, 3D (tcd) toolbar, click 👂 Color Expression.
- 2 In the Settings window for Color Expression, click Replace Expression in the upper-right corner of the Expression section. From the menu, choose Component I (compl)> Tertiary Current Distribution, Nernst-Planck>tcd.llMag Electrolyte current density magnitude A/m².
- 3 Locate the Coloring and Style section. Click Change Color Table.
- 4 In the Color Table dialog box, select Rainbow>CyclicClassic in the tree.
- 5 Click OK.
- 6 In the Settings window for Color Expression, locate the Coloring and Style section.

7 Clear the Color legend check box.

Total Electrode Thickness Change, 3D (tcd)

In the Model Builder window, under Results click Total Electrode Thickness Change, 3D (tcd).

Surface 2

- I In the Total Electrode Thickness Change, 3D (tcd) toolbar, click Surface.
- 2 In the Settings window for Surface, locate the Expression section.
- 3 In the Expression text field, type 1.
- 4 Locate the Coloring and Style section. Clear the Color legend check box.

Selection 1

- I In the Total Electrode Thickness Change, 3D (tcd) toolbar, click 🗣 Selection.
- 2 Select Domain 1 only.

Surface 2

In the Model Builder window, click Surface 2.

Transparency I

- I In the Total Electrode Thickness Change, 3D (tcd) toolbar, click Transparency.
- 2 In the Settings window for Transparency, locate the Transparency section.
- 3 In the Transparency text field, type 0.85.

Surface 2

In the Model Builder window, click Surface 2.

Material Abbearance 1

- I In the Total Electrode Thickness Change, 3D (tcd) toolbar, click Material Appearance.
- 2 In the Settings window for Material Appearance, locate the Appearance section.
- 3 From the Appearance list, choose Custom.
- 4 From the Material type list, choose Water.

Total Electrode Thickness Change, 3D (tcd)

- I In the Model Builder window, under Results click Total Electrode Thickness Change, 3D (tcd).

The ferrous hydroxide precipitation change plot should look like Figure 6.