

INTRODUCTION TO  
Electrochemistry Module

# Introduction to the Electrochemistry Module

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## Introduction

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The Electrochemistry Module is intended for the modeling and simulation of generic electrochemical cells.

The module defines components in 1D, 2D, and 3D geometries that describe the electrochemical reactions, and other surface reactions, at the interface between a metal electrode and an electrolyte, as well as the transport of ions and neutral species in the electrolyte, including possible homogeneous reactions. The current conduction within the metal electrode can also be modeled. The simulations can be used to understand electrolytic processes as well as to design and optimize electrochemical cells.

The functionality in the Electrochemistry Module makes it possible to simulate systems at different scales and at different levels of detail, ranging from rudimentary current distribution analysis of industrial cells in the range of meters down to the detailed chemical and electrochemical phenomena within a pore of a porous electrode, or at, and in the vicinity of, a microelectrode. In terms of size, geometric complexity, and complexity in the described phenomena, the Electrochemistry Module can handle these modeling extremes and anything in between.

### *The Applications*

The modeling and simulation capabilities of the Electrochemistry Module cover processes such as electrode reactions, electrolyte transport and homogeneous reactions. The capabilities also include, for example, transport in porous media and heat transfer.

[Figure 1](#) shows a typical simulation result from a tutorial model, which is available in the module's application library. The plot shows the current density on and the concentration field around a wire mesh electrode. On the electrode, an electrode reaction is consuming a reactant which is present in the surrounding electrolyte. The simulation accounts for the concentration dependent electrode kinetics, the flow of the electrolyte and the transport of the reactant in the electrolyte. (You will explore how to model some of these phenomena in the first modeling example of this introduction book.) The simulation predicts the current distribution in the cell for different cell potentials. This type of simulation may be relevant for any electrolytic manufacturing process. It is then important to estimate the optimum

usage and distribution of catalytic material, which is often based on expensive noble metals.

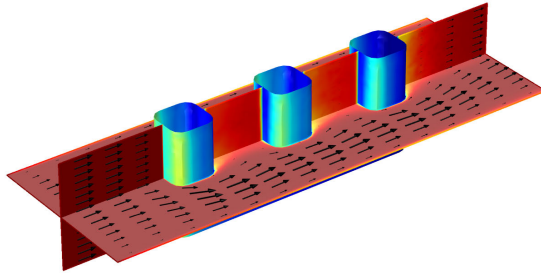


Figure 1: Current distribution and surrounding concentration field of a wire mesh electrode.

Possible applications include the study and design of chlor-alkali and chlorate electrolysis, water electrolysis for hydrogen and oxygen production, waste water treatment, desalination of seawater, electrophoretic separation of proteins, fundamental electrochemical studies in electrocatalysis and electroanalysis, and sensors for glucose, pH, hydrogen, and other gases. In the field of electroanalysis, the Electrochemistry Module offers tailor-made interfaces for cyclic voltammetry and impedance analysis (Figure 2).

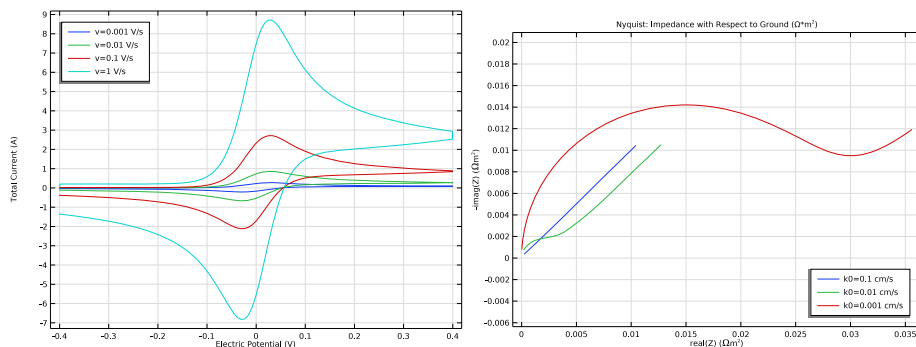


Figure 2: Simulated cyclic voltammograms (left) and Nyquist plots (right) in COMSOL Multiphysics.

## The Electrochemistry Module Physics Interfaces

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The module has a number of physics interfaces, which describe the transport and reaction of charged and neutral ions in aqueous electrolytes, surface reactions (electrochemical and chemical) and the formation of adsorbed species or coatings on metal surfaces. It also describes transport of current in electrolytes and metals, transport of current in thin metal structures (treated as shells), fluid flow, and heat transfer.

Figure 3 shows the available physics interfaces as displayed in the Model Wizard for a 3D model.

- ▷ AC/DC
- ▷ Acoustics
- ▲ Chemical Species Transport
  - Transport of Diluted Species (tds)
  - Chemistry (chem)
  - Nernst-Planck-Poisson Equations
  - Transport of Diluted Species in Porous Media (tds)
  - Electrophoretic Transport (el)
  - ▲ Reacting Flow
    - Laminar Flow, Diluted Species
  - Surface Reactions (sr)
- ▲ Electrochemistry
  - ▲ Primary and Secondary Current Distribution
    - Primary Current Distribution (cd)
    - Secondary Current Distribution (cd)
  - ▲ Tertiary Current Distribution, Nernst-Planck
    - Tertiary, Electroneutrality (tcd)
    - Tertiary, Water-Based with Electroneutrality (tcd)
    - Tertiary, Supporting Electrolyte (tcd)
  - Electroanalysis (tcd)
  - Electrode, Shell (els)
- ▲ Fluid Flow
  - ▷ Single-Phase Flow
  - ▷ Porous Media and Subsurface Flow
  - ▷ Nonisothermal Flow
- ▲ Heat Transfer
  - Heat Transfer in Solids (ht)
  - Heat Transfer in Fluids (ht)
  - Heat Transfer in Solids and Fluids (ht)
  - ▷ Conjugate Heat Transfer
  - ▷ Electromagnetic Heating
  - Heat Transfer in Porous Media (ht)
- ▷ Structural Mechanics
- ▷ Mathematics

Figure 3: The physics interfaces for the Electrochemistry Module as shown in the Model Wizard for a 3D model.

## THE CURRENT DISTRIBUTION INTERFACES


The Electrochemistry interfaces include the generic Primary Current Distribution (  ), Secondary Current Distribution (  ), and Tertiary Current Distribution, Nernst Planck (  ) interfaces.

The Primary Current Distribution interface neglects the activation losses for the charge transfer reactions. It may only be used in the cases where the activation losses are substantially smaller than the conductivity losses. The Secondary




Current Distribution interface accounts for the activation losses for the charge transfer reactions.


The Primary and Secondary Current Distribution interfaces may be combined with a Chemical Species Transport interface (described below) in order to incorporate kinetics effects of active species in the electrolyte or adsorbed species on an electrode surface.


The Tertiary Current Distribution, Nernst Planck () interface accounts for the transport of species through diffusion, migration, and convection and is therefore able to describe the effects of variations in composition on the electrochemical processes. The kinetics expressions for the electrochemical reactions account for both activation and concentration overpotential.


## THE ELECTROANALYSIS INTERFACE


The Electroanalysis interface () models mass transport of diluted species in electrolytes using the diffusion-convection equation, solving for electroactive species concentrations. The physics interface is applicable for electrolyte solutions containing a large quantity of excess (supporting) electrolyte. Ohmic losses are assumed to be negligible. The physics interface includes tailor-made functionality for setting up cyclic voltammetry problems.


## THE CHEMICAL SPECIES TRANSPORT


The Transport of Diluted Species interface () is available under the Chemical Species Transport branch. This physics interface can be used to model transport of species due to diffusion, migration and convection.

The Nernst-Planck-Poisson Equations () interface can be used for investigation of charge and ion distributions within the electrochemical double layer where charge neutrality cannot be assumed. A requisite when using this interface is that the double layer, which typically is in the range of tens nanometers, is fully resolved in the mesh.


The Transport of Diluted Species in Porous Media interface () is also available and describes species transport between the fluid, solid, and gas phases in saturated and variably saturated porous media. The interface for instance be used to model mass transport of non-charged particles within porous electrodes filled with aqueous electrolyte.


The Electrophoretic Transport () interface can be used to investigate the transport of weak acids, bases, and ampholytes in aqueous solvents. The physics interface is typically used to model various electrophoresis modes, such as zone electrophoresis, isotachopheresis, isoelectric focusing, and moving boundary electrophoresis, but is applicable to any aqueous system involving multiple acid-base equilibria.

The Surface Reactions interface () can be used model reactions and translateral transport of surface (adsorbed) species.


The Chemistry interface () can be used to define systems of reacting species, electrode reactions and ordinary chemical reactions. As such, it serves as a reaction kinetics and material property provider to the space dependent transport interfaces, such as the Tertiary Current Distribution, Nernst-Planck interface, or Transport of Diluted Species interface.


## POROUS MEDIA FLOW

The Fluid Flow interfaces () can be combined with the Electrochemistry Module interfaces to model free and forced convection in electrochemical cells.


The Darcy's Law interface () is used to model fluid movement through interstices in a porous medium where a homogenization of the porous and fluid media into a single medium is done. Together with the continuity equation and equation of state for the pore fluid (or gas) this physics interface can be used to model low velocity flows, for which the pressure gradient is the major driving force. The penetration of electrolyte through a porous electrode is a classic example for the use of Darcy's Law in electrochemical engineering.




Darcy's law can be used in porous media where the fluid is mostly influenced by the frictional resistance within the pores. Its use is within very low flows, or media where the porosity is very small. Where the size of the interstices is larger, and the fluid is also influenced by itself, the gradients in fluid velocity, pressure, and gravity must be considered. This is done in the Brinkman Equations interface.

The Brinkman Equations interface () is used to model compressible flow at speeds of less than Mach 0.3, but control over the density and any of the mass balances that are deployed must be maintained to help with this.

The Free and Porous Media Flow interface () is useful for equipment that contain domains where free flow is connected to porous media, such as concrete structures immersed in water.

## HEAT TRANSFER










The Heat Transfer interfaces () have in-built formulations for the contribution of Joule heating, and other electrochemical heat sources, to the thermal balance of electrochemical cells.












The features of the various Heat Transfer interfaces include Heat Transfer in Fluids (), Heat Transfer in Solids (), and Heat Transfer in Porous Media (), and account for conductive and convective heat transfer. These features interact seamlessly and can be used in combination in a single model.





The detailed equations and assumptions that are defined by the physics interfaces are formulated in the *Electrochemistry Module User's Guide* and the *COMSOL Multiphysics Reference Manual*.

### Physics Interface Guide by Space Dimension and Study Type

The table lists the physics interfaces available with this module in addition to those included with the COMSOL Multiphysics basic license.

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
 <b>Chemical Species Transport</b>				
Surface Reactions		sr	all dimensions	stationary (3D, 2D, and 2D axisymmetric models only); time dependent
Transport of Diluted Species		tds	all dimensions	stationary; time dependent
Transport of Diluted Species in Porous Media		tds	all dimensions	stationary; time dependent
Electrophoretic Transport		el	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization
Chemistry		chem	all dimensions	stationary; time dependent
Nernst-Planck-Poisson Equations		tds+es	all dimensions	stationary; time dependent; stationary source sweep; small-signal analysis, frequency domain
 <b>Reacting Flow</b>				
Laminar Flow, Diluted Species		—	3D, 2D, 2D axisymmetric	stationary; time dependent

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
 <b>Electrochemistry</b>				
Primary Current Distribution		cd	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent
Secondary Current Distribution				
Tertiary Current Distribution, Nernst-Planck (Electroneutrality, Water-Based with Electroneutrality, Supporting Electrolyte)		tcd	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent
Electroanalysis		tcd	all dimensions	stationary; time dependent; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent; cyclic voltammetry
Electrode, Shell		els	3D, 2D, 2D axisymmetric	stationary; time dependent
 <b>Fluid Flow</b>				
 <b>Porous Media and Subsurface Flow</b>				
Brinkman Equations		br	3D, 2D, 2D axisymmetric	stationary; time dependent
Darcy's Law		dl	all dimensions	stationary; time dependent
Free and Porous Media Flow		fp	3D, 2D, 2D axisymmetric	stationary; time dependent

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
 <b>Nonisothermal Flow</b>				
Brinkman Equations		—	3D, 2D, 2D axisymmetric	stationary; time dependent; stationary, one-way NITF; time dependent, one-way NITF
 <b>Heat Transfer</b>				
Heat Transfer in Porous Media		ht	all dimensions	stationary; time dependent

# Orange Battery

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This tutorial model serves as an introduction to electrochemistry modeling in COMSOL Multiphysics and models the currents and the concentration of dissolved metal ions in a battery (corrosion cell) made from an orange and two metal nails.

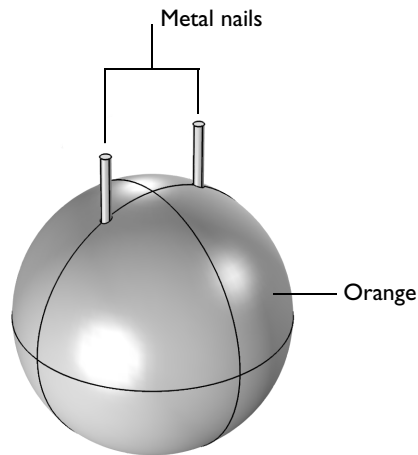


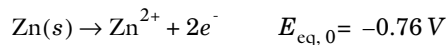
Figure 4: Modeled geometry. Orange and two metal nails.

This type of battery is commonly used in chemistry class demonstrations. Instead of an orange, lemons or potatoes can also be used.

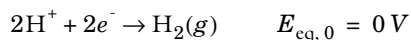
## Model Definition

The citric acid and various other ions in the orange serve as electrolyte, and using nails of different metals as electrodes creates a galvanic potential over the cell.

In this example a zinc nail is used as one of the electrodes, giving rise to the following electrode reaction:



The other nail consists of copper, and here hydrogen evolution is assumed to take place:



$E_{\text{eq},0}$  above denotes the equilibrium potentials at standard conditions versus a standard hydrogen electrode (SHE). In the model, the equilibrium potentials are corrected for the pH and zinc concentration of the orange pulp using the Nernst equation.

The model for the currents in the orange and electrodes is set up using the Secondary Current Distribution interface. The electrolyte current in the orange is thereby solved for by Ohm's law. The conductivity of the metal nails is so high that the electrode domains are not included in the model, instead boundary conditions on the nail surfaces are used to set the nail potentials. One nail is grounded and the other one is set to a cell potential to comply with a total current condition. This would correspond to a situation where the cell is controlled galvanostatically, for instance by the use of a potentiostat.

Butler–Volmer type expressions, with concentration dependent exchange current density for the zinc reaction, are used for the electrode kinetics on the surface of the nails within the orange.

The initial values electrolyte potential is set to correspond to the potential of a cell at open circuit (that is, no activation potential). Following the definition of the overpotential:

$$\eta = \phi_s - \phi_l - E_{\text{eq}}$$

the initial value becomes:

$$\phi_{l, \text{init}} = \phi_s - E_{\text{eq}} - \eta = 0 - E_{\text{eq}, \text{Zn}} - 0 = -E_{\text{eq}, \text{Zn}}$$

In an extension of the model, the diffusion and migration of the dissolved zinc ions in the orange from the zinc electrode reaction is modeled by the Transport of Diluted Species interface in a time-dependent simulation. This assumes that the zinc ion transport can be described by the Nernst-Planck equations (without an electroneutrality condition due to a supporting electrolyte). In addition, the zinc electrode kinetics are modified to be dependent on the zinc concentration, which increases in the orange as more and more zinc is dissolved. The zinc concentration is set to 0.001 mol/m<sup>3</sup> at the start of the simulation. All boundaries except the zinc electrode are insulated.

## RESULTS AND DISCUSSION

Figure 5 shows the potential field in the orange. The potential decreases as the current flows from the zinc electrode (left) to the upper electrode (right). The main part of the cell voltage loss is due to ohmic losses in the electrolyte.

The performance of the battery could probably be increased by using an electrolyte of higher conductivity (for example, a lemon instead of an orange) or by decreasing the distance between the nails.

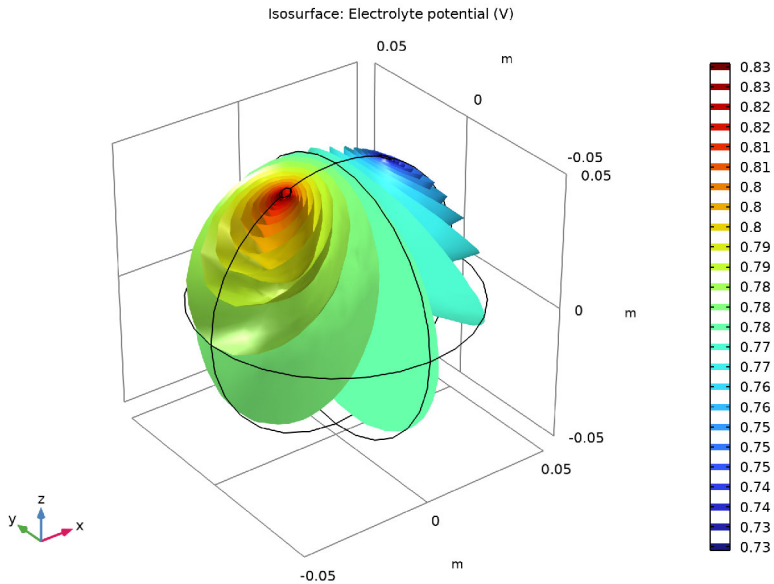


Figure 5: Potential field in the electrolyte at  $t=0$ .



Figure 6 shows a polarization plot as the total current of the battery increases from 0 to 1 mA. The large change in cell voltage seen at low currents is due to overpotential losses at the zinc electrode. Increasing the area of the zinc electrode would decrease this effect.

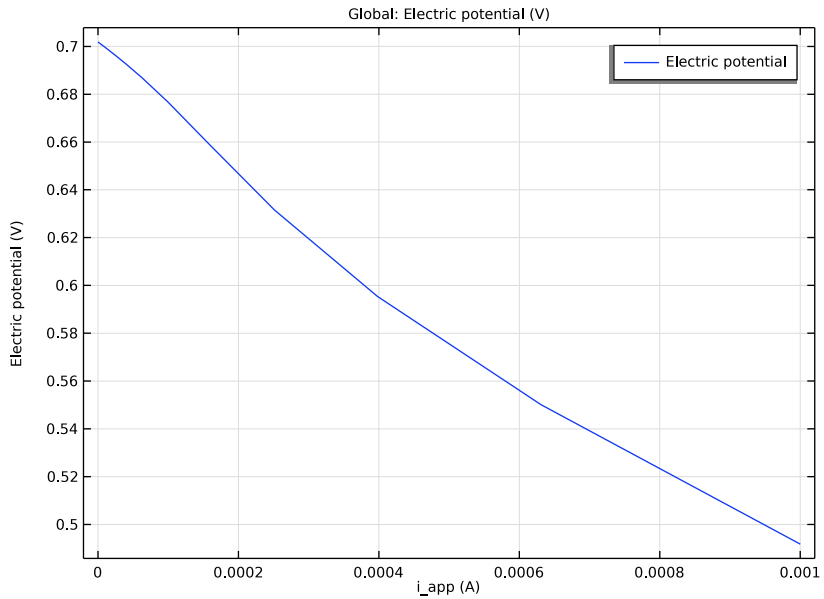


Figure 6: Polarization plot for the initial concentrations.

Figure 7 shows an isosurface for the  $0.2 \text{ mol/m}^3$  concentration level of zinc ions after running the battery for five minutes.

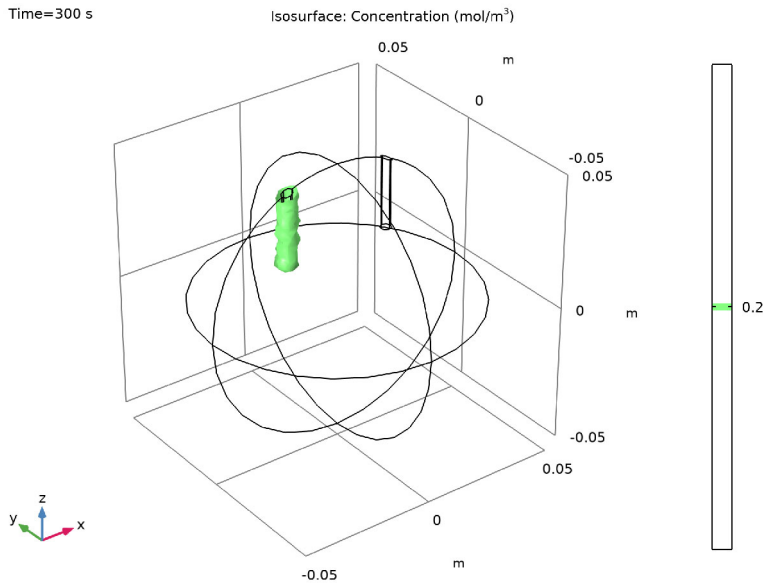


Figure 7:  $0.2 \text{ mol/m}^3$  zinc concentration isosurface after five minutes.

Figure 8 shows how far the  $0.2 \text{ mol/m}^3$  isosurface level has reached after one hour.

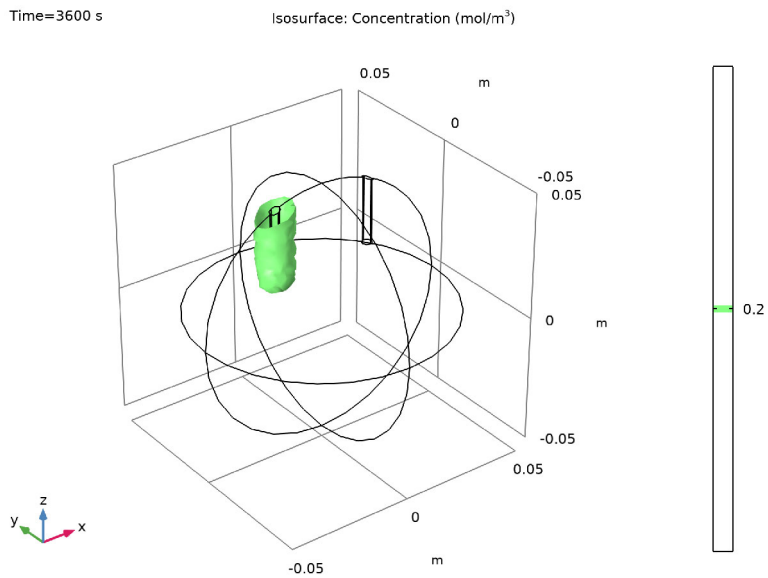


Figure 8:  $0.2 \text{ mol/m}^3$  zinc concentration isosurface after one hour.

Figure 9 shows how the cell current evolves with time. Due to the increase of zinc ions at the zinc nail electrode, the battery current decreases for a constant cell current.

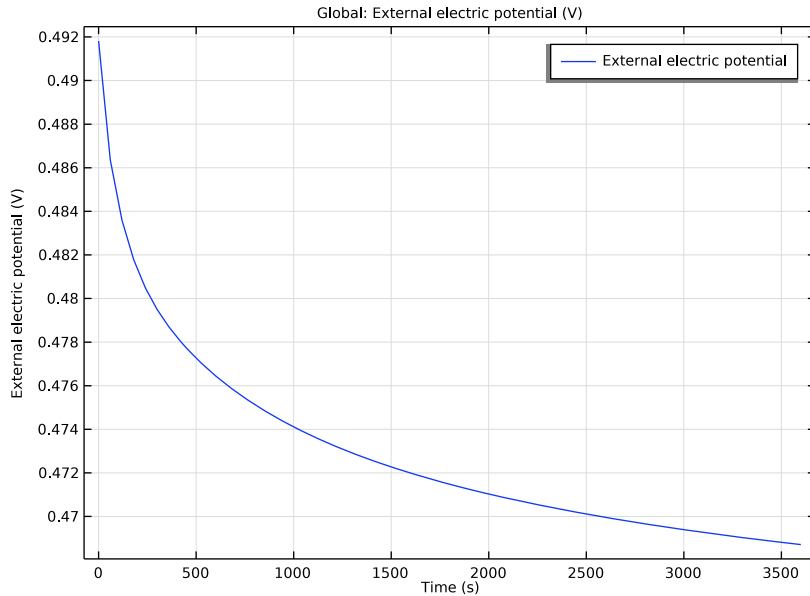


Figure 9: Cell current vs. time.

## SUGGESTED EXERCISES AND EXTENSIONS OF THE MODEL

Change the radius of the nails and the value of the electrolyte conductivity and investigate how this affects the polarization plot.



The dissolved zinc ions may form a layer of zinc hydroxide on the zinc surface, giving rise to an additional potential drop. You may use the Film Resistance section on the Electrode Surface Boundary node to include this potential drop. The value of the film resistance could for instance be a function of the zinc ion concentration variable in the pulp. Alternatively you may add a Surface Reactions interface to model the buildup of the surface concentration of zinc hydroxide, and then couple the film resistance to the hydroxide concentration.

## Model Wizard






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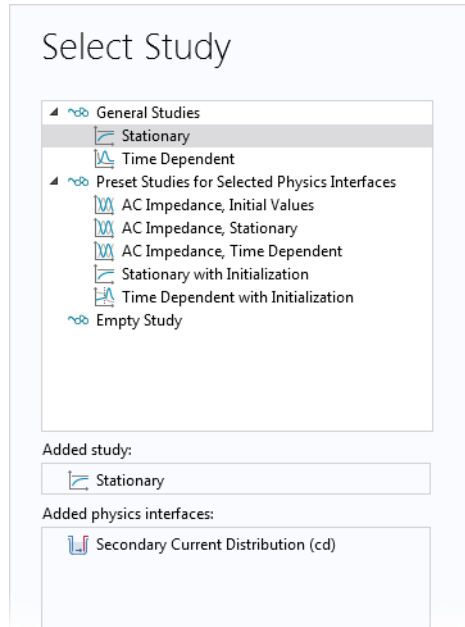
**Note:** These instructions are for the user interface on Windows but apply, with minor differences, also to Linux and Mac.

1 To start the software, double-click the COMSOL icon on the desktop. When the software opens, you can choose to use the Model Wizard to create a new COMSOL Multiphysics model or Blank Model to create one manually. For this tutorial, click the Model Wizard button.

If COMSOL Multiphysics is already open, you can start the Model Wizard by selecting New  from the File menu and then click Model Wizard .

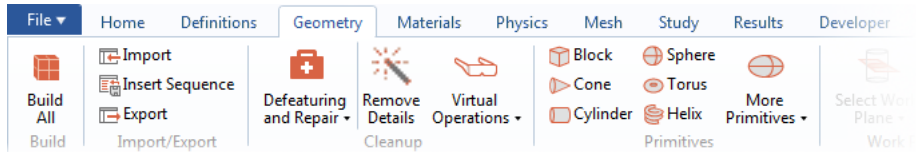
The Model Wizard guides you through the first steps of setting up a model. The next window lets you select the dimension of the modeling space.

- 2 In the Space Dimension window click the 3D button .
- 3 In the Select Physics tree under Electrochemistry>Primary and Secondary Current Distribution, click Secondary Current Distribution .
- 4 Click Add then click the Study  button.
- 5 In the tree under General Studies, click Stationary .
- 6 Click Done , when the Added study and Added physics interfaces lists look as to the right.




# Geometry I


Start by drawing the geometry; one sphere (the orange) and two cylinders (the metal nails, zinc and copper). Both shapes are available in the Geometry toolbar.



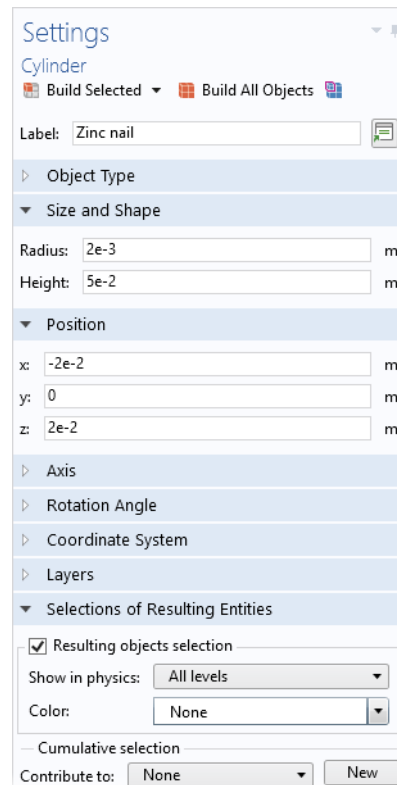
## Sphere I

- 1 On the Geometry toolbar, click Sphere .
- 2 In the Settings window for Sphere, locate the Size section and type  $5e-2$  in the Radius text field.




## Zinc nail

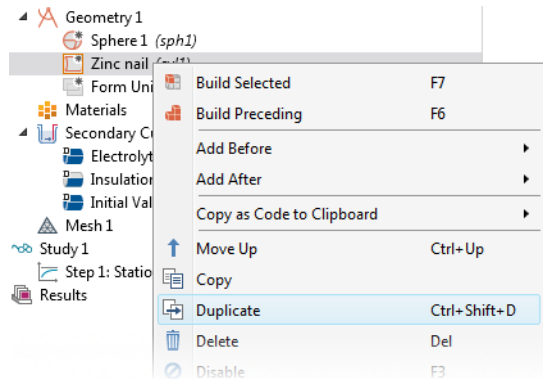
- 1 On the Geometry toolbar, select Cylinder .
- 2 In the Settings window for Cylinder, type Zinc nail in the Label text field.
- 3 Locate the Size and Shape section.
  - In the Radius text field, type  $2e-3$ .
  - In the Height text field, type  $5e-2$ .
- 4 Locate the Position section.
  - In the x text field, type  $-2e-2$ .
  - In the z text field, type  $2e-2$ .
- 5 Locate the Selections of Resulting Entities section. Select the Resulting objects selection check box and choose All levels in the Show in physics list. By enabling this setting you can easily select all boundaries of the nail later on when setting up the physics.

Duplicate the cylinder and change the x position to draw the second nail.



### Copper nail

- 1 Right-click Component 1>Geometry 1>Zinc nail and click Duplicate .
- 2 In the Settings window for Cylinder, type Copper nail in the Label text field.
- 3 In the Position section enter  $2e-2$  in the x text field.
- 4 Finally, to inspect in the Graphics window that the geometry becomes identical to that in [Figure 4](#), click Build all  on the Geometry toolbar and Zoom Extents  on the Graphics toolbar.



## Global Definitions

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Load the model parameters from a text file.

The location of the files used in this exercise may vary based on the installation. For example, if the installation is on your hard drive, the file path might be similar to C:\Program Files\COMSOL61\Multiphysics\applications\.

### Parameters

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

**Note:** On Linux and Mac, the Home toolbar refers to the specific set of controls near the top of the Desktop.


- 2 In the Settings window for Parameters click the Load from File button .

- Browse to the application library folder, Electrochemistry Module>Tutorials, and double-click the file orange\_battery\_parameters.txt.

Parameters

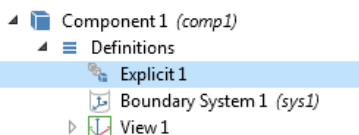
Name	Expression	Value	Description
i_app	1e-3[A]	0.001 A	Applied Current
sigma	0.35[S/m]	0.35 S/m	Electrolyte conductivity
T	293.15[K]	293.15 K	Cell temperature
c_ref	1[mol/l]	1000 mol/m <sup>3</sup>	Reference concentration
c_H0	10^-4[mol/l]	0.1 mol/m <sup>3</sup>	Proton concentration, pH 4
c_Zn20	1e-6[mol/l]	0.001 mol/m <sup>3</sup>	Initial zinc ion concentration
E_eq_Zn0	-0.76[V]+R_const*T/(2*F_const)*log(c_Zn20/c_ref)	-0.9345 V	Initial Zn electrode equilibrium potential
alpha_c_Zn	1.5	1.5	Cathodic Transfer Coefficient, Zn reaction
alpha_a_Zn	2-alpha_c_Zn	0.5	Anodic Transfer Coefficient, Zn reaction
i0_H2	10[A/m^2]	10 A/m <sup>2</sup>	Exchange current density for H2 evolution on Copper electrode
Eeqref_Zn	-0.76[V]	-0.76 V	Zn electrode reference equilibrium potential
i0ref_Zn	10[A/m^2]	10 A/m <sup>2</sup>	Zn electrode reference exchange current density

## Definitions

Add a manual explicit selection for the orange domain. This will facilitate if the geometry needs to be changed in the future. Selections is generally a convenient way to group different parts of the geometry together. Selections of the two nails are already available under the Geometry node  in the Model Builder Window.

### Explicit 1

- On the Definitions toolbar, click Explicit .




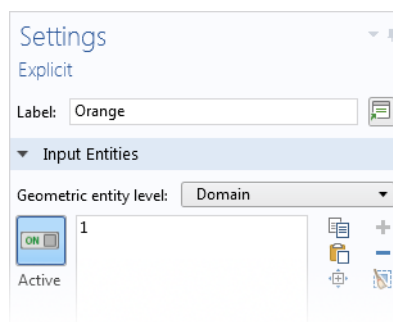
- In the Settings window for Explicit, type Orange in the Label text field.

- Select Domain 1 only.

Load some variable definitions from a file. The location of the file should be the same as the parameter file.


### Variables 1

- In the Model Builder window, under Component 1 right-click Definitions .






and select Variables  $a=$ . Alternatively, click the Definitions toolbar and select Local Variables  $a=$ .

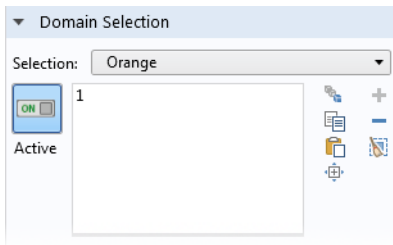
- 2 In the Settings window for Variables click the Load from File button .
- 3 Browse to the application's Application Library folder and double-click the file `orange_battery_variables.txt`.

## Secondary Current Distribution

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Now, start setting up the current distribution model. Change the selection of the entire physics interface to the orange domain only.

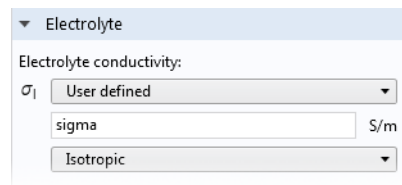
- 1 In the Model Builder window, click Secondary Current Distribution.
- 2 In the Settings window for Secondary Current Distribution , locate the Domain Selection section and choose Orange from the Selection list.



### *Electrolyte 1*

The selection is locked to all selected domains of the physics interface, which in this case is the orange only.

- 1 In the Model Builder window, under Component 1>Secondary Current Distribution click Electrolyte 1 . The 'D' in the upper left corner of a node means it is a default node.
- 2 In the Settings window for Electrolyte, locate the Electrolyte section. Here the electrolyte conductivity can be set. From the  $\sigma_1$  list choose User defined and type `sigma` in the associated text field. `sigma` is defined in the Parameters  $P_1$  node.

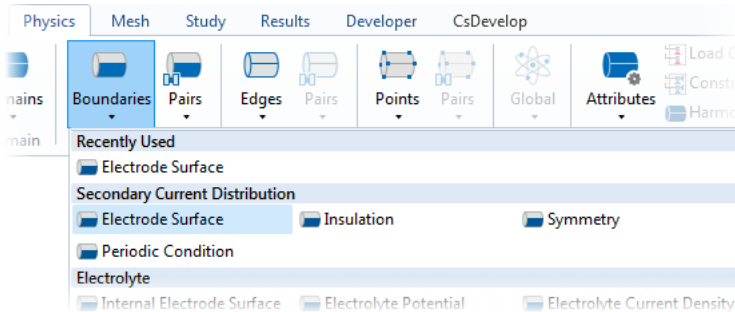



### *Electrode Surface 1*

Use Electrode Surface nodes to define both a metal electrode potential and an electrode electrolyte interface. Use a Butler–Volmer expression for the zinc


electrode. The hydrogen kinetics are assumed to be very fast so that a linearized Butler–Volmer expression is applicable. Start with the Zinc nail (electrode).

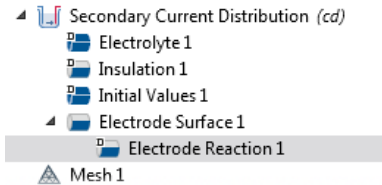
- 1 On the Physics toolbar, click Boundaries  and choose Electrode Surface .



- 2 In the Settings window for Electrode Surface locate the Boundary Selection section and select Zinc nail from the Boundary Selection.
- 3 Click the Transparency  button on the Graphics toolbar to enable transparency and inspect the active boundaries in the Graphics window.

### Electrode Reaction 1

- 1 In the Model Builder, expand the Electrode Surface 1 node and click Electrode Reaction 1 .



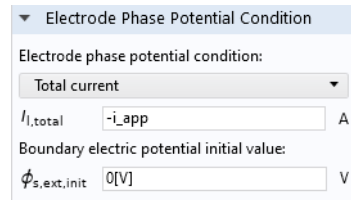
- 2 In the Settings window for Electrode Reaction, locate the Equilibrium Potential section.
- 3 From the Eeq list, choose Nernst equation.
- 4 In the Eeq, ref(T) text field, type Eeqref\_Zn.
- 5 In the CO text field, type  $c_{\text{Zn}^{2+}}/c_{\text{ref}}$ .
- 6 Locate the Stoichiometric Coefficients section. In the n text field, type 2.
- 7 Locate the Electrode Kinetics section. From the Kinetics expression type list, choose Butler–Volmer.
- 8 From the Exchange current density type list, choose From Nernst Equation.
- 9 In the  $i_{0,\text{ref}}(T)$  text field, type  $i_{0\text{ref\_Zn}}$ .

10 In the  $\alpha_a$  text field, type `alpha_a_Zn`.

### *Electrode Surface 2*

Define the copper nail (electrode) in a similar way with an Electrode Surface. First add a parameter for the total current. This parameter will also be used in the study to perform a galvanic polarization sweep over the cell.

- 1 On the Physics toolbar, Click Boundaries and choose Electrode Surface
- 2 In the Settings window for the Electrode Surface, locate the Boundary Selection section. In the Selection list there, choose Copper nail.
- 3 This cell is under galvanic control. Specify this in the Electrode Phase Potential Condition section by selecting Total current in the Boundary condition list and typing `-i_app` in the  $I_{i,total}$  text field that appears. This parameter will also be used in the study to perform a galvanic polarization sweep over the cell.



## Electrode Reaction 1

- 1 In the Model Builder window, expand the Electrode Surface 2 node, then click Electrode Reaction 1
- 2 In the Settings window for Electrode Reaction, locate the Equilibrium Potential section.
- 3 From the Eq list, choose Nernst equation.
- 4 In the  $C_O$  text field, type  $c_{H_0}/c_{ref}$ .
- 5 Locate the Electrode Kinetics section. In the  $i_0$  text field, type  $i_{0\_H_2}$ .

**▼ Stoichiometric Coefficients**

Number of participating electrons:  
 $n$   1

**▼ Equilibrium Potential**

Equilibrium potential:  
 $E_{eq}$   ▼

Reference equilibrium potential:  
 $E_{eq,ref}(T)$   V

Reduced species expression:  
 $C_R$   1

Oxidized species expression:  
 $C_O$   1

$$E_{eq} = E_{eq,ref}(T) - \frac{RT}{nF} \ln \frac{C_R}{C_O}$$

**▼ Electrode Kinetics**

Local current density expression:  
 $i_{loc,expr}$   ▼

Kinetics expression type:  
 ▼

Exchange current density type:  
 ▼

Exchange current density:  
 $i_0$   A/m<sup>2</sup>

Anodic transfer coefficient:  
 $\alpha_a$   1


Cathodic transfer coefficient:  
 $\alpha_c$   1

$$i_{loc,expr} = i_0 \left( \frac{(\alpha_a + \alpha_c)F}{RT} \right) \eta$$

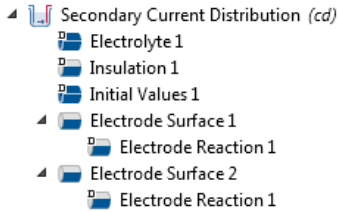
Limiting current density  
 $i_{loc} = i_{loc,expr}$

## Initial Values 1

We are using nonlinear kinetics in the model. Provide an initial value for the electrolyte potential in order to reduce solver time and improve convergence. As a rule of thumb one can often use the negative of the equilibrium potential of the grounded electrode as initial value for the electrolyte potential.

- 1 In the Model Builder window, under Secondary Current Distribution click Initial Values 1 .
- 2 In the Settings window for Initial Values, locate the Initial Values section.
- 3 As a rule of thumb one can often use the negative of the equilibrium potential of the grounded electrode as initial value for the electrolyte potential. Therefore, in the *phil* text field, type  $-E_{eq\_Zn0}$ .

The interface node sequence in the Model Builder should match this figure:



## 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


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The default mesh settings can be used in this model and therefore no changes need to be made here.

## Study 1

---



The model is now ready for solving.

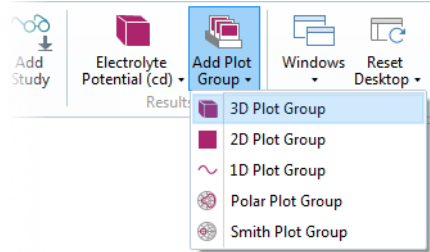
- 1 On the Study toolbar click Compute .

## Results






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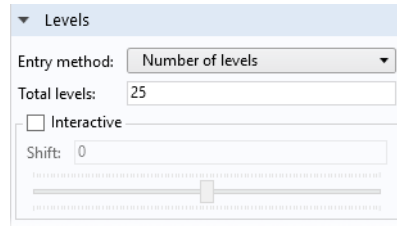
Use a 3D isosurface plot for visualizing the potential field in the electrolyte.

- 1 On the Home toolbar, click Add Plot Group  and choose 3D Plot Group .
- 2 In the Settings window for the 3D Plot Group, type **Potential Isosurface** in the Label text field.



### *Potential Isosurface*




- 1 Right-click the Potential Isosurface  node and choose Isosurface .
- 2 In the Settings window for Isosurface, locate the Levels section and in the Total levels text field, type 25.
- 3 Click Zoom Extents  and Transparency  on the Graphics toolbar before clicking the Plot button  on the Potential Isosurface toolbar. A plot identical to [Figure 5](#) will now appear in the Graphics window.



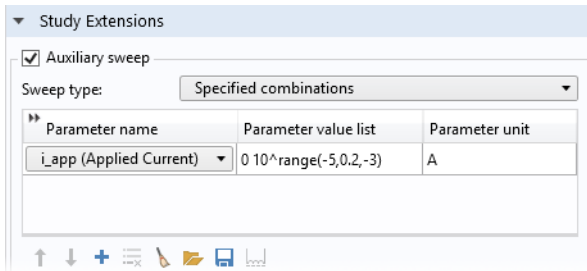
## Study 1

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Now use an Auxiliary Sweep available in Stationary study step to solve over a range of cell currents in order to create a polarization plot.

- 1 In the Model Builder window, under Study 1  click Step 1: Stationary .
- 2 In the Settings window for Stationary, click to expand the Study extension section and select the Auxiliary sweep check box.
- 3 Click the  Add button under the table. In the Parameter name column, select `i_app` (Applied Current) from the list that appears.

- 4 In the Parameter value column enter  $0 \cdot 10^{\text{range}(-5,0.2,-3)}$  and in the Parameter unit column enter A.





- 5 On the Study toolbar click Compute  $\text{=}$ .


## Results


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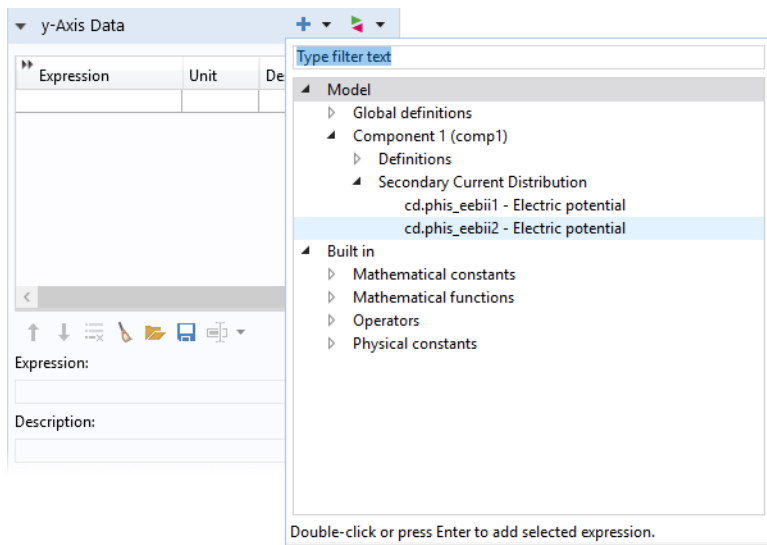
The results from this last run can be used to set up a polarization plot:

- 1 On the Home toolbar, click Add Plot Group  and choose 1D Plot Group .
- 2 In the Settings window for 1D Plot Group, type Polarization Plot in the Label text field.

### *Polarization Plot*

- 1 On the Polarization Plot toolbar, click Global .

- 2 In the Settings window for Global, locate the y-Axis Data section and click Add Expression . Select Component 1>Secondary Current Distribution>Electric potential (siec.phis\_eebii2) from the list that appears.








- 3 On the Polarization plot toolbar, click Plot . This generates [Figure 6](#) above.

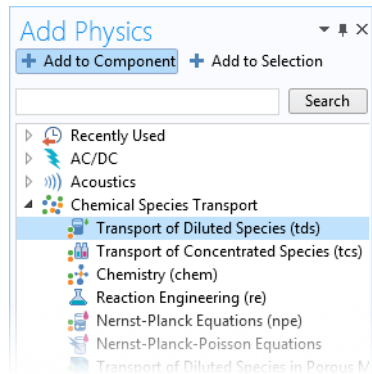
## Adding Mass Transport

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Move on to extend the model to investigate the battery voltage over time at a certain load current. Start by adding a physics interface to handle the mass transport of zinc ions. The ions can be regarded as diluted in the orange interior making the Transport of Diluted Species interface suitable for modeling the mass transport.

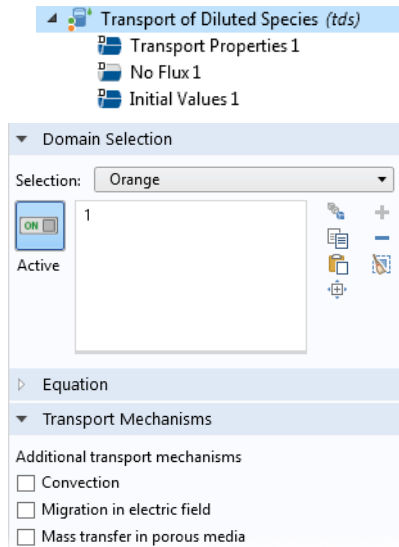


- 1 On the Home toolbar, click Add physics . This opens the Add Physics window.
- 2 Here, locate the Transport of Diluted Species (tds)  under Chemical Species Transport  and click Add to component .
- 3 To close the Add physics window, click Add Physics  on the Home toolbar.





## Transport of Diluted Species

- 1 In the Model Builder window, under Component 1 click Transport of Diluted Species .
- 2 In the Settings window for Transport of Diluted Species, locate the Domain Selection section and in the Selection list choose Orange.
- 3 The orange pulp is quiescent so convection can be ignored in the model. This is done in the Transport Mechanisms section by clearing the Convection check box. Additionally, due to the presence of a lot of other ions in the pulp, acting as supporting electrolyte, we assume the potential gradients to be small and hence also ignore the effect of migrative transport of the zinc ions.




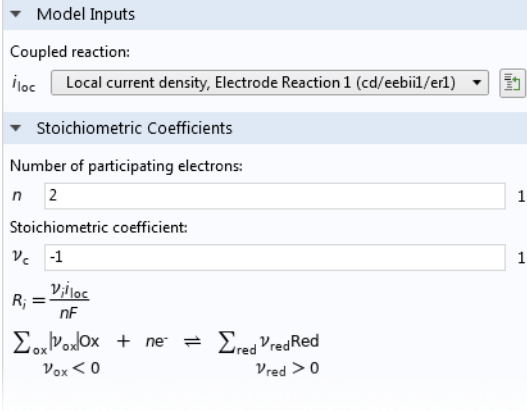
### *Electrode Surface Coupling I*

For this example we will use the default diffusion coefficient value in the Transport Properties node so no settings are needed on the default domain node. The following steps couple the electrochemical reaction currents to the ion flux at the electrode surface.

- 1 On the Physics toolbar, click Boundaries  and choose Electrode Surface Coupling  in which the coupling can be enabled.
- 2 In the Settings window for Electrode Surface Coupling, locate the Boundary Selection section and in the Selection list select Zinc nail.

### Reaction Coefficients 1

- 1 In the Model Builder window, expand the Electrode Surface Coupling 1 node and click the Reaction Coefficients 1  node.
- 2 In the Model Inputs section, the Coupled reaction  $i_{loc}$  list setting should be that of the Zinc nail. Therefore, choose Local current density (siec/eebiil/er1).
- 3 In the Stoichiometric Coefficients section, enter In the  $n$  text field type 2, and in the  $\nu_c$  text field type -1. These stoichiometric coefficients refer to the stoichiometric number of the reacting species when written as a reduction reaction.




The screenshot shows the 'Model Inputs' and 'Stoichiometric Coefficients' sections of a software interface. In the 'Model Inputs' section, the 'Coupled reaction:' dropdown is set to 'Local current density, Electrode Reaction 1 (cd/eebiil/er1)'. In the 'Stoichiometric Coefficients' section, the 'Number of participating electrons:' is set to 2, and the 'Stoichiometric coefficient:' is set to -1. Below these fields, the following equations are displayed:

$$R_i = \frac{\nu_i i_{loc}}{nF}$$

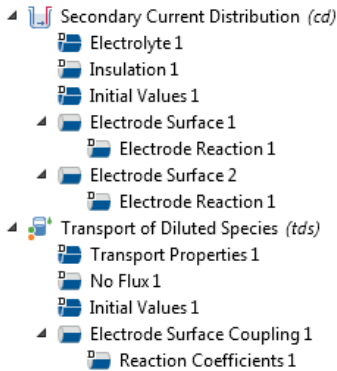
$$\sum_{\nu_{ox} < 0} |\nu_{ox}| Ox + ne^- = \sum_{\nu_{red} > 0} \nu_{red} Red$$

### Initial Values 1

The initial zinc ion concentration at the start of the time-dependent simulation is required.

- 1 In the Model Builder window, under Component 1 and Transport of Diluted Species click Initial Values 1 .
- 2 Locate the Initial Values section and enter c\_Zn20 in the  $c$  text field.

The node sequence of the interfaces in the Model Builder should now match this figure:



## Definitions

The zinc ion concentration is no longer constant. Modify the equilibrium potential and exchange current density variables for the zinc electrode to be dependent on the local concentration of zinc ions. This can be done by defining the following variable.

### Variables 1

- 1 In the Model Builder window, under Component 1 and Definitions click Variables 1  $a=$ .
- 2 In the table, add the following settings:





NAME	EXPRESSION	UNIT	DESCRIPTION
c_Zn2	c	mol/m <sup>3</sup>	Zinc ion concentration (used in above expressions)

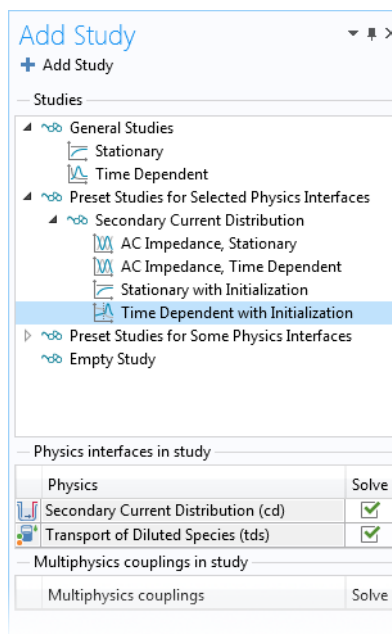
The name of this variable is 'c' by default in the Transport of Diluted Species interface.

Variables			
Name	Expression	Unit	Description
E_eq_Zn	$-0.76[V] + R_{\text{const}} \cdot T / (2 \cdot F_{\text{const}}) \cdot \log(c_{\text{Zn2}} / c_{\text{ref}})$	V	Zinc electrode equilibrium potential
i0_Zn	$10 [A/m^2] \cdot (c_{\text{Zn2}} / c_{\text{ref}})^{\alpha_{\text{a\_Zn}} / 2}$	A/m <sup>2</sup>	Zinc electrode exchange current density
c_Zn2	c_Zn20	mol/m <sup>3</sup>	Zinc ion concentration (used in above expressions)

## Add Study

Create a new time-dependent study for the concentration simulation.

- 1 On the Home toolbar, click Add Study  to open the Add Study window.
- 2 In the Add Study window select Time Dependent with Initialization  under Preset Studies for Selected Physics Interfaces . This study type computes the necessary initial values facilitating the computations to start.
- 3 To close the Add Study window, click Add Study  on the Home toolbar.





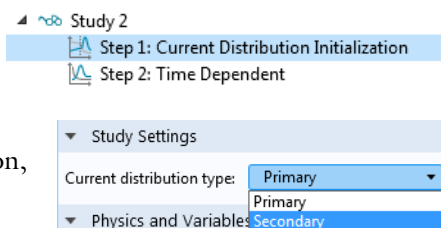
## Study 2

The Time Dependent with Initialization study consists of two steps.



### Step 1: Current Distribution Initialization

In Step I, use a secondary current distribution initialization step which works well when concentration dependent electrode kinetics are modeled.

- 1 In the Model Builder, under Study 2  click Step 1: Current Distribution Initialization .
- 2 From the Current distribution type list available in the Study Settings section, choose Secondary.



### Step 2: Time Dependent




- 1 Now click Step 2: Time Dependent  Under Study 2 to select the times that are solved for.
- 2 In the Study Settings section enter range (0,60,3600) in the Times text field.
- 3 On the Home toolbar, click Compute  .

## Results







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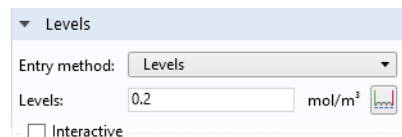
Plot the zinc concentration in the orange.

### 3D Plot Group 14

- 1 On the Home toolbar, click Add Plot Group  and choose 3D Plot Group  .
- 2 In the Settings window for 3D Plot Group  , type Concentration Isosurface in the Label text field.
- 3 Locate the Data section. From the Dataset list in the Data section, choose Study 2/Solution 2. From the Time (s) list that appears, select 300.





### Concentration Isosurface

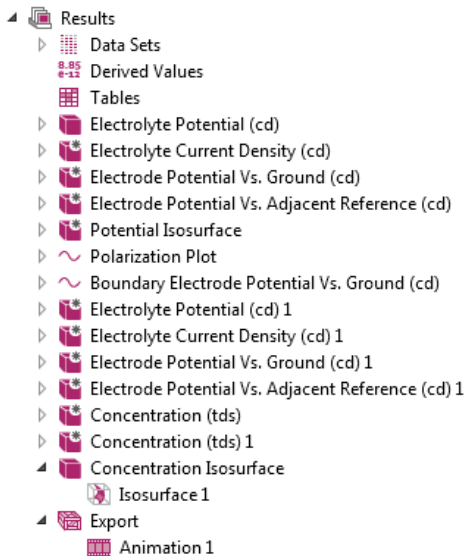
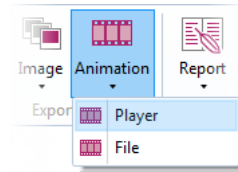
- 1 Right-click Concentration Isosurface  under Results and choose Isosurface  . Alternatively, this can be done by clicking Isosurface  on the Concentration Isosurface toolbar.
- 2 Click Replace Expression  in the upper-right corner of the Expression section in the Isosurface Settings window. From the menu, choose Component 1>Transport of Diluted Species>c - Concentration -mol/m<sup>3</sup>.
- 3 In the Levels section, from the Entry method list, choose Levels and type 0.2 in the Levels text field.
- 4 After you have clicked the Zoom Extents  button on the Graphics toolbar, click Plot  on the Concentration Isosurface toolbar. This will create [Figure 7](#) showing Zinc concentration isosurface.






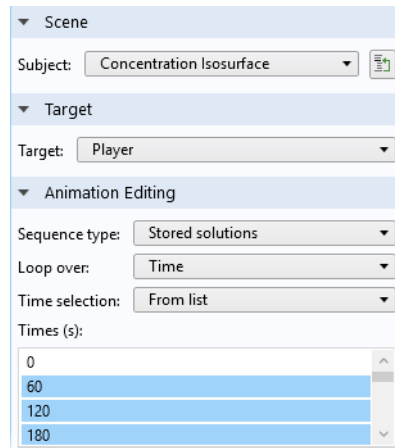
### Export

An animation can be used to visualize the zinc ion isosurface during the simulated time:

- On the Results toolbar, click Animation  and select Player . This generates an Animation 1  node under the Export  node.





- In the Settings window for Animation, locate the Target section and select Player from the Target list. Locate the Scene section. From the Subject list, choose Concentration Isosurface.
- In the Animation Editing section, choose From list in the Time selection list.
- At  $t=0$  there is no concentration gradient in the orange, so deselect the first time step. To do this, select all steps except 0 in the Times (s) list.
- Click Zoom Extents in the Graphics toolbar followed by right-click of Animation 1  under the Export  node and choose Play . The last frame at 3600 s should match [Figure 8](#).

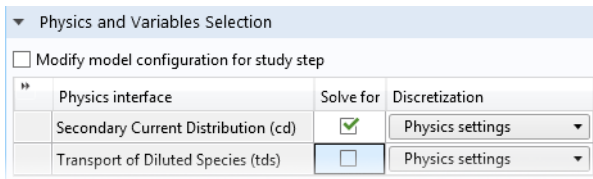


## Further Simulations

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If you want to experiment with the model by changing parameter values and simulate new polarization plots, you have to disable the Transport of Diluted Species interface in the stationary study as follows:

- 1 In the Model Builder window under Study 1  click Step 1: Stationary .
- 2 Disable the Transport of Diluted Species interface in the table shown in the Physics and Variables Selection section by clearing the check box in the ‘Solve for’ column.



## Cyclic Voltammetry at a Macroelectrode in 1D

---

*Cyclic voltammetry* is a common analytical technique for investigating electrochemical systems. In this method, the potential difference between a working electrode and a reference electrode is swept linearly in time from a start potential to a vertex potential, and back again (see Figure 10). The resulting current at the working electrode is recorded and is plotted against the applied electrode potential in a *voltammogram*.

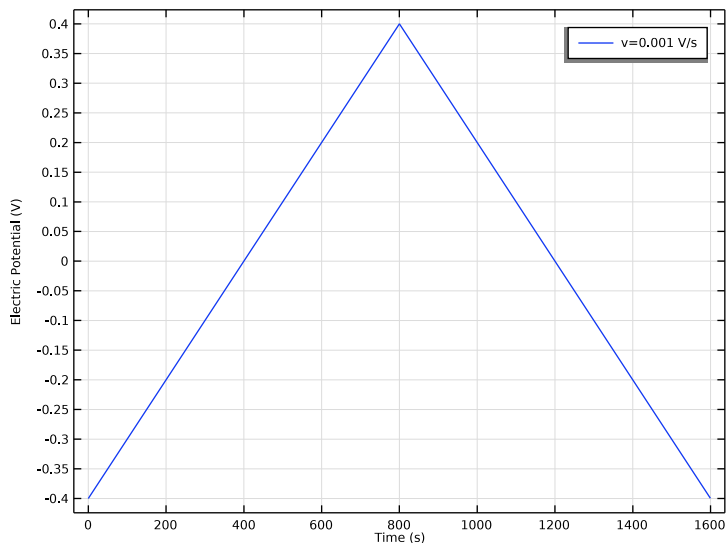


Figure 10: Potential of the working electrode during one voltammetric cycle. The potential is cycled between the vertex potentials 0.4 V and -0.4 V. The scan rate is 1 mV/s.

Voltammetry is a valuable technique because information about both the electrochemical reactivity and the transport properties of a system can be extracted simultaneously. For quantitative interpretation of voltammetry, however, we must use numerical methods to solve the physical equations that describe voltammetry. Then, unknown physical quantities in the system can be inferred by ‘fitting’ to experimental data.

This example demonstrates the use of a common approximation in which a large electrode (macroelectrode) is assumed to have uniform transport behavior across its surface, so only physics occurring normal to the surface need to be considered. By simplifying the model to 1D, an efficient time-dependent analysis is possible. In this model, a Parametric Sweep is used to compare voltammetry recorded at different voltammetric scan rates.



## Model Definition

The model contains a single 1D domain of length  $L$ , which is the maximum extent of the diffusion layer over the duration of the voltammetry experiment. A conservative setting for  $L$  is set to greatly exceed the mean diffusion layer thickness:

$$L = 6\sqrt{Dt_{\max}}$$

Here,  $D$  is the diffusion coefficient of the reactant and  $t_{\max}$  is the duration of the cyclic voltammogram.

## DOMAIN EQUATIONS

We assume the presence of a large quantity of supporting electrolyte. This is inert salt that is added in electroanalytical experiments to increase the conductivity of the electrolyte without otherwise interfering with the reaction chemistry. Under these conditions, the resistance of the solution is sufficiently low that the electric field is negligible, and we can assume  $\phi_l = 0$ .

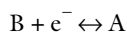
The Electroanalysis interface implements chemical transport equations for the reactant and product species of the redox couple subject to this assumption. The domain equation is the diffusion equation (also known as Fick's second law) to describe the chemical transport of the electroactive species A and B:

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (D_i \nabla c_i)$$

## BOUNDARY EQUATIONS

At the bulk boundary ( $x = L$ ), we assume a uniform concentration equal to the bulk concentration for the reactant. The product has zero concentration here, as in bulk.

At the electrode boundary ( $x = 0$ ), the reactant species A oxidizes (loses one electron) to form the product B. By convention, electrochemical reactions are written in the reduction direction:



The stoichiometric coefficient is  $-1$  for B, the “reactant” in the reduction direction, and  $+1$  for A, the “product” in the reduction direction. This formulation is consistent even in examples such as this model where at certain applied potentials, the reaction proceeds favorably to convert A to B. The number of electrons transferred,  $n$ , equals one.

The current density for this reaction is given by the electroanalytical Butler–Volmer equation for an oxidation reaction:

$$i_{\text{loc}} = nFk_0 \left( c_A \exp\left(\frac{(n - \alpha_c)F\eta}{RT}\right) - c_B \exp\left(\frac{-\alpha_c F\eta}{RT}\right) \right)$$

in which  $k_0$  is the *heterogeneous rate constant* of the reaction,  $\alpha_c$  is the *cathodic transfer coefficient*, and  $\eta$  is the overpotential at the working electrode. This overpotential is the difference between the applied potential and the *equilibrium potential* (formal reduction potential) of the redox couple of species A and B.

According to Faraday’s laws of electrolysis, the flux of the reactant and product species are proportional to the current density drawn:

$$-\mathbf{n} \cdot \mathbf{N}_i = \frac{v_i i_{\text{loc}}}{nF}$$

This is expressed in the Electrode Surface boundary condition in the Electroanalysis Module.

The applied triangular waveform for the cyclic voltammetry study is specified in the Electrode Surface boundary condition according to two vertex potentials—forming a *potential window* between  $-0.4$  V and  $+0.4$  V, either side of the equilibrium reduction potential—and a *voltammetric scan rate*,  $v$  (SI unit: V/s), which is the rate at which the applied potential is changed.

In the 1D approximation, the total current is related to the current density simply by multiplying by the electrode area  $A$ :

$$I_{\text{cl}} = i_{\text{loc}}A$$

## CYCLIC VOLTAMMETRY STUDY

In the cyclic voltammetry experiment, the potential applied to the working electrode surface is varied linearly as a function of time. A Parametric Sweep is used to compare the voltammetry recorded at different scan rates.

## Results and Discussion

The shape of the cyclic voltammogram (Figure 11) shows the relation between electrode kinetics and chemical species transport (diffusion).

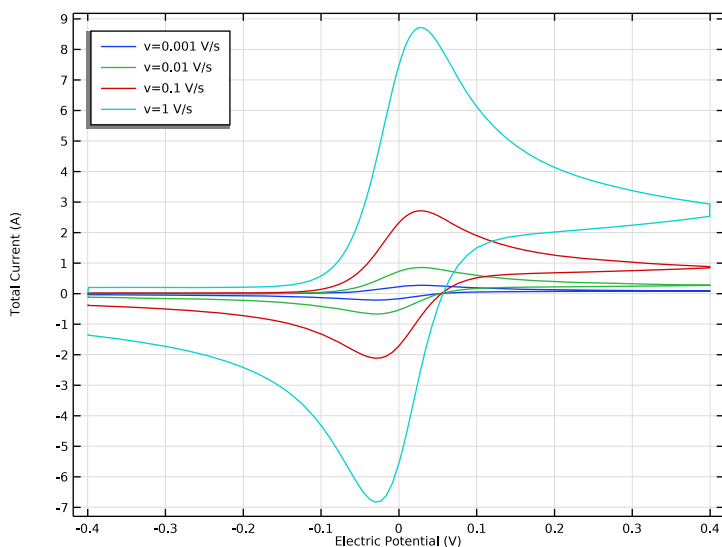


Figure 11: Cyclic voltammetry recorded at a macroelectrode.

Initially, at reducing potentials, the oxidation reaction is not driven and negligible current is drawn. As the potential is ramped conversion toward the reduction potential of the redox couple, the oxidation reaction is accelerated and the current increases. Once the oxidation reaction has consumed the reactant at the electrode surface, the current becomes limited by the rate of transport of A toward the working electrode. Therefore, a peak current is observed, and at higher potentials, the voltammetric current falls off at a potential-independent rate; this region is termed “diffusion-controlled” or “transport-controlled”.

On sweeping back toward more reducing potentials, the conversion of the product B into the original reactant A gives a negative (cathodic, reduction) current. Depletion of the reacting species B causes a negative peak current and conversion thereafter proceeds at a diffusion-controlled rate.

The magnitude of the current on the forward peak,  $I_{pf}$ , is a common diagnostic variable in voltammetry. For fast electrode kinetics and at a macroelectrode under the 1D approximation, its value is given theoretically by the Randles–Ševčík equation (see Ref. 1 and Ref. 2 for a detailed discussion and derivation):

$$I_{pf} = 0.446nFAc \sqrt{\frac{nF}{RT}Dv}$$

where  $A$  is the electrode area,  $c$  is the bulk concentration of the reactant, and  $D$  is the diffusion coefficient of the reactant.








The square-root relationship between peak current and scan rate is characteristic of macroelectrode cyclic voltammetry under the above conditions.

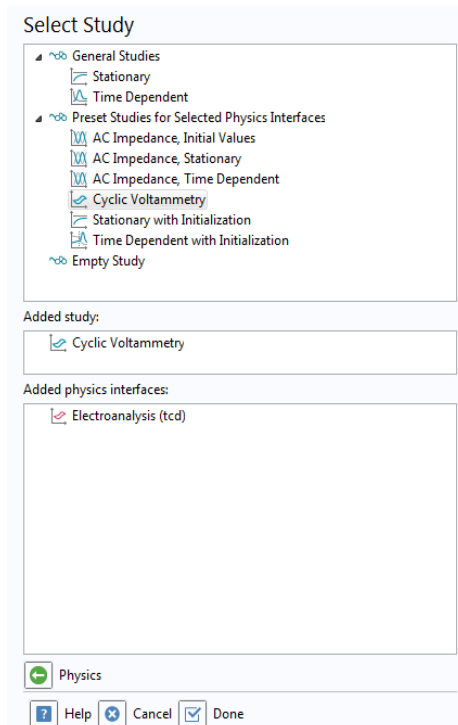
## REFERENCES

- 1 R.G. Compton and C.E. Banks, *Understanding Voltammetry*, 2nd ed., London, 2011.
- 2 A.J. Bard and L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, 2nd ed., Wiley, New York, 2001.

## Model Wizard

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- 1 If COMSOL Multiphysics is already open, you can start the Model Wizard by selecting New  from the File menu and then click Model Wizard .
- 2 In the Space Dimension Window click the 1D button .
- 3 In the Select Physics tree under Electrochemistry, click Electroanalysis (tcd) .
- 4 Click Add.
- 5 This model will solve for the two concentrations of a redox couple, change the default concentration variable names to  $c_A$  and  $c_B$  in the Concentrations table.
- 6 Click the Study  button.
- 7 In the tree under Preset Studies for Selected Physics Interfaces, select Cyclic Voltammetry .
- 8 Click Done  when the Added study and Added physics interfaces lists look as to the right.




## Global Definitions

Load the model parameters from a text file.

The location of the files used in this exercise may vary based on the installation. For example, if the installation is on your hard drive, the file path might be similar to C:\Program Files\COMSOL61\Multiphysics\applications\.


### Parameters

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

**Note:** On Linux and Mac, the Home toolbar refers to the specific set of controls near the top of the Desktop.

2 In the Settings window for Parameters click the Load from File button .

3 Browse to the application library folder, Electrochemistry Module>Tutorials, and double-click the file `cyclic_voltammetry_1d_parameters.txt`.


The figure shows what the parameter list should look like after loading the text file. For any model, you can create your own parameter lists and store these in text files to reuse them in your models. To create your own text file, click the Save to File button .

Name	Expression	Value	Description
v	1[V/s]	1 V/s	Voltammetric scan rate
c_bulk	1[mmol/L]	1 mol/m <sup>3</sup>	Reactant bulk concentration
DA	1e-9[m <sup>2</sup> /s]	1E-9 m <sup>2</sup> /s	Reactant diffusion coefficient
DB	1e-9[m <sup>2</sup> /s]	1E-9 m <sup>2</sup> /s	Product diffusion coefficient
k0	1e10	1E10	Reaction rate (dimensionless)
re	10[mm]	0.01 m	Electrode radius
k0	k0*DA/re	1000 m/s	Reaction rate
Cdl	0.2[F/m <sup>2</sup> ]	0.2 F/m <sup>2</sup>	Double layer capacity
T	298.15[K]	298.15 K	Temperature
E_vertex1	-0.4[V]	-0.4 V	Start potential
E_vertex2	0.4[V]	0.4 V	Switching potential
L	6*sqrt(DA*2*abs(E_vertex1-E_vertex2)/v)	2.4E-4 m	Outer bound on diffusion layer
cB0	c_bulk/(1+exp(-E_vertex1*F_const/(R_const*T)))	1.7322E-7 mol/m <sup>3</sup>	Initial product concentration at electrode

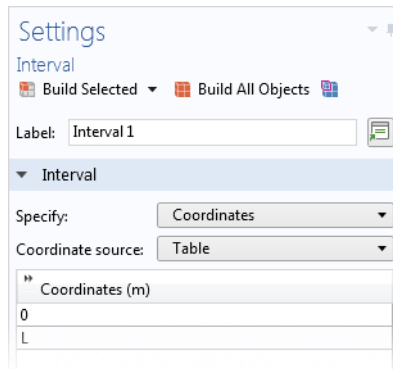
## Geometry I


Build the model geometry as a single interval, where the left boundary will later be defined as the electrode surface, and the right boundary will be the boundary toward the bulk.

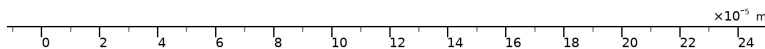
## Interval $l$

- 1 On the Geometry toolbar, click Interval .

In the Settings window for Interval type  $L$  in the Right endpoint text field. This sets the interval length to  $L$ . The value of  $L$  is defined in the Parameters node. Note that  $L$  will vary with the Voltammetric scan rate parameter  $v$ , which is also defined in the Parameters node. This is done to ensure the length of the electrolyte domain is always greater than diffusion length.



- 2 On the Geometry toolbar, click Build all . The completed geometry is now built and appears in the Graphics window:




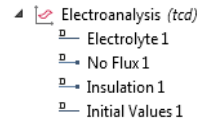
## Electroanalysis

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Start defining the physics by setting the diffusion coefficients for the two species of the redox couple.


## Electrolyte 1

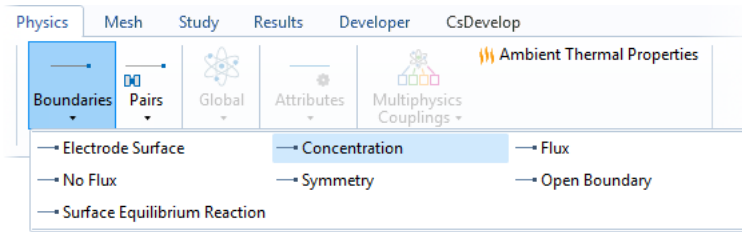
- 1 In the Model Builder window, under Component 1 > Electroanalysis, Click Electrolyte 1 . The 'D' in the upper left corner of a node means it is a default node.
- 2 Locate the Diffusion section in the settings window.
- 3 In the  $D_{cA}$  and  $D_{cB}$  text fields, type DA and DB, respectively.



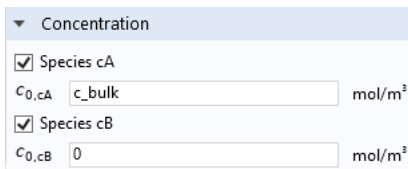
## Concentration 1

Set the boundary to the right to bulk concentration values.

- 1 On the Physics toolbar, click Boundaries  and choose Concentration .





- 2 Select Boundary 2 only.
- 3 In the Concentration section of the Concentration Settings window, select the Species cA and Species cB check boxes.
- 4 In the  $c_{0,cA}$  text field, type  $c_{bulk}$ .



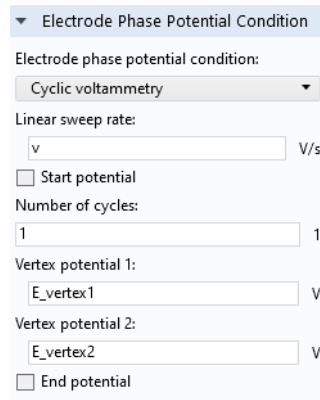
## Electrode Surface 1

Set up the electrode surface and the cyclic voltammetry settings on the left boundary.

- 1 On the Physics toolbar, click Boundaries  and click Electrode Surface .
- 2 Select Boundary 1 only.
- 3 In the Electrode Phase Potential Condition section of the Electrode Surface Settings window, choose Cyclic voltammetry from the Boundary condition list.
- 4 In the Linear sweep rate, type  $v$ .
- 5 The voltage will be cycled between the vertex potentials. When the start potential is not specified, the sweep will start at Vertex potential 2. Enter the following:

-  $E_{\text{vertex1}}$ , in the Vertex potential 1 text field.

-  $E_{\text{vertex2}}$ , in the Vertex potential 2 text field.



Electrode Phase Potential Condition

Electrode phase potential condition:  
Cyclic voltammetry

Linear sweep rate:  
v V/s

Start potential

Number of cycles:  
1

Vertex potential 1:  
E\_vertex1 V

Vertex potential 2:  
E\_vertex2 V

End potential

## Electrode Reaction 1

Specify the electrode reaction as an Electroanalytical Butler–Volmer reaction, which is concentration dependent as defined by the stoichiometric coefficients in the reaction.

- 1 In the Model Builder window, expand the Electrode Surface 1 node and click Electrode Reaction 1.
- 2 In the settings window for Electrode Reaction 1, locate the Stoichiometric Coefficients section.
- 3 In the  $\nu_{\text{cA}}$  and  $\nu_{\text{cB}}$  text fields, type 1 and -1, respectively.
- 4 Locate the Electrode Kinetics section and type in  $i_{0,\text{ref}}$  in the  $i_{0,\text{ref}}(T)$  field.



▼ Electrode Kinetics

Kinetics expression type:  
Butler-Volmer

Exchange current density type:  
Mass action law

Reference exchange current density:  
 $i_{0,\text{ref}}(T)$   A/m<sup>2</sup>

Anodic transfer coefficient:  
 $\alpha_a$   1

$$i_{\text{loc}} = i_0 \left( \exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(-\frac{\alpha_c F \eta}{RT}\right) \right) = i_{0,\text{ref}}(T) \left( \prod_{i: \nu_i > 0} \left(\frac{c_i}{c_{i,\text{ref}}}\right)^{\nu_i} \exp\left(\frac{\alpha_a F \eta_{\text{ref}}}{RT}\right) - \prod_{i: \nu_i < 0} \left(\frac{c_i}{c_{i,\text{ref}}}\right)^{-\nu_i} \exp\left(-\frac{\alpha_c F \eta_{\text{ref}}}{RT}\right) \right)$$

$$i_0 = i_{0,\text{ref}}(T) \prod_{i: \nu_i > 0} \left(\frac{c_i}{c_{i,\text{ref}}}\right)^{\alpha_c \nu_i / n} \prod_{i: \nu_i < 0} \left(\frac{c_i}{c_{i,\text{ref}}}\right)^{-\alpha_a \nu_i / n}$$

$$\alpha_c = n - \alpha_a$$

$$\eta_{\text{ref}} = E_{\text{ct}} - E_{\text{eq,ref}}(T)$$


Limiting current density

### Double Layer Capacitance

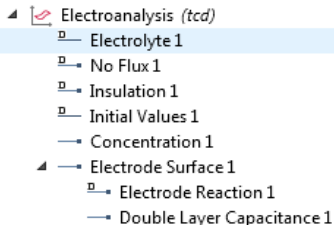
- 1 In the Model Builder window, right-click Electrode Surface 1 and choose the boundary condition Double Layer Capacitance.
- 2 Click the Double Layer Capacitance node and type Cd1 in the  $C_{dl}$  text field.

### Initial Values 1

Continue with specifying the initial concentration values. This will set the concentration values when the simulation starts at  $t=0$ .

- 1 In the Model Builder window under Component 1>Electroanalysis, click Initial Values 1 .
- 2 In the Settings window for Initial Values, locate the Initial Values section.
- 3 In the  $cA$  text field, type  $c_{\text{bulk}} - cB0 * (1 - x/L)$ .
- 4 In the  $cB$  text field, type  $cB0 * (1 - x/L)$ .

The node sequence in the Model Builder under the Electroanalysis interface should match this figure:



## Global Definitions

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### *Default Model Input*

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, locate the Browse Model Inputs sections.
- 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 I

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The default mesh settings can be used in this model and therefore no changes need to be made here.

## Study I

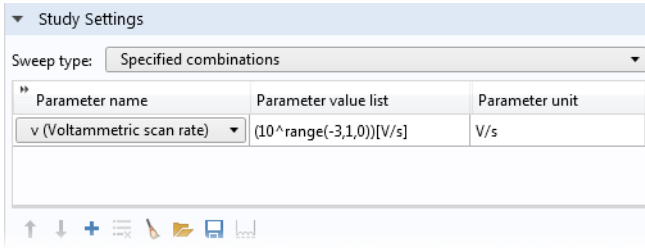
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The problem is now ready for solving. Use a parametric sweep to solve the problem for various sweep rates.

### *Parametric Sweep*

- 1 On the Study toolbar, click Parametric Sweep .

- Under Study Settings in Parametric Sweep Settings window, click the + Add button under the table. In the Parameter name column, select v (Voltammetric scan rate) from the list that appears.
- In the Parameter value column enter  $(10^{\text{range}(-3,1,0)})[\text{V/s}]$ .




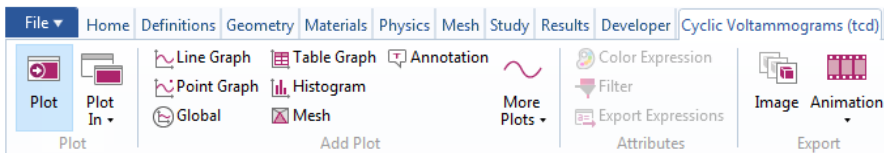
- On the Study toolbar click Compute = .



## Results

A number of plots are created by default. The first default plot group shows voltammograms that are automatically created together with the Cyclic Voltammetry feature in the Electrode Surface node.

### Cyclic Voltammograms

- On the Cyclic Voltammograms (tcd) toolbar, click Plot  to see the simulated voltammograms in the Graphics window.



- If the Legend box covers the graph, go to the Settings window for the 1D Plot Group denoted Cyclic Voltammograms (tcd)  and click to expand the Legend section. Switch for instance to Upper left in the Position list. Doing so and clicking Plot  will reproduce [Figure 11](#).

