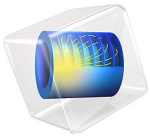


Zinc Bromine Redox Flow Battery

Introduction

The zinc bromine redox flow battery is an electrochemical energy storage technology suitable for stationary applications.

Compared to other flow battery chemistries, the Zn-Br cell potentially features lower cost, higher energy densities and better energy efficiencies.

In the cell during charge, zinc metal is deposited on the negative electrode, whereas bromine is produced on the positive electrode. The electrolyte in the two porous electrodes compartments is continuously replaced in the cell by the use of external pumps and recirculation tanks as depicted in Figure 1. A separator of low permeability separates the two electrode compartments. During discharge of the cell, the bromine stored in the positive electrolyte tank and the zinc deposited in the negative electrode are consumed.

This tutorial models the cell voltage, as well as the bromine and zinc production-consumption, during a charge-discharge cycle. The model is mainly based on the experimental work and results described in Ref. 1, with some additional model parameters taken from Ref. 2.

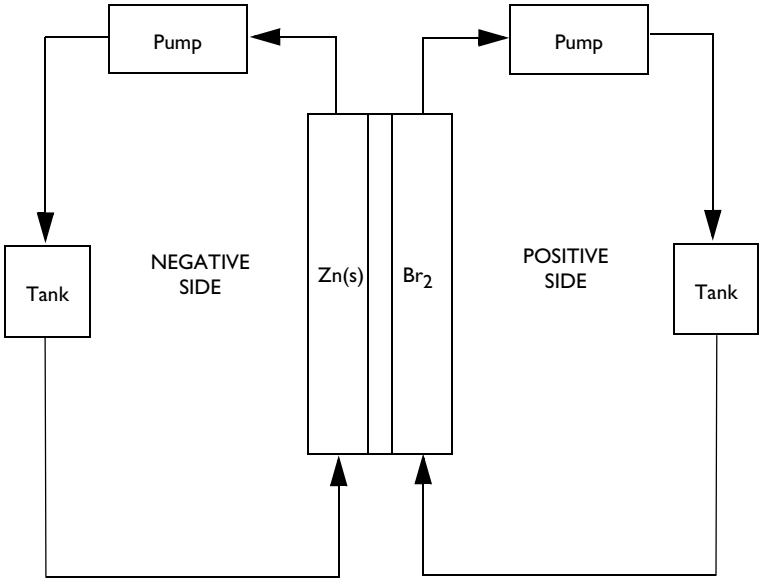


Figure 1: Working principle of a zinc bromine redox flow battery.

Model Definition

Figure 2 shows the model geometry. The geometry consists of three rectangular domains, a negative (left-hand side) carbon felt porous electrode, a separator (center), and a positive (right-hand side) carbon felt porous electrode. On the positive side, the electrolyte (posolyte) enters the cell from the bottom and exits the cell at the top.

The bromine-containing posolyte exiting the cell passes an external tank, and is then reinserted at the posolyte cell inlet at a constant volumetric flow rate. Note that in a real cell there is also a recirculation tank for the negative side (see Figure 1). Negative recirculation is however neglected in this model.

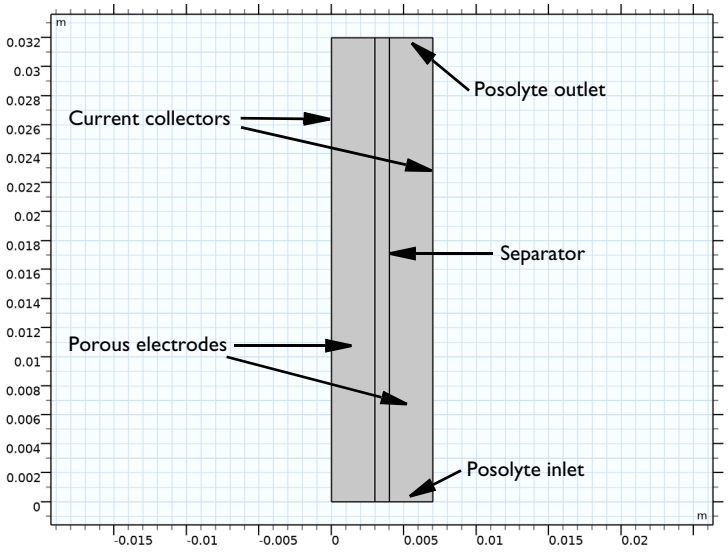


Figure 2: Model Geometry.

During charge in the negative porous electrode, zinc metal is deposited according to

$$\mathrm{Zn}^{2+} + 2e^{-} \Leftrightarrow \mathrm{Zn(s)} \tag{1}$$

In the positive porous electrode, bromine is produced according to

$$2\mathrm{Br}^{-} + 2e^{-} \Leftrightarrow \mathrm{Br}_2 \tag{2}$$

Bromine would normally be evolved as a gas, but due to the presence of a complexing agent Q, a complex is formed

$$Br_2 + Q \Leftrightarrow Br_2Q \tag{3}$$

This second complexing reaction step is assumed to be fast and at equilibrium, and the complexing agent Q is assumed to be excess. When referring to Br_2 or bromine in the reminder of this document, we hence actually refer to the complexed form of bromine, Br_2Q.

The model solves for the electrolyte phase potential and the concentration of the complexed form of bromine in the electrolyte in all three domains using transport equations based on Ohm's law and the Nernst–Planck equations, respectively. A supporting electrolyte assumption is made, treating all other species concentrations in the electrolyte as constants as well as the electrolyte conductivity. In the two porous electrode domains, also the electrode phase potential is solved for using Ohm's law.

As mentioned above, convection effects and the corresponding recirculation tank on the negative side are neglected in this tutorial. Convection effects are also neglected in the separator due to a low permeability. In the positive electrode, a uniform velocity in the y direction is assumed.

Due to the lower potential of the negative electrode, bromine is assumed to be instantly oxidized when reaching the negative electrode-separator boundary, setting the Br_2 concentration to 0. The corresponding current density, calculated by Faraday's law of electrolysis, is added as a boundary current density to the charge balance equations.

The left-hand side negative current collector boundary is grounded, whereas at the corresponding positive boundary an average current density boundary condition is applied, featuring a 30 min charge at a constant current density followed by a discharge at an equal current density magnitude.

TANK MODEL

Assuming a well-mixed system, the recirculation tank is modeled by using an ordinary differential equation, solving for a global dependent variable for the tank concentration of bromine, c_{tank} (mol/m^3):

$$V_{\text{tank}} \frac{\mathrm{d}c_{\text{tank}}}{\mathrm{d}t} = -\int_{\delta\Omega_{\text{in}}} c(\mathbf{n} \cdot \mathbf{u}) - \int_{\delta\Omega_{\text{out}}} c_{\text{tank}}(\mathbf{n} \cdot \mathbf{u}) \tag{4}$$

Here, V_{tank} is the tank volume (m^3), c is the concentration of bromine in the cell (mol/m^3), $\mathbf{n}$ is the normal vector at the boundary, and $\mathbf{u}$ is the convective flow velocity vector (m/s). Furthermore, $\delta\Omega_{\text{in}}$ and $\delta\Omega_{\text{out}}$ are the posolyte inlet and outlet boundaries, respectively.

The above expression is valid for the case when the nonconvective parts of the molar flux at the inlet and outlet fluxes are zero. This is accomplished in the electrolyte transport model by the use of a Danckwerts inflow condition at the inlet and an outflow condition at the outlet.

Results and Discussion

Figure 3 shows the cell voltage versus time for various constant current charge/discharge current densities. The cell voltages during the 30 min charging period feature a flat, constant, voltage profile, whereas there is a pronounced decline in voltage towards the end of the discharge period. The voltage curves also feature higher polarization for higher currents, stemming from the ohmic and electrode activation voltage losses in the cell, which increase with a higher current density level.

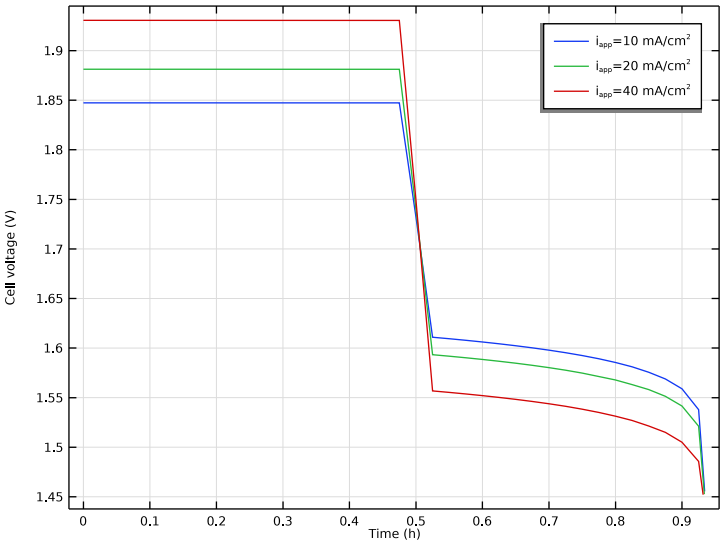


Figure 3: Cell voltage versus time for various current densities.

Figure 4 depicts the tank concentration levels of bromine versus time for the various current density levels. The levels vary linearly with time. At the end of discharge, the tank concentration levels are not zero, indicating that it is not possible to completely discharge the cell at the chosen current density level.

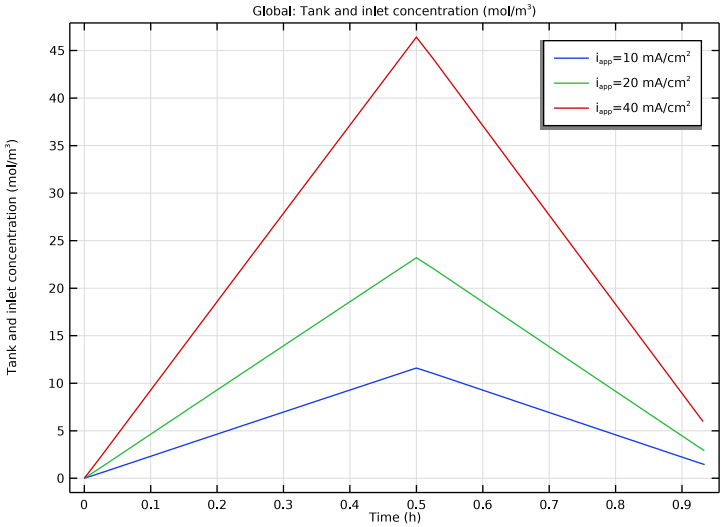


Figure 4: Tank concentrations versus time for various current densities.

Figure 5 and Figure 6 show the bromine concentration levels in the cell at the end of the charging and the discharging periods, respectively. At the end of charge, the cell concentration is more or less uniform, but at the end of discharge, depletion of bromine becomes more severe for longer distances from the posolyte inlet.

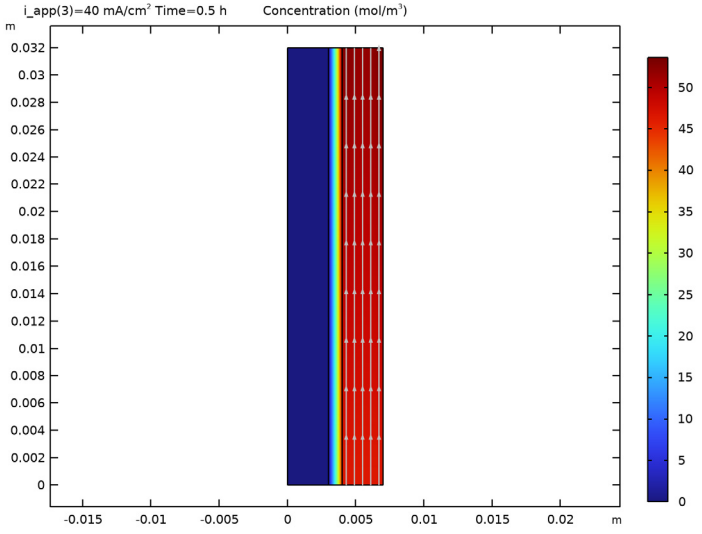


Figure 5: Bromine concentration at the end of the 30 min charge at 40 mA/cm^2.

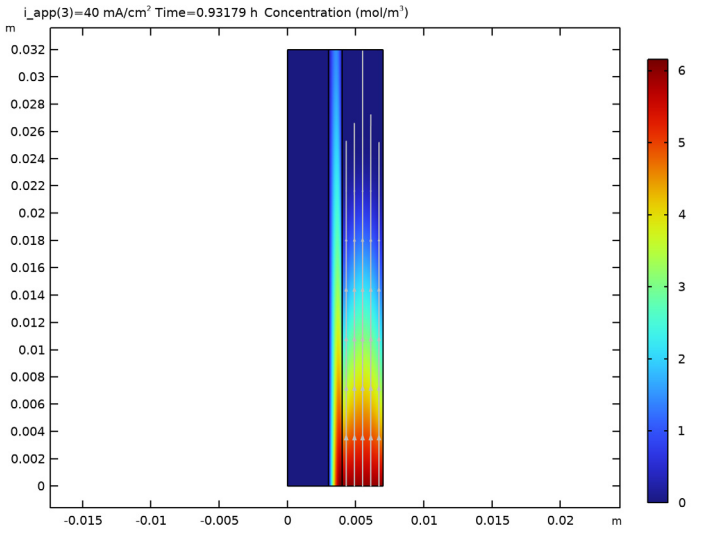


Figure 6: Bromine concentration at the end of the discharge at 40 mA/cm^2.

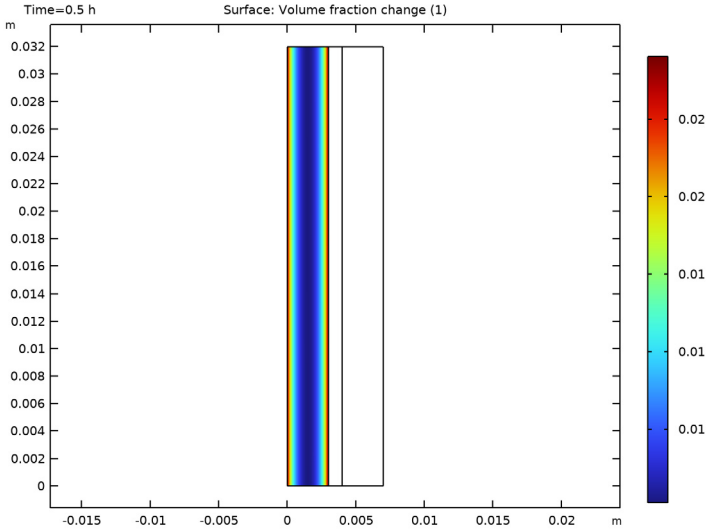


Figure 7: Electrode volume fraction change due to Zn(s) deposition at the end of the 30 min charge period.

Finally, Figure 7 shows the electrode volume fraction change at the end of charge as a result of the deposition of zinc metal. Due to current distribution effects, the highest amount of deposited zinc (2%) is found close to the current collector and separator boundaries. The almost symmetric deposition pattern is a result of the electrolyte and electrode conductivities having similar values in the model parameters.

References

1. S. Suresh, M. Ulaganathan, N. Venkatesan, P. Periasamy, and P. Ragupathy, "High performance zinc-bromine redox flow batteries: Role of various carbon felts and cell configurations," *J. Energy Storage*, vol. 20, pp. 134–139, 2018.

2. Z. Xu, J. Wang, S.C. Yan, Q. Fan, and P.D. Lund, "Modeling of Zinc Bromine redox flow battery with application to channel design, *J. Power Sources*, vol. 450, p. 227436, 2020.

Application Library path: `Battery_Design_Module/Flow_Batteries/znbr_flow_battery`

Modeling Instructions

This tutorial consists of two parts. In the first part we will set up the electrochemical reactions, the electrolyte transport and the recirculation tank model, and solve for 1 h charge at a constant current. In the second part, we will add the deposition of zinc metal, as well as a charge-discharge current load profile, and solve for a range of different current loads.

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

NEW

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

MODEL WIZARD

1. In the **Model Wizard** window, click **2D**.
2. In the **Select Physics** tree, select **Electrochemistry>Tertiary Current Distribution, Nernst-Planck>Tertiary, Supporting Electrolyte (tcd)**.
3. Click **Add**.

   In this tutorial, we will model the transport of one electrolyte species only (Bromine).
4. In the **Number of species** text field, type `1`.
5. In the **Concentrations** table, enter the following settings:

`cBr2`

   Also add an ODE interface which will be used for setting up the tank model.
6. In the **Select Physics** tree, select **Mathematics>ODE and DAE Interfaces>Global ODEs and DAEs (ge)**.
7. Click **Add**.
8. Click **Study**.
9. In the **Select Study** tree, select **Preset Studies for Selected Physics Interfaces>Tertiary Current Distribution, Nernst-Planck>Time Dependent with Initialization**.
10. Click **Done**.

GLOBAL DEFINITIONS

Parameters 1

Load some 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 `znbr_flow_battery_parameters.txt`.

GEOMETRY 1

The geometry is composed of a single rectangle.

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 `W_cell`.

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

Use **Layers** to define the internal carbon felt and separator boundaries.

5 Click to expand the **Layers** section. In the table, enter the following settings:

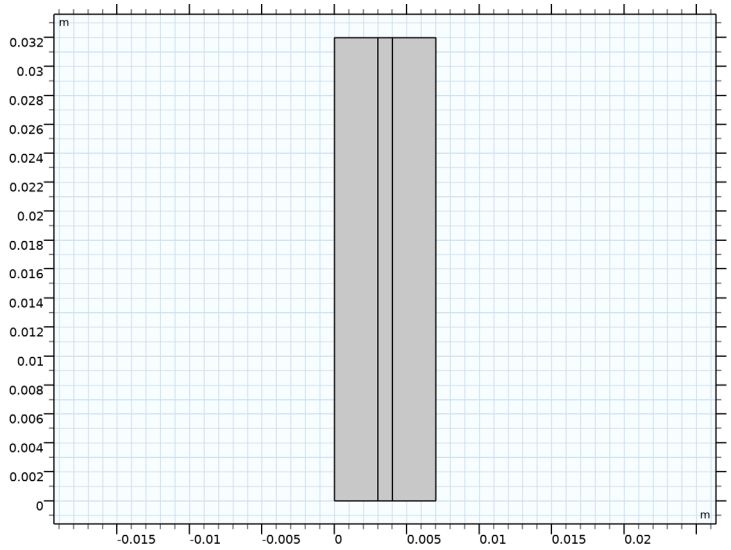
Layer name	Thickness (m)
`Layer 1`	`W_cf`
`Layer 2`	`W_sep`

6 Select the **Layers to the right** check box.

7 Clear the **Layers on bottom** check box.

8 Click **Build All Objects**.

The finalized geometry should look as follows:



DEFINITIONS

Add some explicitly named selections. These will facilitate setting up the physics later on.

Separator

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

2 In the **Settings** window for **Explicit**, type `Separator` in the **Label** text field.

3 Select Domain 2 only.

Negative Carbon Felt

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

2 In the **Settings** window for **Explicit**, type `Negative Carbon Felt` in the **Label** text field.

3 Select Domain 1 only.

Positive Carbon Felt

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

2 In the **Settings** window for **Explicit**, type `Positive Carbon Felt` in the **Label** text field.

3 Select Domain 3 only.

Posolyte Inlet

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

2 In the **Settings** window for **Explicit**, type `Posolyte Inlet` in the **Label** text field.

3 Locate the **Input Entities** section. From the **Geometric entity level** list, choose **Boundary**.

4 Select Boundary 8 only.

Posolyte Outlet

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

2 In the **Settings** window for **Explicit**, type `Posolyte Outlet` in the **Label** text field.

3 Locate the **Input Entities** section. From the **Geometric entity level** list, choose **Boundary**.

4 Select Boundary 9 only.

TERTIARY CURRENT DISTRIBUTION, NERNST-PLANCK (TCD)

Now start defining the current distribution part of the physics, beginning with the separator.

Separator 1

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Tertiary Current Distribution, Nernst-Planck (tcd)** and choose **Separator**.

2 In the **Settings** window for **Separator**, locate the **Domain Selection** section.

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

4 Locate the **Diffusion** section. In the D_{cBr2} text field, type `D_Br2`.

5 Locate the **Solvent** section. From the σ_l list, choose **User defined**. In the associated text field, type `sigmal`.

6 Locate the **Porous Matrix Properties** section. In the ε_l text field, type `epsl_sep`.

Porous Electrode - Negative

Continue with the negative carbon felt electrode as follows:

1 In the **Physics** toolbar, click **Domains** and choose **Porous Electrode**.

2 In the **Settings** window for **Porous Electrode**, type `Porous Electrode - Negative` in the **Label** text field.

3 Locate the **Domain Selection** section. From the **Selection** list, choose **Negative Carbon Felt**.

4 Locate the **Diffusion** section. In the D_{cBr2} text field, type `D_Br2`.

5 Locate the **Solvent** section. From the σ_l list, choose **User defined**. In the associated text field, type `sigmal`.

6 Locate the **Electrode Current Conduction** section. From the σ_s list, choose **User defined**. In the associated text field, type `sigmas_cf`.

7 Locate the **Porous Matrix Properties** section. In the ε_s text field, type `1-epsl_cf`.

8 In the ε_l text field, type `epsl_cf`.

Porous Electrode Reaction 1

Set up the zinc deposition reaction as follows:

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

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

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

4 Locate the **Equilibrium Potential** section. In the $E_{\mathrm{eq,ref}}(T)$ text field, type `Eeq_ref_Zn`.

5 Locate the **Electrode Kinetics** section. In the $i_{0,\mathrm{ref}}(T)$ text field, type `i0_ref_Zn`.

6 In the α_a text field, type `alpha_a_Zn`.

7 Locate the **Active Specific Surface Area** section. In the a_v text field, type `Av_cf`.

Porous Electrode - Positive

1 In the **Physics** toolbar, click **Domains** and choose **Porous Electrode**.

2 In the **Settings** window for **Porous Electrode**, type `Porous Electrode - Positive` in the **Label** text field.

3 Locate the **Domain Selection** section. From the **Selection** list, choose **Positive Carbon Felt**.

In the separator and the negative electrode, the velocity is assumed to be 0. Set the electrolyte to flow at a constant rate in the y direction in the positive carbon felt electrode as follows:

4 Locate the **Convection** section. Specify the $\mathbf{u}$ vector as

0	x
U	y

5 Locate the **Diffusion** section. In the D_{cBr2} text field, type `D_Br2`.

6 Locate the **Solvent** section. From the σ_l list, choose **User defined**. In the associated text field, type `sigmal`.

7 Locate the **Electrode Current Conduction** section. From the σ_s list, choose **User defined**. In the associated text field, type `sigmas_cf`.

8 Locate the **Porous Matrix Properties** section. In the ε_s text field, type `1-epsl_cf`.

9 In the ε_l text field, type `epsl_cf`.

Porous Electrode Reaction 1

Set up the bromine redox reaction as follows:

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

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

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

4 In the ν_{cBr2} text field, type `-1`.

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

6 Locate the **Electrode Kinetics** section. In the $i_{0,ref}(T)$ text field, type `i0_ref_Br`.

7 In the α_a text field, type `alpha_a_Br`.

8 Locate the **Active Specific Surface Area** section. In the a_v text field, type `Av_cf`.

The domain physics settings for the current distribution model are now complete. Continue to define the boundary conditions.

The cell will be set to run galvanostatically, using the negative electrode as ground.

Electric Ground 1

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

2 Select Boundary 1 only.

Electrode Current 1

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

2 Select Boundary 10 only.

3 In the **Settings** window for **Electrode Current**, locate the **Electrode Current** section.

4 From the list, choose **Average current density**.

5 In the $i_{s,average}$ text field, type `i_app`.

6 In the $\phi_{s,bnd,init}$ text field, type `E_cell_init`.

Internal Electrode Surface 1

Add the parasitic oxidation reaction of bromine at the negative electrode-separator boundary.

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

2 Select Boundary 4 only.

Electrode Reaction 1

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

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

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

4 In the ν_{cBr2} text field, type `-1`.

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

6 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Fast irreversible electrode reaction**.

GLOBAL ODES AND DAES - TANK MODEL

Now define the tank model. The tank model will provide the inflow concentration to the posolyte inlet boundary.

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Global ODEs and DAEs (ge)**.

2 In the **Settings** window for **Global ODEs and DAEs**, type `Global ODEs and DAEs - Tank Model` in the **Label** text field.

Global Equations 1

Load the needed equation definitions from a text file.

1 In the **Model Builder** window, under **Component 1 (comp1)>Global ODEs and DAEs - Tank Model (ge)** click **Global Equations 1**.

2 In the **Settings** window for **Global Equations**, locate the **Global Equations** section.

3 Click **Load from File**.

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

The imported expression is marked in orange, indicating a missing operator. Add the operator as follows:

DEFINITIONS

Integration - Posolyte Outlet

1 In the **Definitions** toolbar, click **Nonlocal Couplings** and choose **Integration**.

2 In the **Settings** window for **Integration**, type `Integration - Posolyte Outlet` in the **Label** text field.

3 In the **Operator name** text field, type `intop_pos_out`.

4 Locate the **Source Selection** section. From the **Geometric entity level** list, choose **Boundary**.

5 From the **Selection** list, choose **Posolyte Outlet**.

The `intop_pos_out` operator can now be used to integrate any variable along the posolyte outlet boundary.

GLOBAL ODES AND DAES - TANK MODEL (GE)

Global Equations 1

The global equation expression is still marked in orange, indicating a unit error. Set the correct units as follows:

1 In the **Model Builder** window, under **Component 1 (comp1)>Global ODEs and DAEs - Tank Model (ge)** click **Global Equations 1**.

2 In the **Settings** window for **Global Equations**, locate the **Units** section.

3 Click **Select Dependent Variable Quantity**.

4 In the **Physical Quantity** dialog box, type `concentration` in the text field.

5 Click **Filter**.

6 In the tree, select **General>Concentration (mol/m^3)**.

7 Click **OK**.

8 In the **Settings** window for **Global Equations**, locate the **Units** section.

9 Click **Define Source Term Unit**.

10 In the **Source term quantity** table, enter the following settings:

Source term quantity	Unit
Custom unit	`mol/s`

TERTIARY CURRENT DISTRIBUTION, NERNST-PLANCK (TCD)

Now go back to the current distribution model and set the inflow and outflow conditions.

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Tertiary Current Distribution, Nernst-Planck (tcd)**.

Inflow 1

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

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

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

4 Locate the **Concentration** section. In the $c_{0,\mathrm{cBr2}}$ text field, type `cBr2_tank`.

5 Locate the **Boundary Condition Type** section. From the list, choose **Flux (Danckwerts)**.

The Danckwerts condition will set an inflow molar flux based on the tank concentration and the electrolyte convective velocity. This will ensure that the amount of Bromine that enters domain equals that of what exits the tank.

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 **Posolyte Outlet**.

To finalize the setup of the model, provide also initial values for potentials in the different domains. This will improve convergence of the Current Distribution Initialization study step.

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 *phil* text field, type `-Eeq_ref_Zn`.

Initial Values 2

1 In the **Physics** toolbar, click **Domains** and choose **Initial Values**.

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

3 From the **Selection** list, choose **Positive Carbon Felt**.

4 Locate the **Initial Values** section. In the *phil* text field, type `-Eeq_ref_Zn`.

5 In the *phis* text field, type `E_cell_init`.

MESH 1

A mapped mesh is suitable for this rectangular geometry.

Mapped 1

In the **Mesh** toolbar, click **Mapped**.

Distribution 1

Use **Distribution** nodes to improve the mesh resolution in different parts of the geometry.

1 Right-click **Mapped 1** and choose **Distribution**.

2 Select Boundaries 2 and 3 only.

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

4 From the **Distribution type** list, choose **Predefined**.

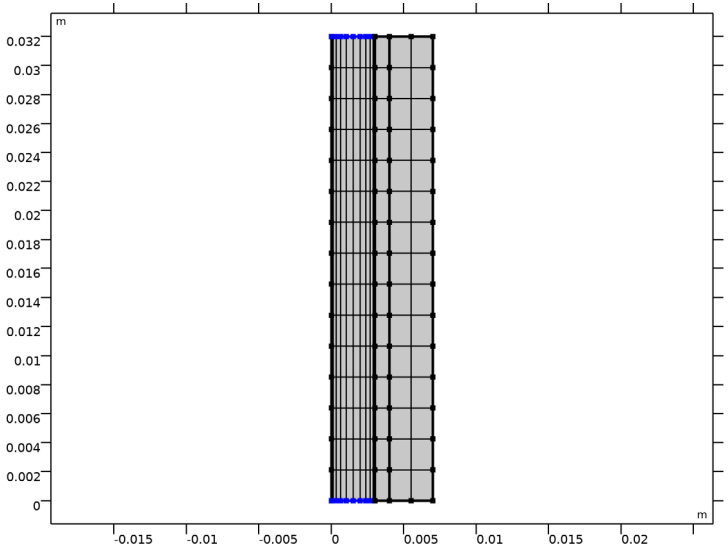
5 In the **Number of elements** text field, type 10.

6 In the **Element ratio** text field, type 4.

As you will see when inspecting the deposited zinc distribution (once the second part of the tutorial has been solved), a symmetric distribution in the x direction is suitable in the negative electrode.

7 Select the **Symmetric distribution** check box.

8 Click **Build Selected**.

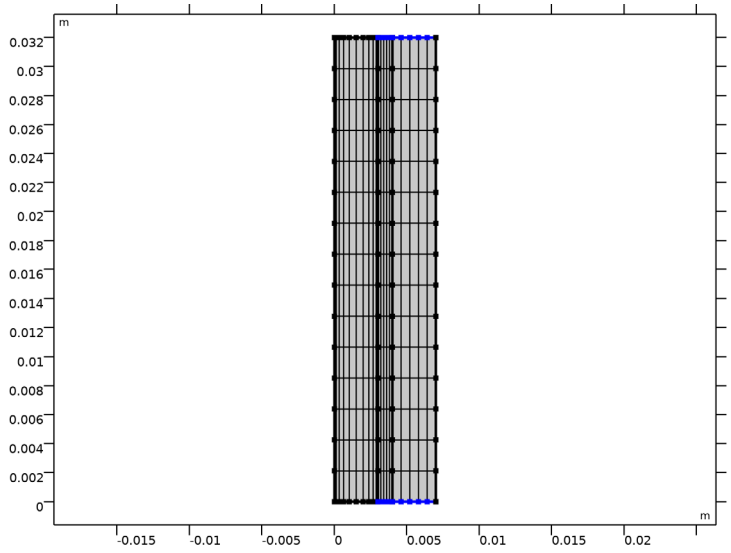


Distribution 2

1 In the **Model Builder** window, right-click **Mapped 1** and choose **Distribution**.

2 Select Boundaries 5, 6, 8, and 9 only.

3 In the **Settings** window for **Distribution**, click **Build Selected**.



Distribution 3

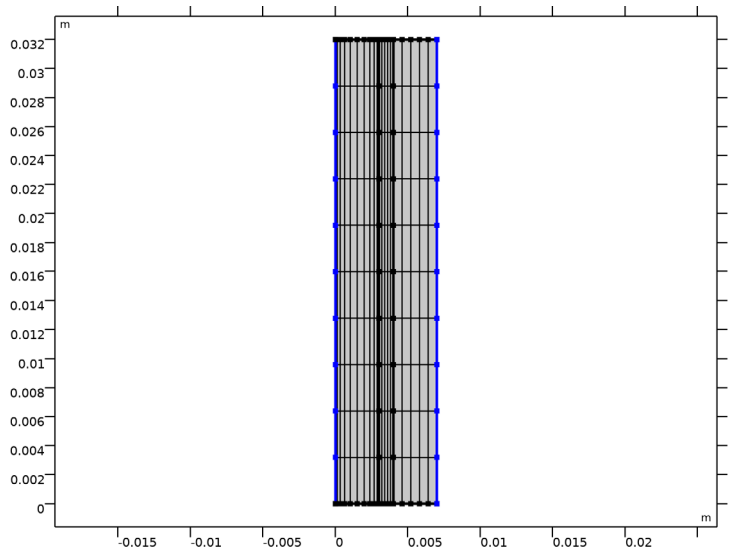
1 Right-click **Mapped 1** and choose **Distribution**.

2 Select Boundaries 1 and 10 only.

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

4 In the **Number of elements** text field, type 10.

5 Click **Build All**.



DEFINITIONS

Before setting up the solver, add a probe to monitor the cell voltage while solving.

Global Variable Probe 1 (var1)

1 In the **Definitions** toolbar, click **Probes** and choose **Global Variable Probe**.

2 In the **Settings** window for **Global Variable Probe**, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Component 1 (comp1)> Tertiary Current Distribution, Nernst-Planck>tcd.phis0_ec1 - Electric potential on boundary - V**.

The variable represents the electrode phase potential of the positive electrode current boundary. The variable is defined by the **Electrode Current** node. (The same variable will also be used in the second part of this tutorial for defining a stop expression for the solver.)

STUDY 1

The study you added at the beginning of the tutorial contains two study steps. The first step is only used to compute suitable potential initial values for the second time-dependent step.

Step 1: Current Distribution Initialization

Since we are using 0 as initial values for the bromine concentration in the cell, the equilibrium potential is not well-defined. Hence a primary current distribution cannot be calculated for the initial values.

1 In the **Model Builder** window, under **Study 1** click **Step 1: Current Distribution Initialization**.

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

3 From the **Current distribution type** list, choose **Secondary**.

The tank model should not be solved for in the first study step.

4 Locate the **Physics and Variables Selection** section. In the table, enter the following settings:

Physics interface	Solve for	Equation form
Tertiary Current Distribution, Nernst-Planck (tcd)	√	Automatic (Current distribution initialization)
Global ODEs and DAEs - Tank Model (ge)		Automatic (Time domain)

Step 2: Time Dependent

Simulate the cell during a 1 h charge.

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

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

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

4 In the **Home** toolbar, click = **Compute**.

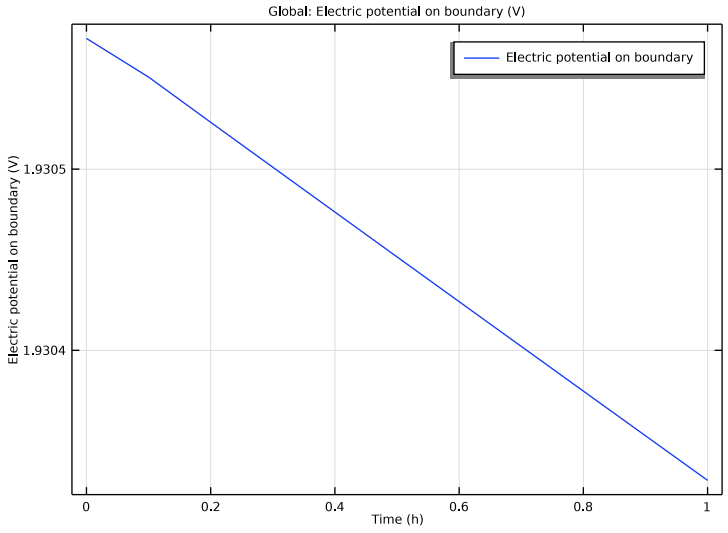
The model should take a few seconds to solve.

RESULTS

Boundary Electrode Potential with Respect to Ground (tcd)

A number of default plots where created. Inspect the plots for the cell voltage, the bromine concentration and the tank concentration.

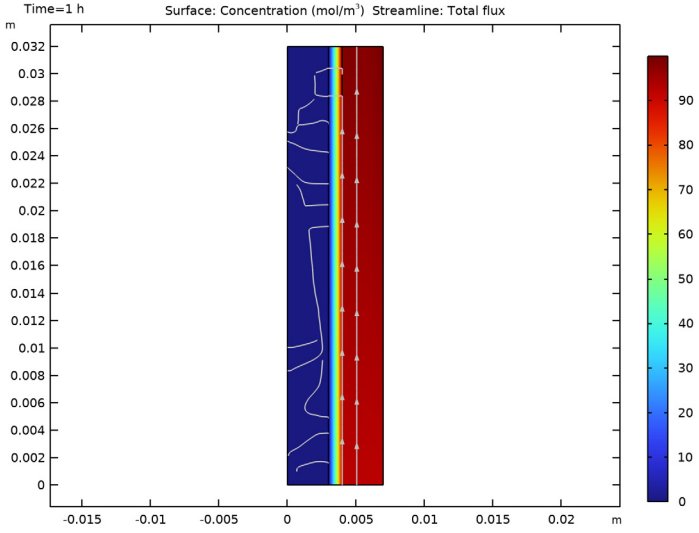
1 In the **Boundary Electrode Potential with Respect to Ground (tcd)** toolbar, click **Plot**.



Concentration (tcd)

1 In the **Model Builder** window, click **Concentration (tcd)**.

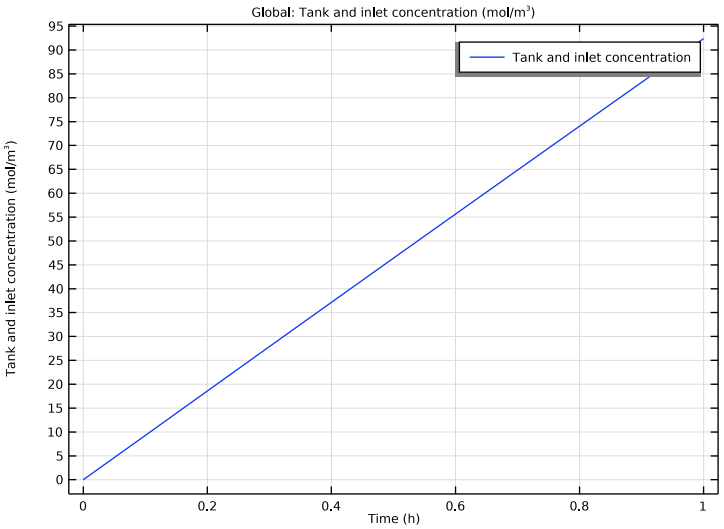
2 In the **Concentration (tcd)** toolbar, click **Plot**.



1D Plot Group 8

1 In the **Model Builder** window, click **1D Plot Group 8**.

2 In the **1D Plot Group 8** toolbar, click **Plot**.



TERTIARY CURRENT DISTRIBUTION, NERNST-PLANCK (TCD)

Now we start with the second part of the tutorial. First add the deposition of zinc metal as follows:

Porous Electrode - Negative

1 In the **Model Builder** window, under **Component 1 (comp1)>Tertiary Current Distribution, Nernst-Planck (tcd)** click **Porous Electrode - Negative**.

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

3 Click **Add**.

4 In the table, enter the following settings:

Species	Density (kg/m^3)	Molar mass (kg/mol)
Zn	rho_Zn	M_Zn

Note that the added the electrolyte volume fraction of deposited zinc is set to be subtracted from the electrolyte volume fraction by default.

Porous Electrode Reaction 1

Set up the stoichiometry for zinc deposition as follows:

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

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

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

Species	Stoichiometric coefficient (1)
Zn	1

DEFINITIONS

Next change the cell current profile to also include discharge. Use a step function for this.

Step 1 (step1)

1 In the **Home** toolbar, click f(x) **Functions** and choose **Local>Step**.

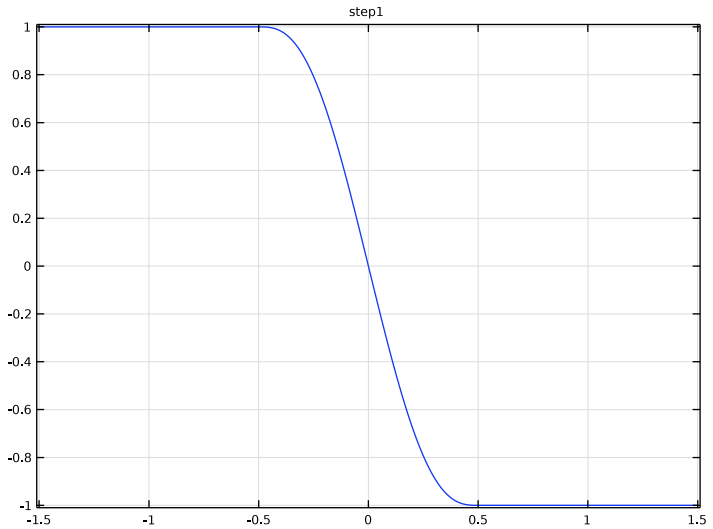
2 In the **Settings** window for **Step**, locate the **Parameters** section.

3 In the **From** text field, type `1`.

4 In the **To** text field, type `-1`.

5 Click to expand the **Smoothing** section. In the **Size of transition zone** text field, type `1`.

6 Click **Plot**.



TERTIARY CURRENT DISTRIBUTION, NERNST-PLANCK (TCD)

This step function will now be used to reverse the current after completion of the charge period (30 min).

Electrode Current 1

1 In the **Model Builder** window, under **Component 1 (comp1)>Tertiary Current Distribution, Nernst-Planck (tcd)** click **Electrode Current 1**.

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

3 In the $i_{\mathrm{s,average}}$ text field, type `i_app*step1((t-t_charge)/1[s])`.

STUDY 1

Solver Configurations

Remove the old solver sequence. This will remove the old default plots, solvers and datasets pertaining to the old study. Also remove the old probe plot.

1 In the **Model Builder** window, under **Study 1** right-click **Solver Configurations** and choose **Delete Configurations**.

RESULTS

Probe Plot Group 9

In the **Model Builder** window, under **Results** right-click **Probe Plot Group 9** and choose **Delete**.

STUDY 1

Parametric Sweep

Add a **Parametric Sweep** to perform the simulation for three different applied current density levels.

1 In the **Study** toolbar, click **Parametric Sweep**.

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

3 Click **Add**.

4 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
i_app (Applied current density)	10 20 40	mA/cm^2

Step 2: Time Dependent

Use a smaller step size to store the solution more often during the charge-discharge cycle. This will render smoother voltage vs time plots later on when post processing the solution.

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

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

3 Click **Range**.

4 In the **Range** dialog box, type `0.025` in the **Step** text field.

5 Click **Replace**.

Solution 1 (sol1)

Generate the solver sequence and modify it by adding a stop condition.

1 In the **Study** toolbar, click **Show Default Solver**.

2 In the **Model Builder** window, expand the **Solution 1 (sol1)** node.

3 Right-click **Study 1>Solver Configurations>Solution 1 (sol1)>Time-Dependent Solver 1** and choose **Stop Condition**.

4 In the **Settings** window for **Stop Condition**, locate the **Stop Expressions** section.

5 Click **Add**.

Define the stop condition to terminate the simulation when the electrode phase potential of the positive electrode drops below 1.45 V.

6 In the table, enter the following settings:

Stop expression	Stop if	Active	Description
`comp1.tcd.phis0_ec1< 1.45[V]`	True (>=1)	√	`Stop expression 1`

7 Locate the **Output at Stop** section. Clear the **Add warning** check box.

8 In the **Study** toolbar, click **Compute**.

The model should take about a minute to solve, depending on computer.

RESULTS

Cell Voltage vs Time

A number new default plots where created. Modify them as follows:

1 In the **Settings** window for **1D Plot Group**, type `Cell Voltage vs Time` in the **Label** text field.

2 Click to expand the **Title** section. From the **Title type** list, choose **None**.

3 Locate the **Plot Settings** section.

4 Select the **y-axis label** check box. In the associated text field, type `Cell voltage (V)`.

Global 1

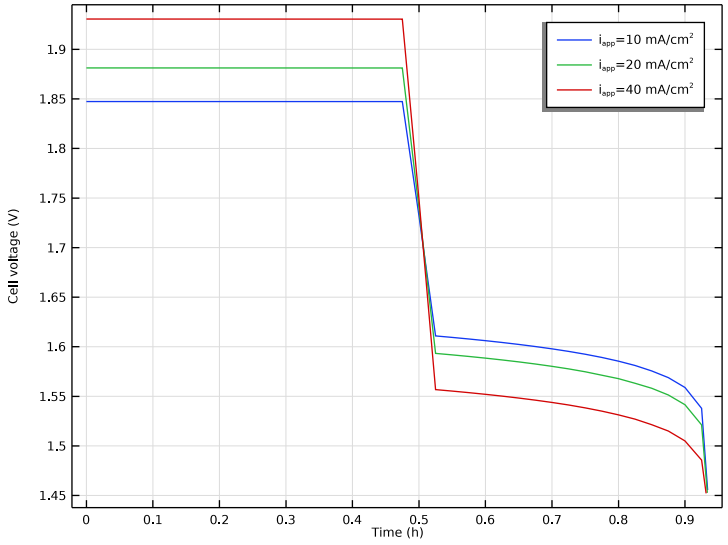
1 In the **Model Builder** window, expand the **Cell Voltage vs Time** node, then click **Global 1**.

2 In the **Settings** window for **Global**, click to expand the **Legends** section.

3 From the **Legends** list, choose **Evaluated**.

4 In the **Legend** text field, type `i<sub>app</sub>=eval(i_app/10) mA/cm<sup>2</sup>`.

5 In the **Cell Voltage vs Time** toolbar, click **Plot**.



Bromine Concentration

1 In the **Model Builder** window, under **Results** click **Concentration (tcd)**.

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

3 Click to expand the **Title** section. Find the **Type and data** subsection. Clear the **Type** check box.

Streamline 1

1 In the **Model Builder** window, expand the **Results>Bromine Concentration** node, then click **Streamline 1**.

2 In the **Settings** window for **Streamline**, click to expand the **Title** section.

3 From the **Title type** list, choose **None**.

4 Locate the **Streamline Positioning** section. From the **Positioning** list, choose **On selected boundaries**.

5 Locate the **Selection** section. From the **Selection** list, choose **Posolyte Inlet**.

6 Locate the **Streamline Positioning** section. In the **Number** text field, type `5`.

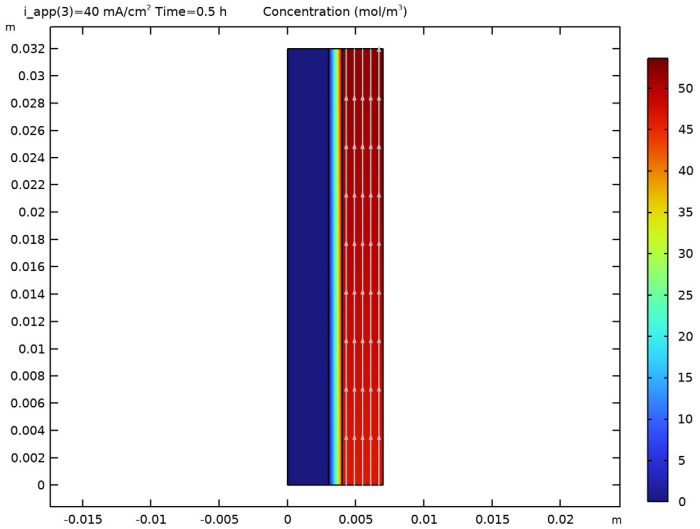
Bromine Concentration

1 In the **Model Builder** window, click **Bromine Concentration**.

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

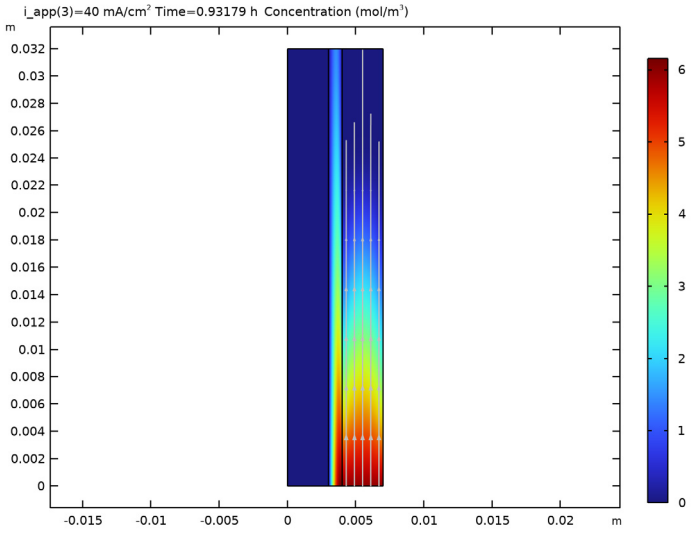
3 From the **Time (h)** list, choose **0.5**.

4 In the **Bromine Concentration** toolbar, click **Plot**.



From the **Time (h)** list, choose the last stored time.

5 Click **Plot**.



Tank concentration

1 In the **Model Builder** window, under **Results** click **1D Plot Group 8**.

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

Global 1

1 In the **Model Builder** window, expand the **Tank concentration** node, then click **Global 1**.

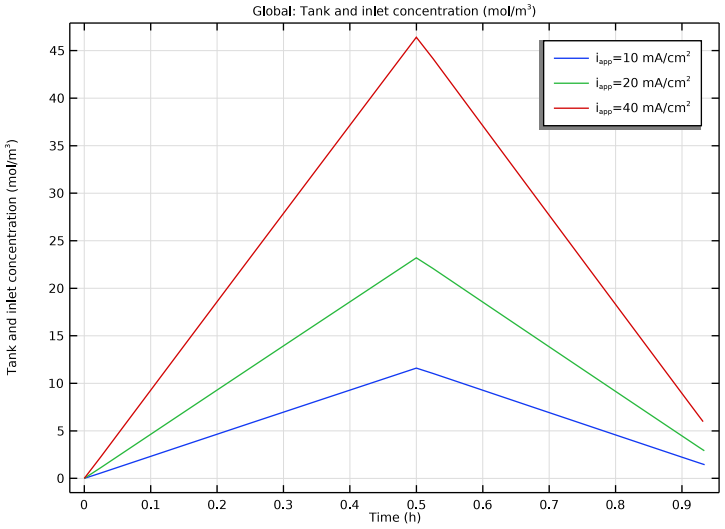
2 In the **Settings** window for **Global**, locate the **x-Axis Data** section.

3 From the **Axis source data** list, choose **Time**.

4 Locate the **Legends** section. From the **Legends** list, choose **Evaluated**.

5 In the **Legend** text field, type `i<sub>app</sub>=eval(i_app/10) mA/cm<sup>2</sup>`.

6 In the **Tank concentration** toolbar, click **Plot**.



Tank concentration

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

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

3 From the **Title type** list, choose **None**.

Deposited Zinc Volume Fraction

You may also add you own plots. Proceed as follows to plot the volume fraction of the deposited zinc layer.

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

2 In the **Settings** window for **2D Plot Group**, type `Deposited Zinc Volume Fraction` in the **Label** text field.

Surface 1

1 Right-click **Deposited Zinc Volume Fraction** and choose **Surface**.

2 In the **Settings** window for **Surface**, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Component 1 (comp1)>Tertiary Current Distribution, Nernst-Planck>Dissolving-depositing species>tcd.deltaeps_pce1_Zn - Volume fraction change**.

Deposited Zinc Volume Fraction

1 In the **Model Builder** window, click **Deposited Zinc Volume Fraction**.

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

3 From the **Time (h)** list, choose **0.5**.

4 Click to expand the **Number Format** section. Select the **Manual color legend settings** check box.

5 From the **Notation** list, choose **Engineering**.

6 In the **Deposited Zinc Volume Fraction** toolbar, click **Plot**.