Model created in COMSOL Multiphysics 6.4

Molten Carbonate Transport

Introduction

This tutorial shows how to model transport of the individual ions in a salt melt comprising two binary salts, where the transport equations are defined using concentrated solution theory. The example model defines the electrolyte ion transport of a molten carbonate fuel cell (or electrolyzer), with a 1D-model geometry consisting of a separator, one negative (hydrogen) and one positive (oxygen) porous electrode.

The model is solved using a time-dependent solver, simulating changes in the ion distribution during a 1 h potentiostatic hold.

The model parameters are taken from a paper by Bodén and others (Ref. 1).

Model Definition

Figure 1 shows the model geometry. The electrodes are porous, where the solid matrix consists of Ni, alloyed with Cr or Al, on the negative side, and lithiated NiO on the positive side, respectively. The separator consists of a ceramic $LiAlO_2$ matrix.

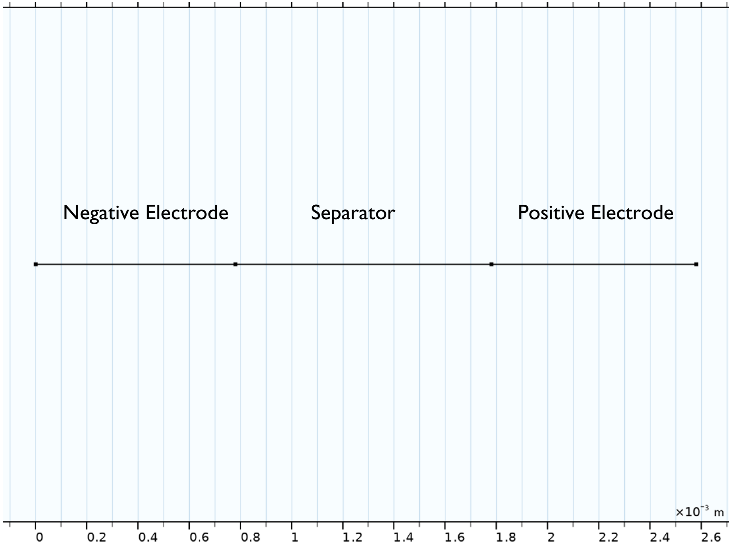


Figure 1: Model geometry.

The electrolyte consists of a $Li^+/K^+/CO_3^{2-}$ salt melt, and the aim of the model is to investigate the ion distribution in the cell during load. The absence of a neutral solvent, and the high concentration of the CO_3^{2-} ions participating in the electrode reactions, makes the problem unsuitable to solve using the Nernst–Planck equations (which are used in the Tertiary Current Distribution, Nernst–Planck interfaces), which assume a diluted electrolyte, implying the presence of a solvent present at a high concentration in relation to all other species. The model is therefore defined using the **Concentrated Electrolyte Transport** interface, solving for an electrolyte phase potential variable and two neutral salt (Li_2CO_3 and K_2CO_3) fraction variables. The electrolyte transport equations in this interface make use of concentrated electrolyte theory, including the assumption of local electroneutrality (Ref. 2).

Charge transfer occurs at the electrode-electrolyte interface within the porous matrix of the negative and positive electrodes. The local current density, i_{loc}, of the negative electrode hydrogen oxidation charge transfer reaction

$$\mathrm{H_2 + CO_3^{2-} \leftrightarrow H_2O + CO_2} + 2e^-$$

is defined as

$$i_{\mathrm{loc,\,neg}} = i_{0,\,\mathrm{neg}}\left(e^{\frac{(1-\beta_{\mathrm{neg}})F\eta_{\mathrm{neg}}}{RT}} - e^{\frac{-(1+\beta_{\mathrm{neg}})F\eta_{\mathrm{neg}}}{RT}}\right) \tag{1}$$

where β is a symmetry factor and the exchange current density $i_{0,\mathrm{neg}}$ is defined as

$$i_{0,\,\mathrm{neg}} = i_{0,\,\mathrm{ref,\,neg}}\, x_{\mathrm{H_2}}^{0.5\beta_{\mathrm{neg}}}\, x_{\mathrm{H_2O}}^{0.5(1-\beta_{\mathrm{neg}})}\, x_{\mathrm{CO_2}}^{0.5(1-\beta_{\mathrm{neg}})}, \tag{2}$$

where x_i denote the molar fractions of the reacting gas species in the gas phase. These molar fractions are set as constant in the model. (The $i_{0,\mathrm{ref}}$ exchange current density refers to the exchange current density for an imaginary reference state of unity molar fractions.)

Correspondingly, on the positive side, the local current density of the oxygen reduction reaction

$$\mathrm{O_2 + 2CO_2} + 4e^- \leftrightarrow \mathrm{2CO_3^{2-}}$$

is defined as

$$i_{\mathrm{loc,\,pos}} = i_{0,\,\mathrm{pos}}\left(e^{\frac{(1+\beta_{\mathrm{pos}})F\eta_{\mathrm{pos}}}{RT}} - e^{\frac{-(1-\beta_{\mathrm{pos}})F\eta_{\mathrm{pos}}}{RT}}\right) \tag{3}$$

with

$$i_{0,\,\mathrm{pos}} = i_{0,\,\mathrm{ref,\,pos}}\, x_{\mathrm{O_2}}^{0.5(1-0.5\beta_{\mathrm{pos}})}\, x_{\mathrm{CO_2}}^{-(1+\beta_{\mathrm{pos}})}. \tag{4}$$

In the kinetic expressions above, the overpotential η is defined as

$$\eta = \phi_s - \phi_l - E_{\mathrm{eq}} \tag{5}$$

Here, the electrode phase potential ϕ_s is set to 0 V in the negative electrode and 0.75 V in the positive electrode. The cell voltage equals the difference between the positive and negative electrode phase potentials

$$E_{\mathrm{cell}} = \phi_{s,\ \mathrm{pos}} - \phi_{s,\ \mathrm{neg}} = 0.75\ \mathrm{V} \tag{6}$$

By defining the **Reference Electrode** node stoichiometry to correspond to the oxidation of CO_3^{2-}, the electrolyte phase potential ϕ_l is inherently defined to include CO_3^{2-} ion concentration overpotentials.

The equilibrium potentials of the two electrode reactions are defined as

$$E_{\mathrm{eq,\ neg}} = E_{\mathrm{eq,\ neg,\ ref}} - \frac{RT}{2F}\log\left(\frac{x_{\mathrm{H_2}}}{x_{\mathrm{H_2O}}x_{\mathrm{CO_2}}}\right) \tag{7}$$

and

$$E_{\mathrm{eq,\ pos}} = E_{\mathrm{eq,\ pos,\ ref}} - \frac{RT}{2F}\log\left(\frac{1}{x_{\mathrm{O_2}}^{0.5}x_{\mathrm{CO_2}}}\right) \tag{8}$$

where the reference equilibrium potentials refer to the reference state of 1 atm for the partial pressures and the cell temperature 650°C.

Finally, the species sources, R (mol/m^{3}s), for the CO_3^{2-} ions are calculated using Faraday's law of electrolysis according to

$$R_{\mathrm{CO_3^{2-}}} = -\frac{A_v i_{\mathrm{loc}}}{2F} \tag{9}$$

where A_v (m^2/m^3) is the specific surface are of the electrodes.

A **Species Sources** domain node is used in the model to define the charge transfer reactions according to the above equations.

As CO_3^{2-} is transferred between the electrolyte and electrode phases, current starts to flow in the cell. The transport in the electrolyte is characterized by the use of composition-dependent binary Maxwell-Stefan diffusivities, these are defined on the **Diffusion Coefficients** node, which is a child node to the **Electrolyte** domain node. One diffusivity for each ion-pair (Li^+-K^+, Li^+-CO_3^{2-}, and K^+-CO_3^{2-}) is required to define the transport.

The Maxwell–Stefan transport model computes diffusive–migrative fluxes of the electrolyte species with respect to the mass-averaged velocity, $\mathbf{u}$ (m/s), of the electrolyte. Instead of computing the velocity using a Fluid Flow interface such as Darcy's Law, the velocity is approximated to be proportional to the electrolyte current vector, $\mathbf{I}_l$ (A/m^2), times the carbonate ion molar mass according to

$$\mathbf{u} = -\frac{\mathbf{I}_l M_{\mathrm{CO}_3^{2-}}}{2F\rho} \tag{10}$$

The electrolyte density, ρ (kg/m^3), will in reality depend on composition, but is treated as a constant in this tutorial.

For this cell, where the carbonate ion is the only ion (CO_3^{2-}) participating in the charge transfer reaction, the above expression for the electrolyte mass-averaged velocity is valid for a stationary current distribution. However, it often serves as a fair approximation also for time-dependent problems.

All the three domains are porous and are defined using a common **Separator** node. By the use of a domain-specific porosity variable, the porosity is defined differently in each domain.

The model is solved in a **Study** comprising a **Current Distribution Initialization** step followed by a **Time Dependent** study step. The first step solves for the electrolyte phase potential dependent variable only, using a stationary solver, and the solution is then passed on as initial values the following time-dependent step.

Results and Discussion

Figure 2 shows the individual ion concentrations at 1 h. As a result of electroneutrality, the concentration of CO_3^{2-} equals half of the sum of Li^+ and K^+.

Interestingly, the concentration gradients of the two cations (Li^+ and K^+) are opposite to each other, and in addition it can be seen that the smaller ion Li^+, which has a higher binary diffusivity value vs CO_3^{2-}, is subject to higher concentration gradient magnitudes than the larger K^+. This segregation effect is related to it being energetically more favorable to have Li^+ fulfill electroneutrality when gradients in the CO_3^{2-} concentration are induced by the electrode reactions. Binary diffusivity coefficients can be seen an as inverse proportionality constants for the friction forces between the electrolyte species — the higher the diffusivity, the lower the friction.

An alternative way of plotting composition changes in the cell is to plot the relative proportions of the two neutral salts (Li_2CO_3 and K_2CO_3) in relation to each other. Figure 3 plots the quantity $x_{Li+}/(x_{Li+}+x_{K+})$ as a measure of the fraction of Li_2CO_3.

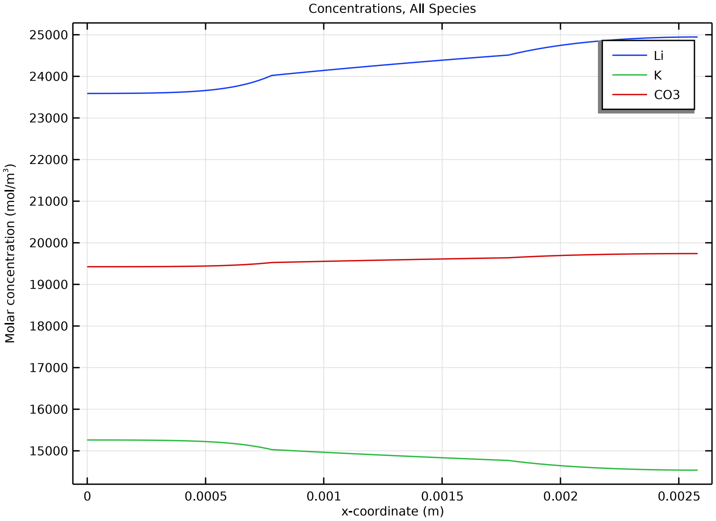


Figure 2: Individual ion concentrations.

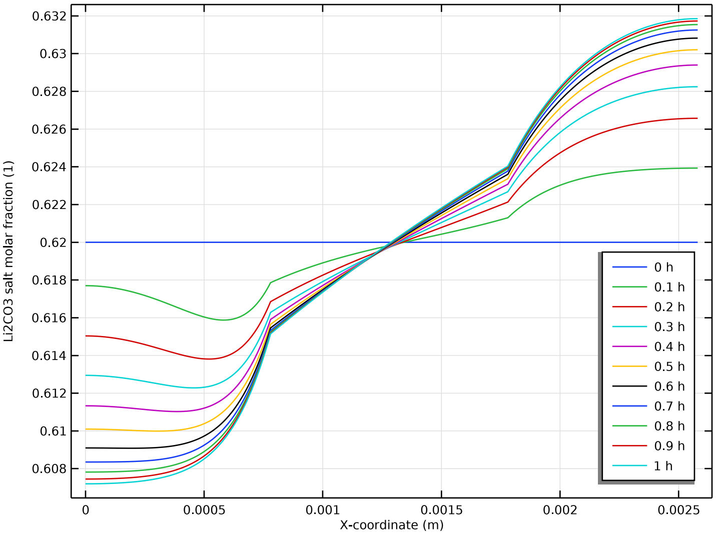


Figure 3: Li_2CO_3 salt fraction.

Figure 4 shows the electrolyte conductivity profile over time. As a result of the concentration changes, the conductivity varies. This is a result of the composition-dependent diffusivities deployed in the model.

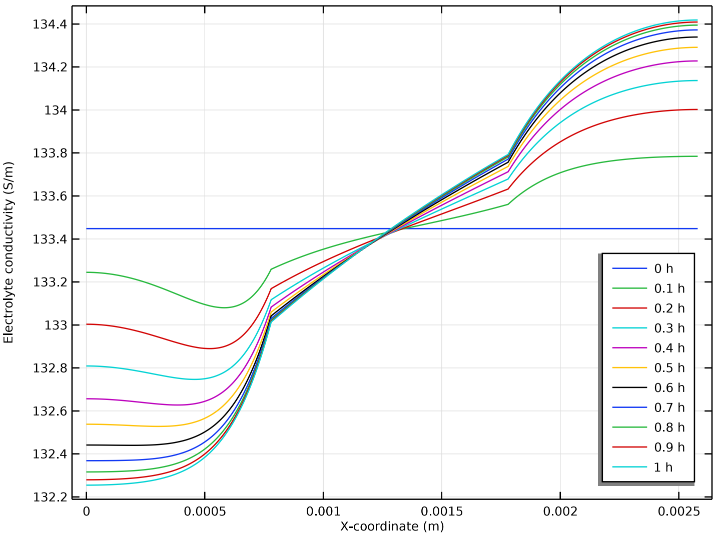


Figure 4: Electrolyte conductivity.

The electrolyte conductivity variations are fairly small. Figure 5 shows the electrolyte phase potential for all simulated times, ranging from 0 to 1 h in steps of 0.1 h. The variations in the potential profile are small and all line graphs more or less coincide.

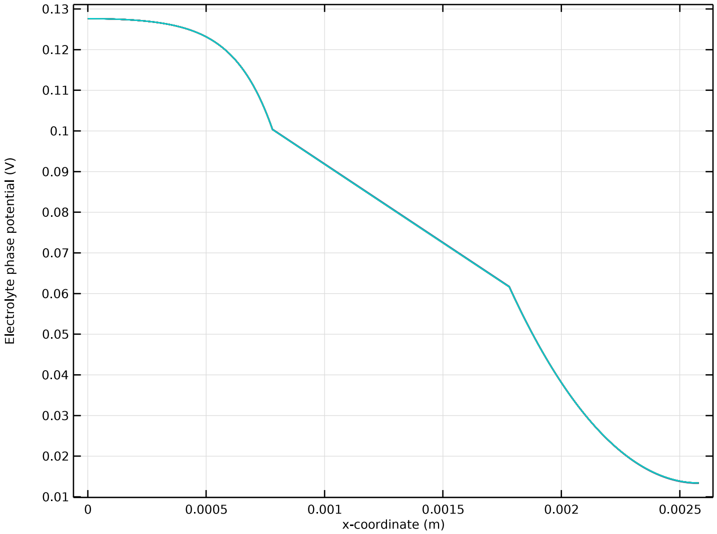


Figure 5: Electrolyte phase potential.

Figure 6 shows the volumetric current densities in the cell stemming from the charge transfer reactions, also here ranging from 0 to 1 h in steps of 0.1 h. These source terms give rise to the corresponding electrolyte current density profiles seen in Figure 7. As for Figure 5, variations over time are small and all line graphs more or less coincide.

It is known that the local composition of the electrolyte impacts the electrolyte wetting of the porous matrix of the electrodes. An extended model could incorporate this effect by defining the local electrolyte volume fraction as a function of the composition. Such a model would likely result in larger spatial and temporal variations in the current distribution.

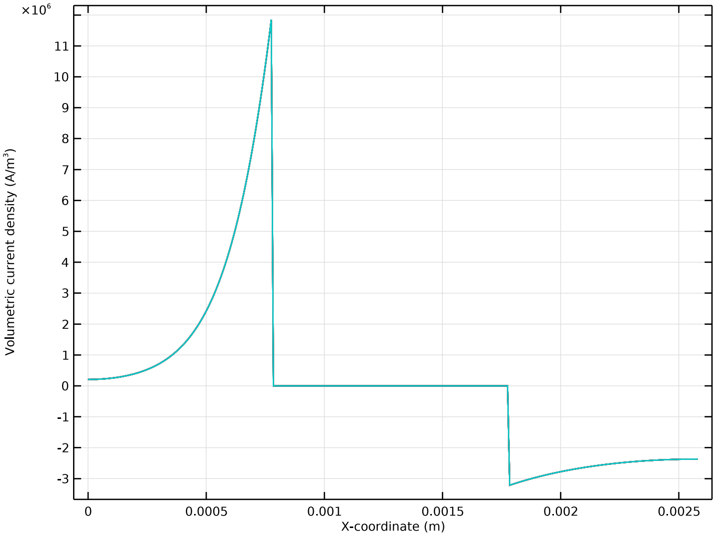


Figure 6: Volumetric (reaction) current density.

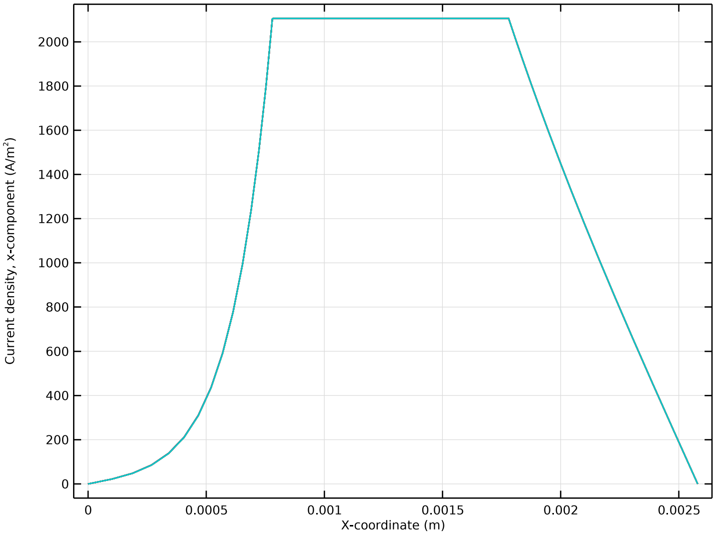


Figure 7: Electrolyte current density in the x direction.

References

1. A. Bodén and G. Lindbergh, “A Model for Mass Transport of Molten Alkali Carbonate Mixtures Applied to the MCFC,” *J. Electrochem. Soc.*, vol. 153, no. 111, pp. A2111–A2119, 2006.

2. A. Van-Brunt, P.E. Farrell, and C.W. Monroe, “Structural electroneutrality in Onsager–Stefan–Maxwell transport with charged species,” *Electrochimica Acta*, vol. 441, p. 141769, 2023, doi.org/10.1016/j.electacta.2022.141769.

Application Library path: `Fuel_Cell_and_Electrolyzer_Module/Fuel_Cells/molten_carbonate_transport`

Modeling Instructions

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

NEW

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

MODEL WIZARD

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

2 In the **Select Physics** tree, select **Electrochemistry** > **Concentrated Electrolyte Transport (cet)**.

3 Click **Add**.

4 Click ➔ **Study**.

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

6 Click ☑ **Done**.

GLOBAL DEFINITIONS

Parameters 1

Load the model parameters from a text file.

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

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

3. Click **Load from File**.
4. Browse to the model's Application Libraries folder and double-click the file `molten_carbonate_transport_parameters.txt`.

GEOMETRY 1

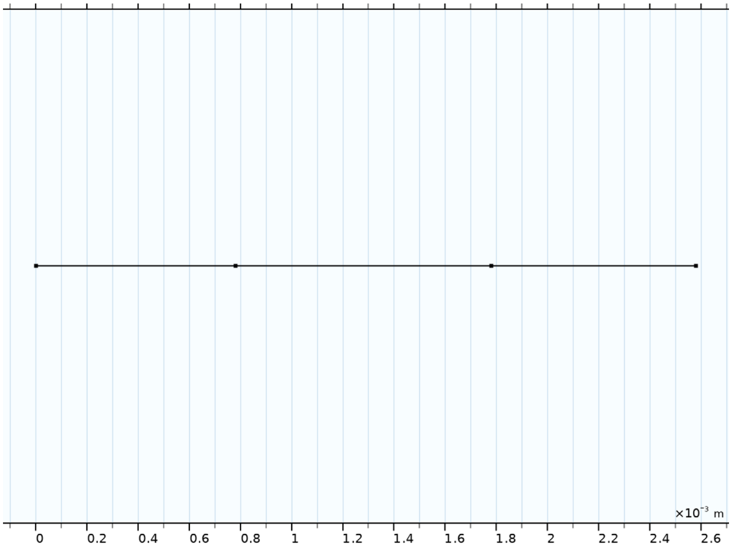
Create the model geometry as follows:

Interval 1 (i1)

1. In the **Model Builder** window, under **Component 1 (comp1)** right-click **Geometry 1** and choose **Interval**.
2. In the **Settings** window for **Interval**, locate the **Interval** section.
3. From the **Specify** list, choose **Interval lengths**.
4. In the table, enter the following settings:

Lengths (m)
`L_neg`
`L_mem`
`L_pos`

5. Click **Build Selected**.



CONCENTRATED ELECTROLYTE TRANSPORT (CET)

The electrolyte consists of two cations (`Li` and `K`) and one anion (`CO3`)

1. In the **Model Builder** window, under **Component 1 (comp1)** click **Concentrated Electrolyte Transport (cet)**.
2. In the **Settings** window for **Concentrated Electrolyte Transport**, locate the **Species** section.
3. Find the **Cations** subsection. In the table, enter the following settings:

Name	Molar mass (kg/mol)	Charge
`Li`	`M_Li`	+1

4. Click + **Add**.
5. In the table, enter the following settings:

Name	Molar mass (kg/mol)	Charge
`Li`	`M_Li`	+1
`K`	`M_K`	+1

6. Find the **Anions** subsection. In the table, enter the following settings:

Name	Molar mass (kg/mol)	Charge
`CO3`	`M_CO3`	-2

7. Find the **Neutral species** subsection. Click to select the first row in the table.
8. Click **Delete**.

Reference Electrode 1

1. In the **Model Builder** window, under **Component 1 (comp1)** > **Concentrated Electrolyte Transport (cet)** click **Reference Electrode 1**.
2. In the **Settings** window for **Reference Electrode**, locate the **Stoichiometric Coefficients** section.
3. In the s_{Li} text field, type `0`.
4. In the s_{CO3} text field, type `1`.

Electrolyte 1

1. In the **Model Builder** window, click **Electrolyte 1**.
2. In the **Settings** window for **Electrolyte**, locate the **Volumetric Equation of State** section.
3. From the **Define** list, choose **Density**.
4. In the ρ text field, type `rho`.

GLOBAL DEFINITIONS

Default Model Inputs

Define the temperature variable under **Default Model Inputs**. This setting will be used by all model nodes.

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`.

DEFINITIONS

Load a number of variable expressions from a text file. These variables expressions will be used when defining the diffusion coefficients and the electrode kinetics.

Variables 1

1. In the **Model Builder** window, under **Component 1 (comp1)** right-click **Definitions** and choose **Variables**.
2. In the **Settings** window for **Variables**, locate the **Variables** section.
3. Click 📂 **Load from File**.
4. Browse to the model's Application Libraries folder and double-click the file `molten_carbonate_transport_variables.txt`.

   Check that no expressions are marked with curly yellow underlines, indicating unknown variables. If missing variables are indicated, you may have misspelled the species names (`Li`, `K` and `CO3`) that you defined earlier in the **Concentrated Electrolyte Transport** parent node.

CONCENTRATED ELECTROLYTE TRANSPORT (CET)

Diffusion Coefficients 1

1. In the **Model Builder** window, under **Component 1 (comp1)** > **Concentrated Electrolyte Transport (cet)** > **Electrolyte 1** click **Diffusion Coefficients 1**.
2. In the **Settings** window for **Diffusion Coefficients**, locate the **Maxwell–Stefan Diffusivities** section.
3. In the $D_{\mathrm{Li,K}}$ text field, type `D_Li_K`.
4. In the $D_{\mathrm{Li,CO3}}$ text field, type `D_Li_CO3`.
5. In the $D_{\mathrm{K,CO3}}$ text field, type `D_K_CO3`.

Initial Values 1

1. In the **Model Builder** window, under **Component 1 (comp1)** > **Concentrated Electrolyte Transport (cet)** click **Initial Values 1**.
2. In the **Settings** window for **Initial Values**, locate the **Initial Values** section.
3. Find the **Electrolyte components** subsection. From the **Define** list, choose **Molar proportions**, and in the corresponding text fields, type `P_Li2CO3` and `P_K2CO3`, respectively.

DEFINITIONS

Add some additional variable nodes to define the local electrolyte volume fractions in the individual domains and the molar source rate of carbonate ions.

Variables 2 (Negative Electrode)

1. In the **Model Builder** window, under **Component 1 (comp1)** right-click **Definitions** and choose **Variables**.
2. In the **Settings** window for **Variables**, type `Variables 2 (Negative Electrode)` in the **Label** text field.
3. Locate the **Geometric Entity Selection** section. From the **Geometric entity level** list, choose **Domain**.
4. Select Domain 1 only.
5. Locate the **Variables** section. In the table, enter the following settings:

Name	**Expression**	**Unit**	**Description**
`R_CO3`	`-iv_neg/(2*F_const)`	mol/(m^3·s)	`Carbonate molar source rate`
`epsl`	`epsl_neg`		`Electrolyte volume fraction`

Variables 3 (Separator)

1. Right-click **Variables 2 (Negative Electrode)** and choose **Duplicate**.
2. In the **Settings** window for **Variables**, type `Variables 3 (Separator)` in the **Label** text field.
3. Locate the **Geometric Entity Selection** section. Click **Clear Selection**.
4. Select Domain 2 only.

5 Locate the **Variables** section. In the table, enter the following settings:

Name	**Expression**	**Unit**	**Description**
`R_CO3`	`0`		`Carbonate molar source rate`
`epsl`	`epsl_mem`		`Electrolyte volume fraction`

Variables 4 (Positive Electrode)

1 Right-click **Variables 3 (Separator)** and choose **Duplicate**.

2 In the **Settings** window for **Variables**, type `Variables 4 (Positive Electrode)` in the **Label** text field.

3 Locate the **Geometric Entity Selection** section. Click **Clear Selection**.

4 Select Domain 3 only.

5 Locate the **Variables** section. In the table, enter the following settings:

Name	**Expression**	**Unit**	**Description**
`R_CO3`	`-iv_pos/(2*F_const)`	mol/(m³·s)	`Carbonate molar source rate`
`epsl`	`epsl_pos`		`Electrolyte volume fraction`

CONCENTRATED ELECTROLYTE TRANSPORT (CET)

Separator (Porous Media)

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

2 In the **Settings** window for **Separator**, type `Separator (Porous Media)` in the **Label** text field.

3 Locate the **Domain Selection** section. From the **Selection** list, choose **All domains**.

4 Locate the **Separator** section. In the ε_l text field, type `epsl`.

Species Sources 1

1 In the **Physics** toolbar, click **Domains** and choose **Species Sources**.

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

3 From the **Selection** list, choose **All domains**.

4 Locate the **Species Sources** section. In the R_{CO3} text field, type `R_CO3`.

MESH 1

Define a mesh with an extra fine resolution at the separator–electrode boundaries as follows:

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

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

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

Size 1

1 In the **Model Builder** window, right-click **Edge 1** and choose **Size**.

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

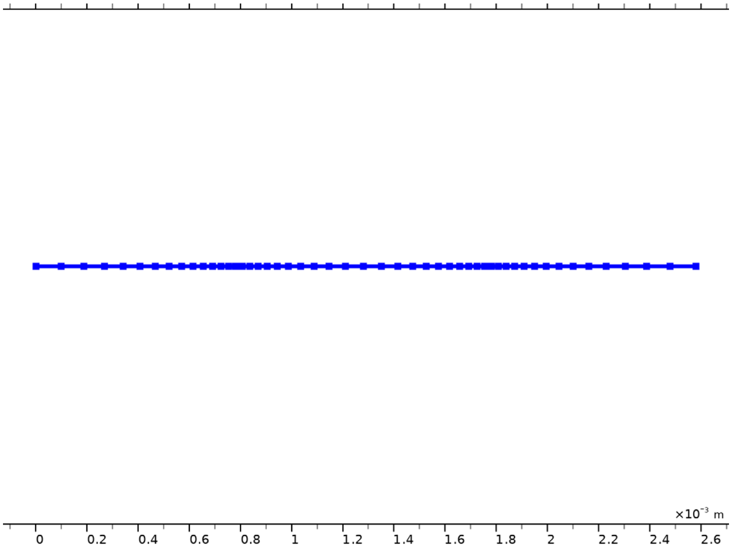
3 From the **Geometric entity level** list, choose **Boundary**.

4 Select Boundaries 2 and 3 only.

5 Locate the **Element Size** section. From the **Predefined** list, choose **Extremely fine**.

Edge 1

Right-click **Edge 1** and choose **Build All**.



STUDY 1

Step 2: Time Dependent

The model is now ready for solving. Change the simulation time to 1 h as follows:

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

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

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

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

RESULTS

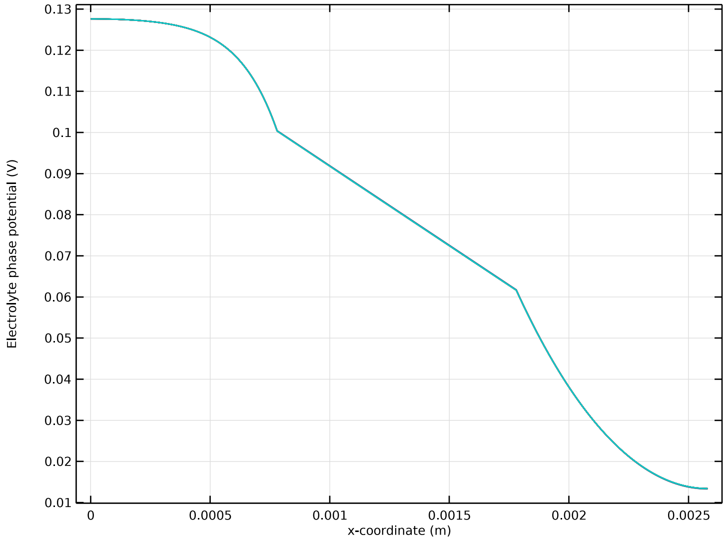
Electrolyte Potential (cet)

Inspect and modify the default plots as follows:

1 In the **Settings** window for **1D Plot Group**, click to expand the **Title** section.

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

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



Concentrations, All Species (cet)

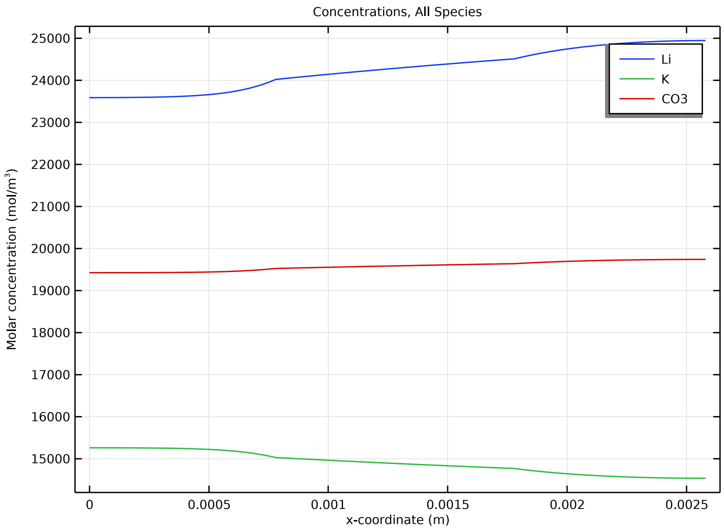
1 In the **Model Builder** window, click **Concentrations, All Species (cet)**.

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

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

4 Locate the **Plot Settings** section.

5 Select the **y-axis label** checkbox. In the associated text field, type `Molar concentration (mol/m<sup>3</sup>)`.



Volumetric Current Density

Create a plot of the volumetric current density as follows:

1 In the **Results** toolbar, click ∿ **1D Plot Group**.

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

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

Line Graph 1

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

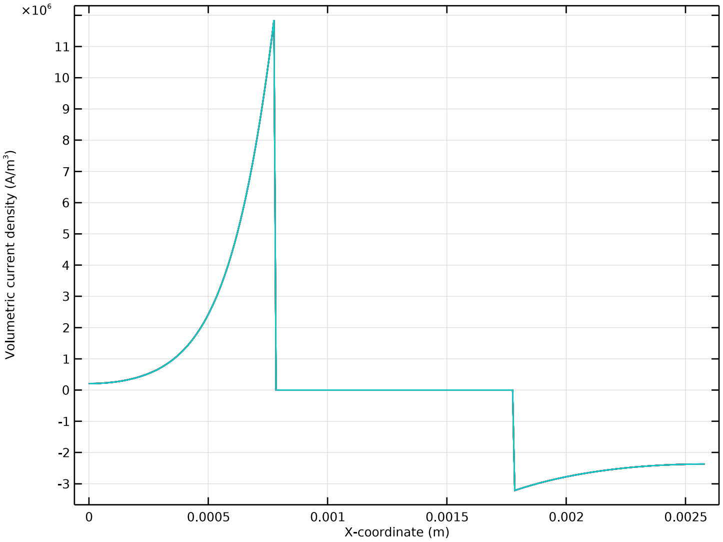
2 In the **Settings** window for **Line Graph**, locate the **Selection** section.

3 From the **Selection** list, choose **All domains**.

4 Click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Concentrated Electrolyte Transport** > **cet.ss1.iv - Volumetric current density - A/m^3**.

5 Locate the **x-Axis Data** section. From the **Parameter** list, choose **Dataset space variable**.

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



The volumetric current density is proportional to the reaction rate in the electrodes.

Electrolyte Current Density

Create a plot of the electrolyte current density as follows:

1 In the **Model Builder** window, right-click **Volumetric Current Density** and choose **Duplicate**.

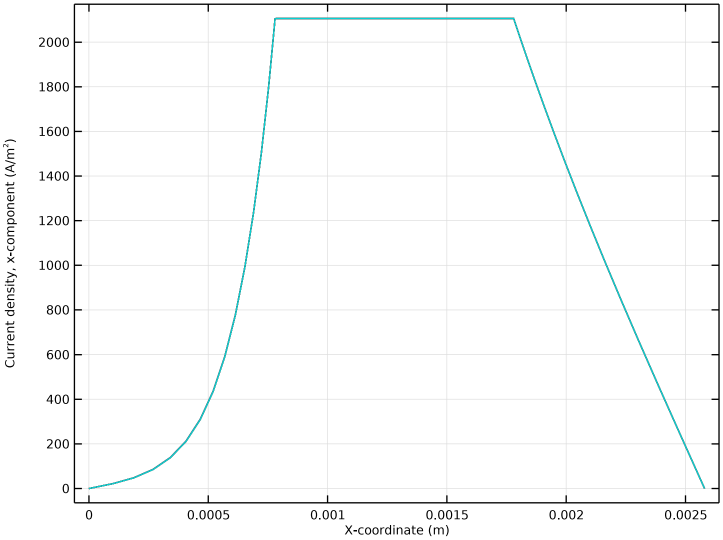
2 In the **Settings** window for **1D Plot Group**, type `Electrolyte Current Density` in the **Label** text field.

Line Graph 1

1 In the **Model Builder** window, expand the **Electrolyte Current Density** node, then click **Line Graph 1**.

2 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Concentrated Electrolyte Transport** > **Electrolyte current densities** > **Current density - A/m²** > **cet.Ilx - Current density, x-component**.

3 In the **Electrolyte Current Density** toolbar, click **Plot**.



This plot shows the magnitude and direction of the current flowing in the electrolyte phase.

Electrolyte Conductivity

As a result of concentration changes over time in the electrolyte, the conductivity will change. Plot the electrolyte conductivity as follows:

1 In the **Model Builder** window, right-click **Electrolyte Current Density** and choose **Duplicate**.

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

Line Graph 1

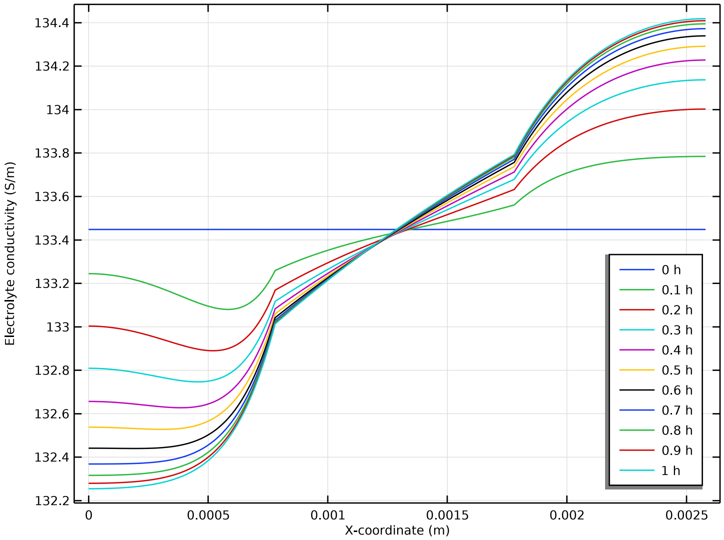
1 In the **Model Builder** window, expand the **Electrolyte Conductivity** node, then click **Line Graph 1**.

2 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Concentrated Electrolyte Transport** > **Electrolyte properties** > **cet.sigmal - Electrolyte conductivity - S/m**.

3 Click to expand the **Legends** section. Select the **Show legends** checkbox.

Electrolyte Conductivity

1. In the **Model Builder** window, click **Electrolyte Conductivity**.
2. In the **Settings** window for **1D Plot Group**, locate the **Legend** section.
3. From the **Position** list, choose **Lower right**.
4. In the **Electrolyte Conductivity** toolbar, click **Plot**.



Finally, plot the molar fraction of the Li2CO3 salt (in relation to the total salt concentration) as follows:

Li2CO3 Salt Fraction

1. Right-click **Electrolyte Conductivity** and choose **Duplicate**.
2. In the **Settings** window for **1D Plot Group**, type `Li2CO3 Salt Fraction` in the **Label** text field.

Line Graph 1

1. In the **Model Builder** window, expand the **Li2CO3 Salt Fraction** node, then click **Line Graph 1**.
2. In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Definitions** > **Variables** > **xA - Li2CO3 salt molar fraction - 1**.

3 In the **Li2CO3 Salt Fraction** toolbar, click **Plot**.