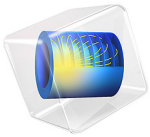

1D Isothermal Nickel–Cadmium Battery

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Introduction

Nickel–Cadmium (Ni–Cd) batteries are rechargeable batteries with nickel-hydroxide as positive electrode material, cadmium as negative electrode material, and hydroxide ions in an aqueous KOH electrolyte as charge carriers. Historically, they were used in many applications, for example those requiring high power. Today, mainly due to the toxicity of cadmium, their use is restricted. In the European Union, for example, they are only allowed in medical equipment and emergency systems and lighting. Lithium-ion and nickel–metal hydroxide batteries have replaced the Ni–Cd battery in many applications.

The present model shows how a typical sealed Ni–Cd battery cell can be described using the Battery with Binary Electrolyte interface.

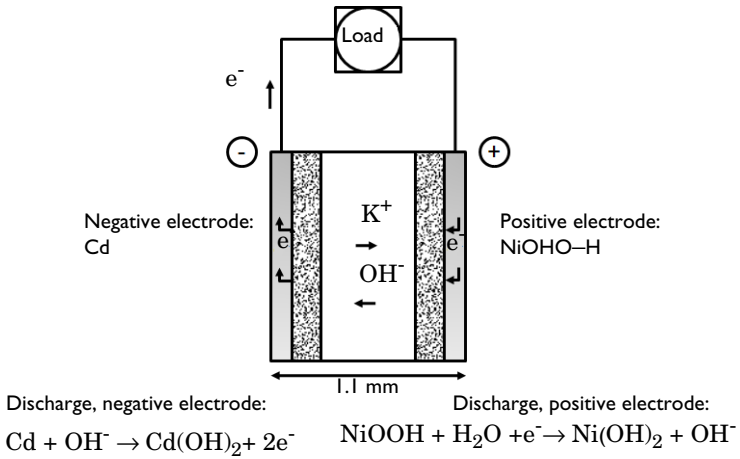


Figure 1: Cross section of a Ni–Cd battery showing the main electrochemical processes that occur during discharge.

The 1D isothermal model includes the following processes:

- Electronic current conduction in the electrodes
- Ionic charge transport in the electrodes and electrolyte/separator
- Material transport in the electrolyte
- Material transport within the cylindrically symmetric particles that form the positive electrode

- Change in porosity of the negative electrode
- Butler–Volmer electrode kinetics using experimentally measured discharge curves for the equilibrium potential. The kinetics for both electrode reactions, as well as for oxygen evolution, are included.

The model is based on a paper by De Vidts and White (Ref. 2) using data for a typical sealed NiCd battery (Ref. 1). In the paper, the authors also included a model for electron transport inside the positive electrode material. However, it was found that this contribution was negligible and it is therefore excluded in the present model.

Model Definition

This example models the battery cross section in 1D, which implies that edge effects in the length and height of the battery are neglected. The example uses the following domains:

- Negative porous electrode (cadmium): 400 μm
- Separator (electrolyte): 250 μm
- Positive porous electrode (nickel oxide): 360 μm

In addition, an extra dimension description of the cylindrically symmetric particles in the positive electrode is included. These particles constitute long "wires", with a central core of inactive support material. The thickness of the inactive core region is 1.5 μm, and the thickness of the active material surrounding it is 1.4 μm.

The electric potential in the electron conducting phase, ϕ_s, is calculated using a charge balance based on Ohm's law, where the charge transfer reactions result in source or sink term. For the porous electrodes effective conductivities, σ_s^{eff}, are used that take porosity and tortuosity into account as given by the following expression:

$$\sigma_s^{\text{eff}} = \sigma_s \varepsilon^{\gamma}$$

where γ is the Bruggeman coefficient, which is set to 1.5 in this model, corresponding to a packed bed of spherical particles. Also, the diffusion coefficient for the electrolyte salt is corrected for the tortuosity and the porosity in this way.

The ionic charge balances and material balances are modeled according to the equations for a binary 1:1 electrolyte, with both the anion (OH^-) and the solvent (H_2O) participating in the electrode reactions (Ref. 2).

Fickian diffusion describes the transport in the cylindrical particles of the positive electrode. The diffusion equation is expressed in cylindrical coordinates for the material balance of protons in the particles.

Butler–Volmer electrode kinetics describes the local charge transfer current density in the electrodes. The Butler–Volmer expressions are introduced as source or sink terms in the charge balances and material balances.

BOUNDARY CONDITIONS

For the electronic current balance, a potential of 0 V is set on the negative electrode's current collector/feeder boundary. At the positive electrode current collector/feeder, the current density is specified. The current density is set to a constant discharge current. The inner boundaries facing the separator are insulating for electric currents.

For the ionic charge balance in the electrolyte, the current collector/feeder boundaries are insulating. Insulating conditions also apply to the material balances.

At the particle surface in the local particle model, the material flux is determined by the local electrochemical reaction rate.

MATERIAL PROPERTIES

The material properties are those of a typical NiCd cell. The electrolyte is KOH, diluted in water to a 30% (wt) solution. The active electrode materials are cadmium for the negative electrode and a nickel oxide ($Ni(OH)_2$) for the positive electrode.

The model uses constant values for the electrolyte conductivity, the electrolyte diffusivity, and the activity variation with concentration in the electrolyte.

The positive Ni electrode limits, and thus determines, the capacity of the battery cell. For this reason, the solid volume fraction of the Ni electrode is computed as

$$\varepsilon_s = \frac{Q_{\text{cell}}}{F c_{\text{H, max}} l_{\text{positive}}} \tag{1}$$

where Q_{cell} is the cell capacity (74.16 C/cm^2 of electrode), F is Faraday's constant, $c_{\text{H, max}}$ is the maximum proton concentration in the positive material and l_{positive} is the thickness of the positive electrode (400 μm).

Simulations of both the discharge and charge behavior of the cell are performed. In both cases, three increasingly high C-rates of C/10, C/2.1, and C/0.7 are applied. The nominal charge/discharge current density, the 1C rate, is 206 A/m^2.

DISCHARGE CURVES

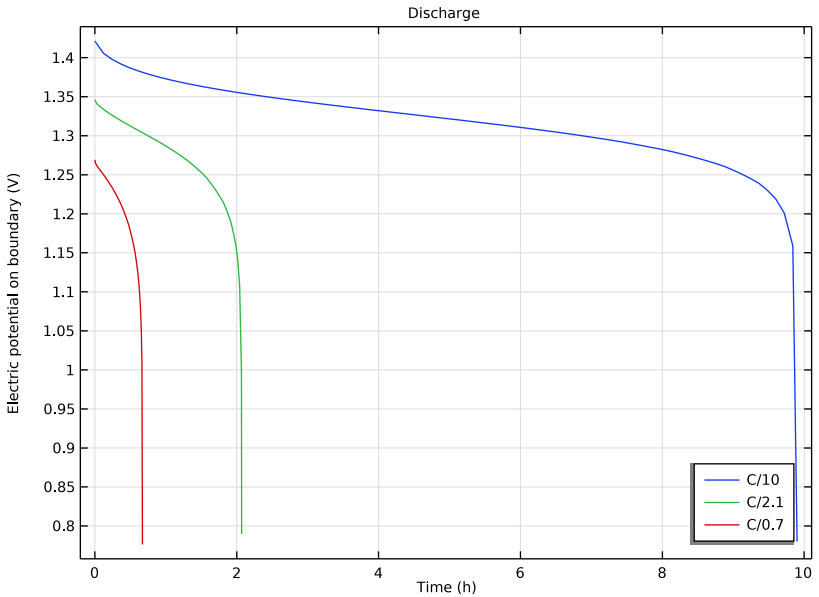


Figure 2: Discharge curves for three C-rates.

Figure 2 shows discharge curves for the three C-rates. The overpotential of the positive electrode reaction increases with increasing C-rate, accounting for most of the difference in cell voltage at the initial time. At the end of discharge, the concentration of protons inside the positive electrode approaches the maximum value and the slopes of the voltage curves decrease drastically.

CHARGE CURVES

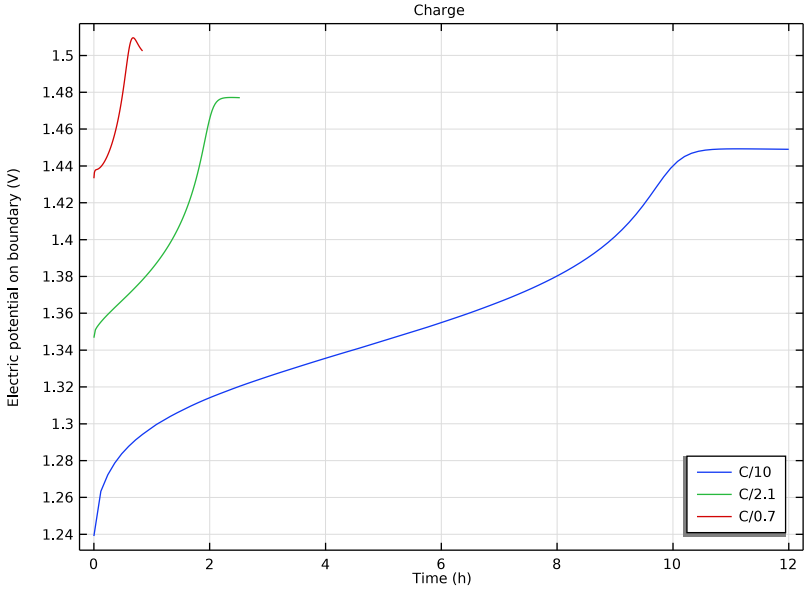


Figure 3: Charge curves for the three C-rates.

Figure 3 shows charge curves for all three C-rates. Again, as for the discharge curves, the difference in initial potential is due mainly to the overpotential of the positive electrode reaction. However, as the cell approaches 100% state of charge (SOC), the oxygen side reaction takes up an increasing fraction of the applied current. The voltage then plateaus, and during overcharging all current goes toward oxygen evolution on the positive Ni electrode and reduction at the negative Cd electrode.

STATE OF CHARGE DURING CHARGING

Figure 4 shows the hydration level of the positive Ni electrode, while Figure 5 shows the volume fraction of the negative Cd electrode, in both cases for charging. The x-axis shows the charge efficiency. Charging should reach completion at $t = 1$ for 100% charge efficiency. Charging causes protons to exit the positive electrode, and causes Cd hydroxide to be converted into metallic Cd. For this reason, decreasing hydration level and decreasing volume fraction both correspond to increasing SOC.

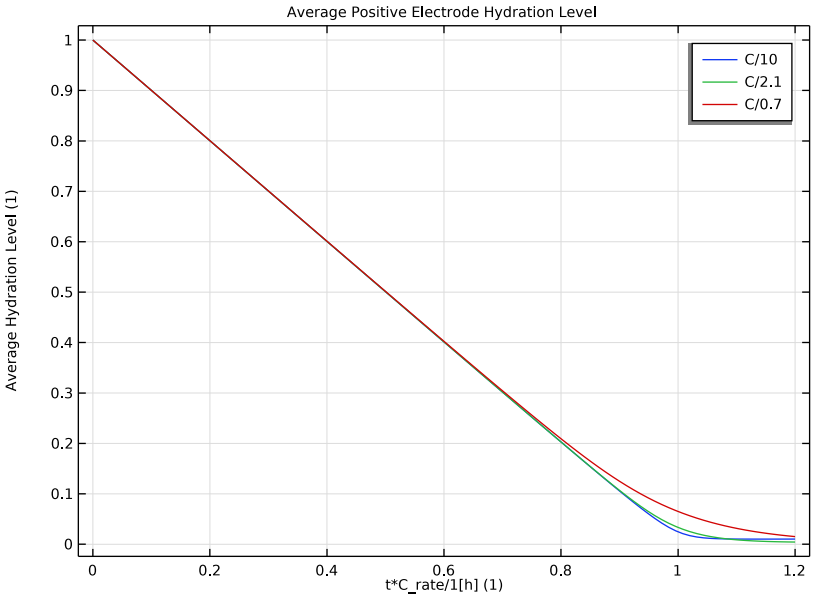


Figure 4: State of charge of the positive Ni electrode during charging at three different C-rates.

Both hydration level and volume fraction decrease in the same way during the initial part of charging, when the main electrode reactions consume almost all of the current. As charging approaches completion, after about $t = 0.8$, increasing C-rates are associated with decreased charge efficiency. Again, at higher C-rates, the oxygen side reaction consumes an increasing fraction of the charging current.

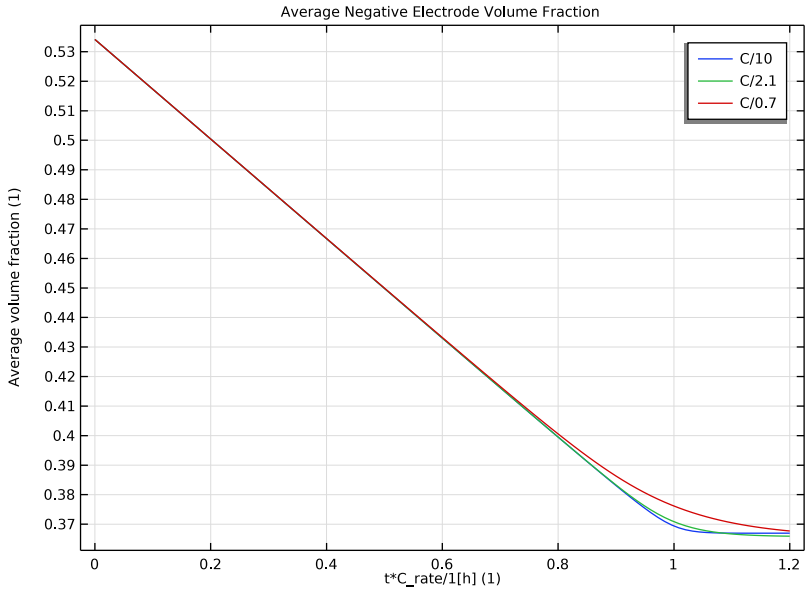


Figure 5: State of charge of the negative Cd electrode during charging at three different C-rates.

Notes About the COMSOL Implementation

ELECTROLYTE MOLAR MASS

By default, the Battery with Binary Electrolyte interface assumes a binary aqueous KOH electrolyte, so the default values for molar masses on the main interface node do not need to be changed.

PROTON DIFFUSION IN EXTRA DIMENSION

Proton diffusion inside the positive Ni active material is modeled inside a cylindrically symmetric Extra Dimension. The following continuity equation, which accounts for the cylindrical symmetry, is applied for protons inside the active positive material:

$$2\pi r\left(\frac{\partial c_{\mathrm{H}}}{\partial t} + -D_{\mathrm{H}}\frac{\partial c_{\mathrm{H}}}{\partial r}\right) = 0 \qquad (2)$$

Furthermore, at the exterior boundary of the Extra Dimension (the active material particle outer surface), the flux of c_H is proportional to the current density of the main Ni electrode reaction. Both expressions are implemented in weak form.

The core of inactive support material is what necessitates the extra dimension description. If the Ni material particles had been assumed to be active throughout the whole radius, the **Particle Properties** of the Ni electrode could instead have been set to **Intercalating Particles**, and the diffusion of protons could have been set up in the associated **Particle Intercalation** child node.

POROUS ELECTRODE ELECTRICAL CONDUCTIVITY

The solid electrical conductivity of each of the two porous electrodes is on the order of 10^5 S/m. However, the electrolyte conductivity is significantly lower, and thus is the main factor limiting the rate of charge transport. This difference in conductivities makes convergence harder to achieve. Using an effective solid phase conductivity of 100 S/m facilitates convergence while having an insignificant effect on the results.

References

1. W.R. Scott and D.W. Rusta, *Sealed-Cell Nickel Cadmium Battery Applications Manual*, 1979.

2. P. De Vidts and R.E. White, "Mathematical Modeling of a Nickel–Cadmium Cell: Proton Diffusion in the Nickel Electrode," *J. Electrochem. Soc.*, vol. 142, p. 1509, 1995.

Application Library path: `Battery_Design_Module/Batteries,_General/nicd_battery_1d`

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>Batteries>Battery with Binary Electrolyte (batbe)**.

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

Define parameters for the model. These include general parameters (for example the geometry), parameters used for each electrode, for the electrode reactions, for initial values of the charging and discharging studies, and finally the different C-rates to use for charge and discharge.

General

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

2 In the **Settings** window for **Parameters**, type `General` in the **Label** text field.

3 Locate the **Parameters** section. Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `nicd_battery_1d_general.txt`.

Cd Electrode

1 In the **Home** toolbar, click **Parameters** and choose **Add>Parameters**.

2 In the **Settings** window for **Parameters**, type `Cd Electrode` in the **Label** text field.

3 Locate the **Parameters** section. Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `nicd_battery_1d_cd_electrode.txt`.

Ni Electrode

1 In the **Home** toolbar, click **Parameters** and choose **Add>Parameters**.

2 In the **Settings** window for **Parameters**, type `Ni Electrode` in the **Label** text field.

3 Locate the **Parameters** section. Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `nicd_battery_1d_ni_electrode.txt`.

Electrode Reactions

1 In the **Home** toolbar, click **Parameters** and choose **Add>Parameters**.

2 In the **Settings** window for **Parameters**, type `Electrode Reactions` in the **Label** text field.

3 Locate the **Parameters** section. Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `nicd_battery_1d_electrode_reactions.txt`.

Charge/Discharge Cases

1 In the **Home** toolbar, click **Parameters** and choose **Add>Parameters**.

2 In the **Settings** window for **Parameters**, type `Charge/Discharge Cases` in the **Label** text field.

3 Locate the **Parameters** section. In the table, enter the following settings:

Name	Expression	Value	Description
`c_H_init`	`c_H_max/500`	104.2 mol/m³	`Initial H concentration in positive electrode`
`epsilon_3_init`	`epsilon_3_max`	0.6365	`Initial porosity of the negative electrode`
`sign`	`-1`	-1	`Sign of applied current, 1 for charge, -1 for discharge`

4 In the **Home** toolbar, click **Parameter Case**.

5 Right-click **Case 1** and choose **Rename**.

6 In the **Rename Case** dialog box, type `Discharge` in the **New label** text field.

7 Click **OK**.

8 In the **Home** toolbar, click **Parameter Case**.

9 In the **Settings** window for **Case**, type `Charge` in the **Label** text field.

10 Locate the **Parameters** section. In the table, enter the following settings:

Name	Expression	Description
c_H_init	`c_H_max`	Initial H concentration in positive electrode
epsilon_3_init	`epsilon_3_min+0.05`	Initial porosity of the negative electrode
sign	1	Sign of applied current, 1 for charge, -1 for discharge

C-rate Cases

1 In the **Home** toolbar, click **Parameters** and choose **Add>Parameters**.

2 In the **Settings** window for **Parameters**, type `C-rate Cases` in the **Label** text field.

3 Locate the **Parameters** section. In the table, enter the following settings:

Name	Expression	Value	Description
`C_rate`	1	1	`Charge/discharge rate`

4 In the **Home** toolbar, click **Parameter Case**.

5 In the **Settings** window for **Case**, locate the **Parameters** section.

6 In the table, enter the following settings:

Name	Expression	Description
C_rate	1/10	Charge/discharge rate

7 In the **Home** toolbar, click **Parameter Case**.

8 In the **Settings** window for **Case**, locate the **Parameters** section.

9 In the table, enter the following settings:

Name	Expression	Description
C_rate	1/2.1	Charge/discharge rate

10 In the **Home** toolbar, click **Parameter Case**.

11 In the **Settings** window for **Case**, locate the **Parameters** section.

12 In the table, enter the following settings:

Name	Expression	Description
C_rate	1/0.7	Charge/discharge rate

Define the cylindrical geometry of the electrode particles in the positive electrode in an **Extra Dimension**.

13 Click the **Show More Options** button in the **Model Builder** toolbar.

14 In the **Show More Options** dialog box, select **Physics>Extra Dimensions** in the tree.

15 In the tree, select the check box for the node **Physics>Extra Dimensions**.

16 Click **OK**.

ADD COMPONENT

In the **Model Builder** window, right-click **Global Definitions** and choose **Extra Dimensions> 1D Axisymmetric**.

EXTRA DIMENSION: POSITIVE ELECTRODE

1 In the **Settings** window for **Extra Dimension**, type `Extra Dimension: Positive Electrode` in the **Label** text field.

2 Locate the **Frames** section. Find the **Spatial frame coordinates** subsection. In the table, enter the following settings:

First	Second	Third
rxd	phi1	z1

GEOMETRY 2

Interval 1 (i1)

1 In the **Model Builder** window, expand the **Global Definitions> Extra Dimension: Positive Electrode (xdim1)>Definitions** node.

2 Right-click **Global Definitions>Extra Dimension: Positive Electrode (xdim1)>Geometry 2** and choose **Interval**.

The geometry of the positive electrode particles consists of an inner core of inactive substrate surrounded by active battery material.

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

4 From the **Specify** list, choose **Interval lengths**.

5 In the **Left endpoint** text field, type `y_positive_substrate`.

6 In the table, enter the following settings:

Lengths (m)
y_positive_active

7 Click **Build Selected**.

Define two integration operators to allow integration of variables in the extra dimension. These will be used later to compute the particle surface proton concentration as well as the average proton concentration inside the particle.

DEFINITIONS (XDIM1)

Extra Dimension Surface Integral

1. In the **Model Builder** window, under **Global Definitions> Extra Dimension: Positive Electrode (xdim1)** right-click **Definitions** and choose **Extra Dimensions>Integration over Extra Dimension**.
2. In the **Settings** window for **Integration over Extra Dimension**, type `Extra Dimension Surface Integral` in the **Label** text field.
3. Locate the **Operator Name** section. In the **Operator name** text field, type `xdsurfop`.
4. Locate the **Source Selection** section. From the **Geometric entity level** list, choose **Boundary**.
5. Select Boundary 2 only.
6. Locate the **Advanced** section. Clear the **Compute integral in revolved geometry** check box.

Extra Dimension Domain Integral

1. In the **Model Builder** window, right-click **Extra Dimensions** and choose **Integration over Extra Dimension**.
2. In the **Settings** window for **Integration over Extra Dimension**, type `Extra Dimension Domain Integral` in the **Label** text field.
3. Locate the **Operator Name** section. In the **Operator name** text field, type `xdintopDomain`.
4. Select Domain 1 only.
5. Locate the **Advanced** section. Clear the **Compute integral in revolved geometry** check box.

Make the mesh finer close to the left and right boundaries of the extra dimension.

MESH 2

1. In the **Model Builder** window, under **Global Definitions> Extra Dimension: Positive Electrode (xdim1)** click **Mesh 2**.
2. In the **Settings** window for **Mesh**, locate the **Sequence Type** section.
3. From the list, choose **User-controlled mesh**.

Distribution 1

1. Right-click **Global Definitions>Extra Dimension: Positive Electrode (xdim1)>Mesh 2** and choose **Distribution**.
2. Drag and drop **Distribution 1** below **Size**.
3. Select Domain 1 only.

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

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

6 In the **Number of elements** text field, type `31`.

7 In the **Element ratio** text field, type `0.1`.

8 Click **Build All**.

Next, define the geometry for the battery cell.

GEOMETRY 1

Interval 1 (i1)

1 In the **Model Builder** window, expand the **Component 1 (comp1)>Geometry 1** node.

2 Right-click **Geometry 1** and choose **Interval**.

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

4 From the **Specify** list, choose **Interval lengths**.

5 In the table, enter the following settings:

Lengths (m)
l_neg
l_sep
l_pos

6 Click **Build All Objects**.

Define the connection between the battery cell geometry and the extra dimension used for the cylindrical battery particles.

DEFINITIONS (COMP1)

Attached Dimensions 1

1 In the **Model Builder** window, expand the **Component 1 (comp1)>Definitions** node.

2 Right-click **Component 1 (comp1)>Definitions** and choose **Extra Dimensions> Attached Dimensions**.

3 In the **Settings** window for **Attached Dimensions**, locate the **Geometric Entity Selection** section.

4 From the **Geometric entity level** list, choose **Domain**.

5 Select Domain 3 only.

6 Locate the **Attached Dimensions** section. Under **Extra dimensions to attach**, click + **Add**.

7 In the **Add** dialog box, select **Extra Dimension: Positive Electrode (xdim1)** in the **Extra dimensions to attach** list.

8 Click **OK**.

Define the variables needed for the SOC of the negative electrode, the SOC and diffusive flux of protons inside the positive electrode, and the surface and average proton concentration and SOC at the positive electrode.

Negative Electrode

1 Right-click **Definitions** and choose **Variables**.

2 In the **Settings** window for **Variables**, type `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
`theta_N`	`(batbe.epsl-epsilon_3_min)/(epsilon_3_max-epsilon_3_min)`		`SOC, negative electrode`

Positive Electrode (Intraparticle)

1 Right-click **Definitions** and choose **Variables**.

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

3 Locate the **Geometric Entity Selection** section. From the **Geometric entity level** list, choose **Domain**.

4 Select Domain 3 only.

5 From the **Extra dimension attachment** list, choose **Attached Dimensions 1**.

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

Name	Expression	Unit	Description
theta_P	cH[mol/m^3]/ c_H_max		SOC, positive electrode
particle_diffusive_flux	-D_H*d(cH[mol/ m^3],rxd)		Fickian diffusive flux in positive electrode

Positive Electrode (Particle Surface)

1 Right-click **Definitions** and choose **Variables**.

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

3 Locate the **Geometric Entity Selection** section. From the **Geometric entity level** list, choose **Domain**.

4 Select Domain 3 only.

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

Name	Expression	Unit	Description
cH_surf	xdim1.xdsurfop(cH)[mol/m^3]		Particle surface H concentration, positive electrode
cH_average	xdim1.xdintopDomain(rxd* cH[mol/m^3])/ xdim1.xdintopDomain(rxd)		Average H concentration, positive electrode
soc_average	cH_average/c_H_max		Average SOC, positive electrode

At this point, all the entries are shown in yellow since further settings are needed to fully define the variables.

Define three operators: one for the positive electrode current collector, one for positive electrode averages, and one for negative electrode averages.

Integration Operator for Positive Electrode Current Collector

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

2 In the **Settings** window for **Integration**, type `Integration Operator for Positive Electrode Current Collector` in the **Label** text field.

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

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

5 Select Boundary 4 only.

Positive Electrode Average Operator

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

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

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

4 Select Domain 3 only.

Negative Electrode Average Operator

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

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

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

4 Select Domain 1 only.

The next step is to set up the description of the chemical processes inside the battery. Begin with the **Battery with Binary Electrolyte** interface.

BATTERY WITH BINARY ELECTROLYTE (BATBE)

By default, the **Battery with Binary Electrolyte** interface assumes a KOH binary electrolyte, so the default values for the **Species** section will be kept. However, properties for the KOH electrolyte for the porous electrodes and separator need to be specified. These are available in the **Material Library**.

ADD MATERIAL

1 In the **Home** toolbar, click **Add Material** to open the **Add Material** window.

2 Go to the **Add Material** window.

3 In the tree, select **Battery>Electrolytes>KOH (Liquid)**.

4 Click **Add to Component** in the window toolbar.

5 In the **Home** toolbar, click **Add Material** to close the **Add Material** window.

Initial Values 1

1 In the **Model Builder** window, under **Component 1 (comp1)> Battery with Binary Electrolyte (batbe)** click **Initial Values 1**.

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

3 In the *cl* text field, type `cl_init`.

Continue by setting up the description for the Ni (positive) electrode.

Porous Electrode: Ni (Positive)

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

2 In the **Settings** window for **Porous Electrode**, type `Porous Electrode: Ni (Positive)` in the **Label** text field.

3 Select Domain 3 only.

4 Locate the **Electrode Properties** section. From the σ_s list, choose **User defined**. In the associated text field, type `sigma_electrode`.

5 Locate the **Particle Properties** section. From the list, choose **Nonintercalating particles**.

6 Locate the **Porous Matrix Properties** section. In the ε_s text field, type `epss`.

7 In the ε_l text field, type `epsilon0_P-epss`.

8 Locate the **Effective Transport Parameter Correction** section. From the **Electrical conductivity** list, choose **No correction**.

Set up the intercalation process for protons at the Ni electrode.

Porous Electrode Reaction: NiOOH + H2O + e- <=> Ni(OH)2 + OH-

1 In the **Model Builder** window, under **Component 1 (comp1)> Battery with Binary Electrolyte (batbe)>Porous Electrode: Ni (Positive)** click **Porous Electrode Reaction 1**.

2 In the **Settings** window for **Porous Electrode Reaction**, type `Porous Electrode Reaction: NiOOH + H2O + e- <=> Ni(OH)2 + OH-` in the **Label** text field.

3 Locate the **Equilibrium Potential** section. From the E_{eq} list, choose **Nernst equation**.

4 In the $E_{eq,ref}(T)$ text field, type `E_ref_pos`.

5 In the C_R text field, type `(cl/c_ref)*(cH_surf/c_H_ref)`.

6 In the C_O text field, type `(c_H_max-cH_surf)/(c_H_max-c_H_ref)`.

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 $i_{0,\mathrm{ref}}(T)$ text field, type `i0_1_ref`.

10 In the α_a text field, type `alpha_a_1`.

11 Locate the **Active Specific Surface Area** section. From the **Active specific surface area** list, choose **User defined**. In the a_v text field, type `a_Ni`.

12 Click to expand the **Heat of Reaction** section. From the list, choose **User defined**.

Add the OER/ORR reaction on the Ni electrode. The mass transport of oxygen inside the battery cell will be set up later.

Porous Electrode: Ni (Positive)

In the **Model Builder** window, click **Porous Electrode: Ni (Positive)**.

Porous Electrode Reaction: 1/2 O2 + H2O + 2e- <=> 2 OH-

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

2 In the **Settings** window for **Porous Electrode Reaction**, type `Porous Electrode Reaction: 1/2 O2 + H2O + 2e- <=> 2 OH-` in the **Label** text field.

3 Locate the **Equilibrium Potential** section. From the E_{eq} list, choose **Nernst equation**.

4 In the $E_{\mathrm{eq,ref}}(T)$ text field, type `E_ref_OER`.

5 In the C_{R} text field, type `1`.

6 In the C_{O} text field, type `c_O2/c_O2_ref`.

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**.

Use a `max()` operator to numerically stabilize the kinetics expression.

9 In the $i_{0,\mathrm{ref}}(T)$ text field, type `i0_2_ref*max(cl/c_ref,1e-20)^2`.

10 In the α_a text field, type `alpha_a_2`.

11 Locate the **Active Specific Surface Area** section. From the **Active specific surface area** list, choose **User defined**. In the a_v text field, type `a_Ni`.

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

13 Locate the **Heat of Reaction** section. From the list, choose **User defined**. Set up the diffusion of protons inside the positive electrode. Add one weak expression for the diffusive flux and one weak expression for the boundary flux due to the NiOOH/Ni(OH)2 electrode reaction.

14 Click the **Show More Options** button in the **Model Builder** toolbar.

15 In the **Show More Options** dialog box, select **Physics>Stabilization** in the tree.

16 In the tree, select the check box for the node **Physics>Stabilization**.

17 In the tree, select **Physics>Stabilization**.

18 In the tree, clear the check box for the node **Physics>Stabilization**.

19 In the tree, select **Physics>Equation-Based Contributions**.

20 In the tree, select the check box for the node **Physics>Equation-Based Contributions**.

21 Click **OK**.

H+ Diffusion Inside Positive Electrode

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

2 In the **Settings** window for **Weak Contribution**, type `H+ Diffusion Inside Positive Electrode` in the **Label** text field.

3 Select Domain 3 only.

4 Locate the **Domain Selection** section. From the **Extra dimension attachment** list, choose **Attached Dimensions 1**.

5 Click to select the **Activate Selection** toggle button.

6 Select Domain 1 only.

7 Locate the **Weak Contribution** section. In the **Weak expression** text field, type `2*pi*rxd*(particle_diffusive_flux*test(cHrxd)-cHt*test(cH))`.

Intraparticle H+ Concentration

1 In the **Physics** toolbar, click **Attributes** and choose **Auxiliary Dependent Variable**.

2 In the **Settings** window for **Auxiliary Dependent Variable**, type `Intraparticle H+ Concentration` in the **Label** text field.

3 Locate the **Domain Selection** section. From the **Extra dimension attachment** list, choose **Attached Dimensions 1**.

4 Click to select the **Activate Selection** toggle button.

5 Select Domain 1 only.

6 Locate the **Auxiliary Dependent Variable** section. In the **Field variable name** text field, type `cH`.

7 In the **Initial value** text field, type `c_H_init`.

Boundary Condition for Concentration at Particle Outer Surface

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

2 In the **Settings** window for **Weak Contribution**, type `Boundary Condition for Concentration at Particle Outer Surface` in the **Label** text field.

3 Select Domain 3 only.

4 Locate the **Domain Selection** section. From the **Extra dimension attachment** list, choose **Attached Dimensions 1**.

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

6 Select Boundary 2 only.

7 Locate the **Weak Contribution** section. In the **Weak expression** text field, type `-2*batbe.pce1.per1.iloc*test(cH)*pi*rxd/(1[m]*F_const)`.

Boundary Condition for Concentration at Particle Outer Surface, H+ Diffusion Inside Positive Electrode

1 In the **Model Builder** window, under **Component 1 (comp1)>Battery with Binary Electrolyte (batbe)**, Ctrl-click to select **H+ Diffusion Inside Positive Electrode** and **Boundary Condition for Concentration at Particle Outer Surface**.

2 Right-click and choose **Group**.

Intraparticle Diffusion of H+

1 In the **Model Builder** window, right-click **Group 1** and choose **Rename**.

2 In the **Rename Group** dialog box, type `Intraparticle Diffusion of H+` in the **New label** text field.

3 Click **OK**.

Continue by defining the separator and the Cd (negative) electrode.

Separator 1

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

2 Select Domain 2 only.

3 In the **Settings** window for **Separator**, locate the **Porous Matrix Properties** section.

4 In the ε_1 text field, type `epsilon_2`.

Porous Electrode: Cd (Negative)

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

2 In the **Settings** window for **Porous Electrode**, type `Porous Electrode: Cd (Negative)` in the **Label** text field.

3 Select Domain 1 only.

4 Locate the **Electrode Properties** section. From the σ_s list, choose **User defined**. In the associated text field, type `sigma_electrode`.

5 Locate the **Particle Properties** section. From the list, choose **Nonintercalating particles**.

6 Locate the **Porous Matrix Properties** section. In the ε_s text field, type `1-epsilon_3_init`.

7 In the ε_l text field, type `epsilon_3_init`.

8 Locate the **Effective Transport Parameter Correction** section. From the **Electrical conductivity** list, choose **No correction**.

9 Click to expand the **Dissolving-Depositing Species** section. Click + **Add**.

10 In the table, enter the following settings:

Species	Density (kg/m^3)	Molar mass (kg/mol)
Cd	rho_Cd	M_Cd

11 Click + **Add**.

12 In the table, enter the following settings:

Species	Density (kg/m^3)	Molar mass (kg/mol)
CdO2H2	rho_CdO2H2	M_CdO2H2

Porous Electrode Reaction: Cd + 2 OH- <=> Cd(OH)2 + 2e-

1 In the **Model Builder** window, under **Component 1 (comp1)>Battery with Binary Electrolyte (batbe)>Porous Electrode: Cd (Negative)** click **Porous Electrode Reaction 1**.

2 In the **Settings** window for **Porous Electrode Reaction**, type `Porous Electrode Reaction: Cd + 2 OH- <=> Cd(OH)2 + 2e-` in the **Label** text field.

3 Locate the **Equilibrium Potential** section. From the E_{eq} list, choose **Nernst equation**.

4 In the $E_{eq,ref}(T)$ text field, type `E_ref_neg`.

5 In the C_R text field, type `(cl/c_ref)^2`.

6 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Butler-Volmer**.

7 From the **Exchange current density type** list, choose **From Nernst Equation**.

8 In the $i_{0,ref}(T)$ text field, type `theta_N*i0_3_ref`.

9 In the α_a text field, type `alpha_a_3`.

10 Locate the **Active Specific Surface Area** section. From the **Active specific surface area** list, choose **User defined**. In the a_v text field, type `a_Cd`.

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

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

Species	Stoichiometric coefficient (1)
Cd	1
CdO2H2	-1

13 Locate the **Heat of Reaction** section. From the list, choose **User defined**.

The oxygen reduction reaction is mass-transport limited at the Cd electrode. Model it using an **Internal Electrode Surface**, with the local current density being given by an oxygen flux at the Cd electrode. In turn, the flux will be obtained from a **Transport of Diluted Species** interface, where the diffusion of oxygen in the battery is also modeled.

Oxygen Recombination at Cd Electrode

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

2 In the **Settings** window for **Internal Electrode Surface**, type `Oxygen Recombination at Cd Electrode` in the **Label** text field.

3 Select Boundary 2 only.

Electrode Reaction: 1/2 O2 + H2O + 2e- <=> 2 OH-

1 In the **Model Builder** window, under **Component 1 (comp1)>Battery with Binary Electrolyte (batbe)>Oxygen Recombination at Cd Electrode** click **Electrode Reaction 1**.

2 In the **Settings** window for **Electrode Reaction**, type `Electrode Reaction: 1/2 O2 + H2O + 2e- <=> 2 OH-` in the **Label** text field.

3 Locate the **Equilibrium Potential** section. From the E_{eq} list, choose **User defined**. Locate the **Electrode Kinetics** section. From the $i_{\mathrm{loc,expr}}$ list, choose **User defined**. In the associated text field, type `tds.tflux_c_O2x*4*F_const`.

4 Click to expand the **Heat of Reaction** section. From the list, choose **User defined**.

Define the boundary conditions for the battery cell.

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 4 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 $i_{\text{s,average}}$ text field, type `sign*i_app`.

Set up the description of the oxygen transport and reaction.

ADD PHYSICS

1 In the **Physics** toolbar, click **Add Physics** to open the **Add Physics** window.

2 Go to the **Add Physics** window.

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

4 Click **Add to Component 1** in the window toolbar.

5 In the **Physics** toolbar, click **Add Physics** to close the **Add Physics** window.

TRANSPORT OF DILUTED SPECIES (TDS)

1 In the **Settings** window for **Transport of Diluted Species**, locate the **Transport Mechanisms** section.

2 Clear the **Convection** check box.

3 Select the **Mass transfer in porous media** check box.

4 Click to expand the **Dependent Variables** section. In the **Concentrations** table, enter the following settings:

c_O2

5 Select Domains 2 and 3 only.

Transport Properties 1

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

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

3 In the D_{cO2} text field, type `D_O2`.

Initial Values 1

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

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

3 In the c_{O2} text field, type `c_O2_init`.

Porous Electrode Coupling: Positive Electrode

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

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

3 Select Domain 3 only.

Reaction Coefficients 1

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

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

3 From the i_v list, choose **Local current source, Porous Electrode Reaction: 1/2 O2 + H2O + 2e- <=> 2 OH- (batbe/pce1/per2)**.

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

5 In the ν_{cO2} text field, type `-1`.

Oxygen Recombination at Cd Electrode

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

2 In the **Settings** window for **Concentration**, type `Oxygen Recombination at Cd Electrode` in the **Label** text field.

3 Select Boundary 2 only.

4 Locate the **Concentration** section. Select the **Species c_O2** check box.

Initial Values 2

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

Add a suitable initial value for the oxygen concentration in the separator.

2 Select Domain 2 only.

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

4 In the c_{O2} text field, type `c_O2_init*((x-l_neg)/l_sep)`.

The battery model, including the oxygen transport and reaction, has now been set up. Now, configure the study to simulate both discharging, and charging, of the battery.

DISCHARGE AND CHARGE

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

2 In the **Settings** window for **Study**, type `Discharge and Charge` in the **Label** text field.

Parametric Sweep

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

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

3 From the **Sweep type** list, choose **Parameter switch**.

4 Click + **Add**.

5 In the table, enter the following settings:

Switch	Cases	Case numbers
Charge/Discharge Cases	All	range(1,1,2)

6 Click + **Add**.

7 In the table, enter the following settings:

Switch	Cases	Case numbers
C-rate Cases	All	range(1,1,3)

Current Distribution Initialization: Primary

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

2 In the **Settings** window for **Current Distribution Initialization**, type `Current Distribution Initialization: Primary` in the **Label** text field.

Current Distribution Initialization: Secondary

1 In the **Study** toolbar, click **Study Steps** and choose **Other> Current Distribution Initialization**.

2 Right-click **Discharge and Charge>Step 3: Current Distribution Initialization 2** and choose **Move Up**.

3 In the **Settings** window for **Current Distribution Initialization**, type `Current Distribution Initialization: Secondary` in the **Label** text field.

Use an additional **Current Distribution Initialization** step, solving for a secondary current distribution, to improve the initial guess further.

4 Locate the **Study Settings** section. From the **Current distribution type** list, choose **Secondary**.

Step 3: Time Dependent

1 In the **Model Builder** window, click **Step 3: 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 **Output times** text field, type `range(0,t_charge_limit/100, t_charge_limit)`.

Before starting to solve, to make convergence easier to achieve, manually set the scaling for the oxygen concentration, and the proton concentration in the extra dimension. The corresponding reference concentrations are suitable values for scaling.

Solution 1 (sol1)

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

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

3 In the **Model Builder** window, expand the **Discharge and Charge>Solver Configurations> Solution 1 (sol1)>Dependent Variables 3** node, then click **Concentration (comp1.c_O2)**.

4 In the **Settings** window for **Field**, locate the **Scaling** section.

5 From the **Method** list, choose **Manual**.

6 In the **Scale** text field, type `c_O2_ref`.

7 In the **Model Builder** window, under **Discharge and Charge>Solver Configurations> Solution 1 (sol1)>Dependent Variables 3** click **Auxiliary dependent variable cH (comp1.cH)**.

8 In the **Settings** window for **Field**, click to collapse the **Scaling** section.

9 Click to expand the **Scaling** section. From the **Method** list, choose **Manual**.

10 In the **Scale** text field, type `c_H_ref`.

Additionally, set up two **Stop** conditions, signaling the solver to stop if the cell voltage gets below 0.8 V or above 1.6 V.

11 In the **Model Builder** window, under **Discharge and Charge>Solver Configurations> Solution 1 (sol1)** right-click **Time-Dependent Solver 1** and choose **Stop Condition**.

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

13 Click **Add**.

14 In the table, enter the following settings:

Stop expression	Stop if	Active	Description
`comp1.intop_posCC(comp1.phis)<0.8`	True (>=1)	√	`Stop expression 1`

15 Click **Add**.

16 In the table, enter the following settings:

Stop expression	Stop if	Active	Description
`comp1.intop_posCC(comp1.phis)>1.6`	True (>=1)	√	`Stop expression 2`

Store the solution just after the stop condition to include the data at the lowest and highest voltages reached in the results.

17 Locate the **Output at Stop** section. From the **Add solution** list, choose **Step after stop**.

Now, run the study for discharge and charge of the battery.

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

RESULTS

Discharge: Boundary Electrode Potential with Respect to Ground (batbe)

Plot the cell voltage for discharge at the three different C-rates.

1 In the **Settings** window for **1D Plot Group**, type `Discharge: Boundary Electrode Potential with Respect to Ground (batbe)` in the **Label** text field.

2 Locate the **Data** section. From the **Parameter selection (c_H_init, epsilon_3_init, sign, C_rate)** list, choose **From list**.

3 In the **Parameter values** list, choose **1: c_H_init=104.2, epsilon_3_init=0.6365, sign=-1, C_rate=0.1**, **2: c_H_init=104.2, epsilon_3_init=0.6365, sign=-1, C_rate=0.47619**, and **3: c_H_init=104.2, epsilon_3_init=0.6365, sign=-1, C_rate=1.4286**.

4 In the **Discharge: Boundary Electrode Potential with Respect to Ground (batbe)** toolbar, click **Plot**.

Global 1

1 In the **Model Builder** window, expand the **Discharge: Boundary Electrode Potential with Respect to Ground (batbe)** 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 **Inner solutions**.

4 From the **Parameter** list, choose **Expression**.

5 In the **Expression** text field, type `t`.

6 From the **Unit** list, choose **h**.

7 Click to expand the **Legends** section. From the **Legends** list, choose **Evaluated**.

8 In the **Legend** text field, type `C/eval(1/C_rate)`.

Discharge: Boundary Electrode Potential with Respect to Ground (batbe)

1 In the **Model Builder** window, click **Discharge: Boundary Electrode Potential with Respect to Ground (batbe)**.

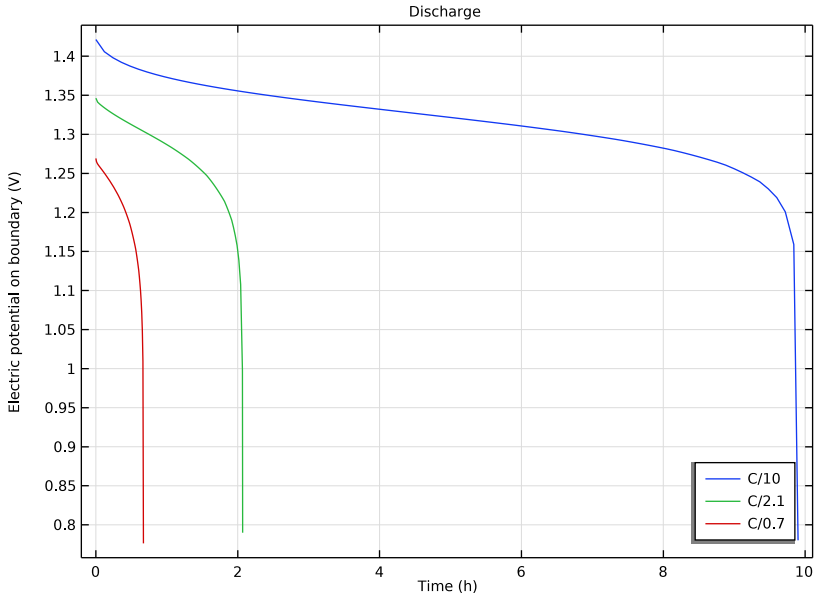
2 In the **Settings** window for **1D Plot Group**, click to expand the **Title** section.

3 From the **Title type** list, choose **Manual**.

4 In the **Title** text area, type `Discharge`.

5 Locate the **Legend** section. From the **Position** list, choose **Lower right**.

6 In the **Discharge: Boundary Electrode Potential with Respect to Ground (batbe)** toolbar, click **Plot**.



Plot the cell voltage for charging. Then, plot the average positive electrode hydration level (SOC) and the average negative electrode volume fraction (SOC).

Charge: Boundary Electrode Potential with Respect to Ground (batbe)

1 Right-click **Discharge: Boundary Electrode Potential with Respect to Ground (batbe)** and choose **Duplicate**.

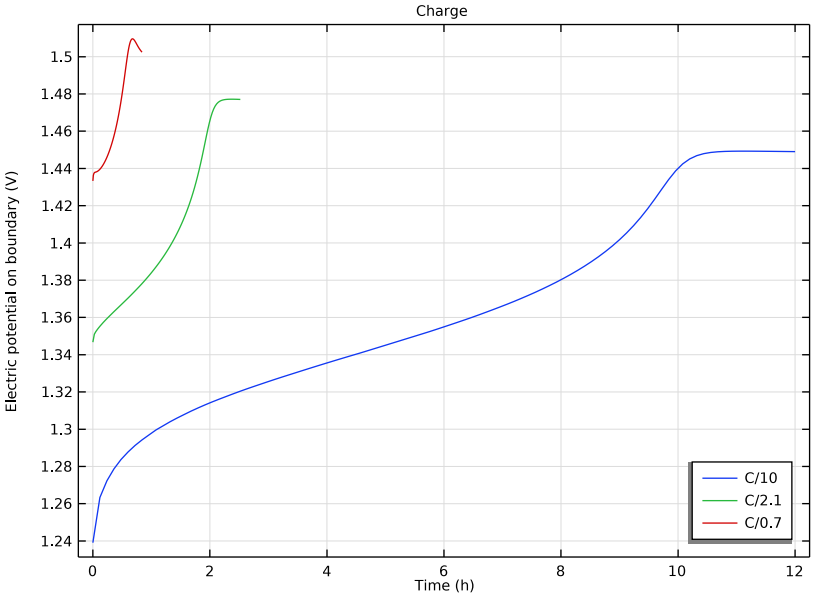
2 In the **Settings** window for **1D Plot Group**, type `Charge: Boundary Electrode Potential with Respect to Ground (batbe)` in the **Label** text field.

3 Locate the **Data** section. In the **Parameter values** list, choose **4: c_H_init=52098, epsilon_3_init=0.46587, sign=1, C_rate=0.1**, **5: c_H_init=52098, epsilon_3_init=0.46587,**

sign=1, C_rate=0.47619, and **6: c_H_init=52098, epsilon_3_init=0.46587, sign=1, C_rate=1.4286**.

4 Locate the **Title** section. In the **Title** text area, type `Charge`.

5 In the **Charge: Boundary Electrode Potential with Respect to Ground (batbe)** toolbar, click **Plot**.



Charge: Average Positive Electrode Hydration Level

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

2 In the **Settings** window for **1D Plot Group**, type `Charge: Average Positive Electrode Hydration Level` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Discharge and Charge/ Parametric Solutions 1 (sol4)**.

4 From the **Parameter selection (c_H_init, epsilon_3_init, sign, C_rate)** list, choose **From list**.

5 In the **Parameter values** list, choose **4: c_H_init=52098, epsilon_3_init=0.46587, sign=1, C_rate=0.1**, **5: c_H_init=52098, epsilon_3_init=0.46587, sign=1, C_rate=0.47619**, and **6: c_H_init=52098, epsilon_3_init=0.46587, sign=1, C_rate=1.4286**.

6 Locate the **Title** section. From the **Title type** list, choose **Manual**.

7 In the **Title** text area, type `Average Positive Electrode Hydration Level`.

Global 1

1 Right-click **Charge: Average Positive Electrode Hydration Level** and choose **Global**.

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

3 In the table, enter the following settings:

Expression	Unit	Description
`comp1.ave_pos(cH_average/c_H_max)`	1	`Average Hydration Level`

4 Locate the **x-Axis Data** section. From the **Parameter** list, choose **Expression**.

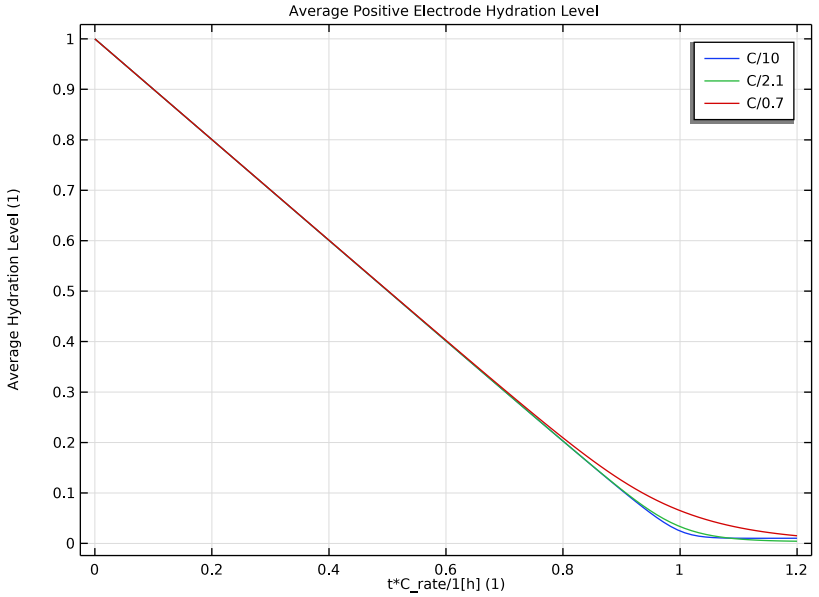
Normalize the time by the C-rate to enable comparing hydration levels for increasing C-rates.

5 In the **Expression** text field, type `t*C_rate/1[h]`.

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

7 In the **Legend** text field, type `C/eval(1/C_rate)`.

8 In the **Charge: Average Positive Electrode Hydration Level** toolbar, click **Plot**.



Charge: Average Negative Electrode Volume Fraction

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

2 In the **Settings** window for **1D Plot Group**, type `Charge: Average Negative Electrode Volume Fraction` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Discharge and Charge/ Parametric Solutions 1 (sol4)**.

4 From the **Parameter selection (c_H_init, epsilon_3_init, sign, C_rate)** list, choose **From list**.

5 In the **Parameter values** list, choose **4: c_H_init=52098, epsilon_3_init=0.46587, sign=1, C_rate=0.1**, **5: c_H_init=52098, epsilon_3_init=0.46587, sign=1, C_rate=0.47619**, and **6: c_H_init=52098, epsilon_3_init=0.46587, sign=1, C_rate=1.4286**.

6 In the **Charge: Average Negative Electrode Volume Fraction** toolbar, click **Plot**.

7 Locate the **Title** section. From the **Title type** list, choose **Manual**.

8 In the **Title** text area, type `Average Negative Electrode Volume Fraction`.

Global 1

1 Right-click **Charge: Average Negative Electrode Volume Fraction** and choose **Global**.

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

3 In the table, enter the following settings:

Expression	Unit	Description
`comp1.ave_neg(batbe.epss)`	1	`Average volume fraction`

4 Locate the **x-Axis Data** section. From the **Parameter** list, choose **Expression**.

5 In the **Expression** text field, type `t*C_rate/1[h]`.

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

7 In the **Legend** text field, type `C/eval(1/C_rate)`.

8 In the **Charge: Average Negative Electrode Volume Fraction** toolbar, click **Plot**.