



Model created in COMSOL Multiphysics 6.4

1D Isothermal Nickel-Metal Hydride Battery

Introduction

This example simulates the discharge of a nickel–metal hydride (Ni–MH) battery using the Battery with Binary Electrolyte interface. The geometry is in one dimension and the model is isothermal. The model serves as an introduction to Ni–MH modeling, and can be further extended to include various side reactions. The model is based on a study by Paxton and Newman (Ref. 1), with updated equilibrium potentials from a more recent study by Albertus and others (Ref. 2).

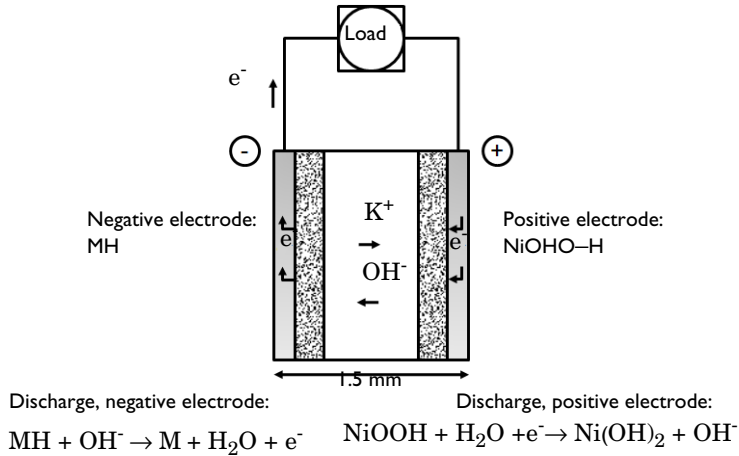


Figure 1: Cross section of a NiMH battery showing the main electrochemical processes that occur during discharge.

The 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 spherical particles that form the electrodes
- Butler–Volmer electrode kinetics using experimentally measured discharge curves for the equilibrium potential.

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 (metal hydride): 350 μm
- Separator (electrolyte): 250 μm
- Positive porous electrode (nickel oxide): 843 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 terms. 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 and corresponds to a packed bed of spherical particles. The diffusion coefficient for the electrolyte salt is corrected for the tortuosity and the porosity in a similar manner.

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. 1).

Fickian diffusion describes the transport in the spherical particles. The diffusion equation is expressed in spherical coordinates for the material balance of intercalated hydrogen atoms 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 to a constant discharge current density. 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 NiMH. The electrolyte is KOH, diluted in water to a 30% (wt) solution. The active electrode materials are a metal hydride (LaNi_5H_x) for the negative electrode and a nickel oxide (NiOHOH_y) for the positive electrode.

The equilibrium potential of the negative and positive electrodes are composition dependent through experimentally measured data. This data is tabulated in interpolation functions in the model and the properties vary significantly during charge and discharge due to the changes in composition.

The model uses constant values for the electrolyte conductivity, the electrolyte diffusivity, and the activity variation with concentration in the electrolyte. The activity coefficients are assumed to be constant in the electrode reactions. For more accurate simulations you can use concentration-dependent expressions for these properties ([Ref. 1](#)).

Figure 2 displays the equilibrium potentials for the negative and positive electrodes as functions of the measured state of charge (SOC).

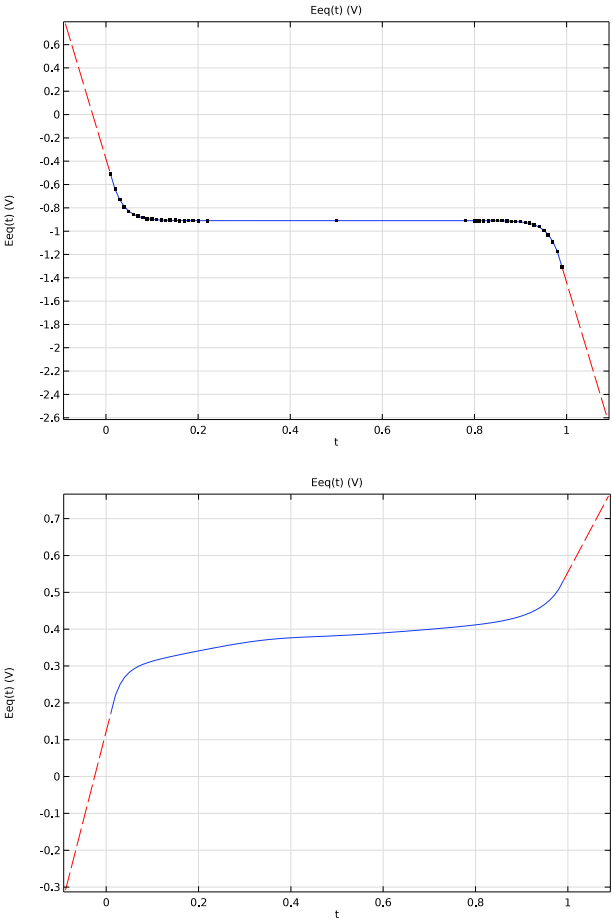


Figure 2: The equilibrium voltage of the electrode materials.

The initial concentration values within the electrode particles are set to correspond to a fully charged battery.

For complete details on the material properties and constants, see Ref. 1.

DISCHARGE CURVES

The battery is initially at a fully charged state. Discharges at two different current densities are simulated and displayed in the figure below. The model defines end-of-discharge as the time when the cell voltage drops below 0.99 V. The nominal discharge current density, corresponding to case 1C below (a current density corresponding to a theoretical full discharge in one hour), is 430 A/m^2 .

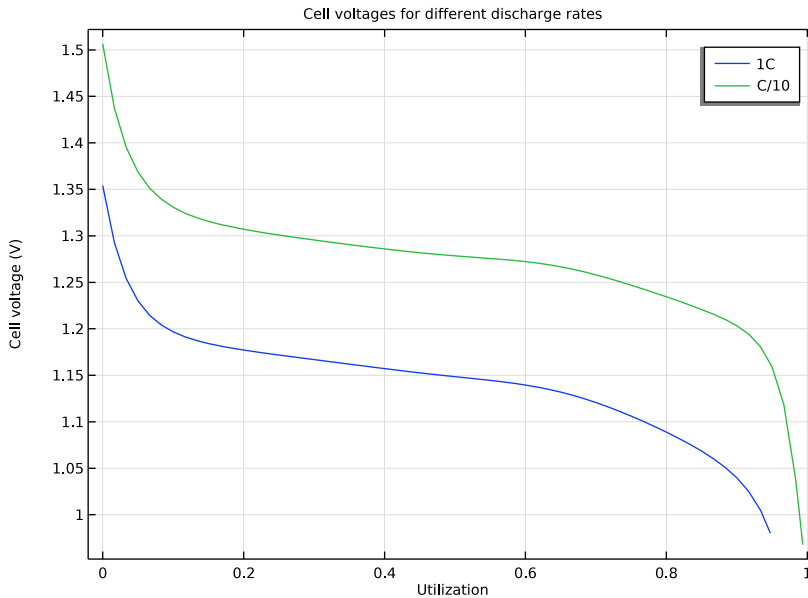


Figure 3: Discharge curves for various discharge rates.

Figure 3 shows that the maximum discharge capacity of 430 Ah/m^2 is obtained for the current density of 43 A/m^2 (0.1C). It can also be seen that the discharge capacity decreases slightly when applying a 1C discharge current. At 1C, the battery delivers approximately 90% of the theoretical capacity before it reaches a cell voltage of 1 V.

At the beginning of the discharge, the voltage is higher than what is normally seen in a NiMH battery. The reason is the absence of side reactions in the model (Ref. 2), specifically the oxygen evolution/reduction side-reaction. The high voltage on the positive electrode results in a self-discharge process in which oxygen is evolved on the positive electrode and transported over to the negative electrode where it is reduced.

The discharge curves are similar to those presented in [Ref. 1](#), with slight deviation due to different sources of experimental data for the equilibrium potentials.

ANALYSIS OF VOLTAGE LOSSES

It is possible to visualize the contributions of the different losses to the total overpotential. You can compare the contribution from the activation overpotential and the electrolyte potential by plotting the electrolyte potential with a bias of 0.91 V as shown in [Figure 4](#). In this way the two plots are within a similar potential range.

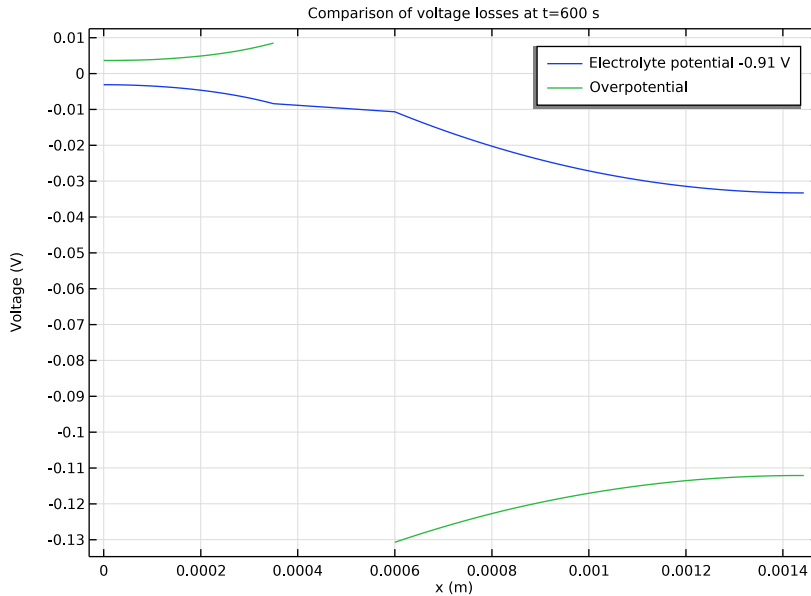


Figure 4: Voltage losses in the battery during discharge.

The overpotential at the positive electrode is the largest contributor to the potential losses during a 1C discharge. The figure does not include the electronic potential profile in the solid phase, but the simulations show that contributions from the ohmic losses in the electronic conductors are negligible.

To further investigate the reason for the steep voltage decrease, you can plot the concentration profile in the electrolyte. Figure 5 depicts the profile at several stages during the discharge of the cell.

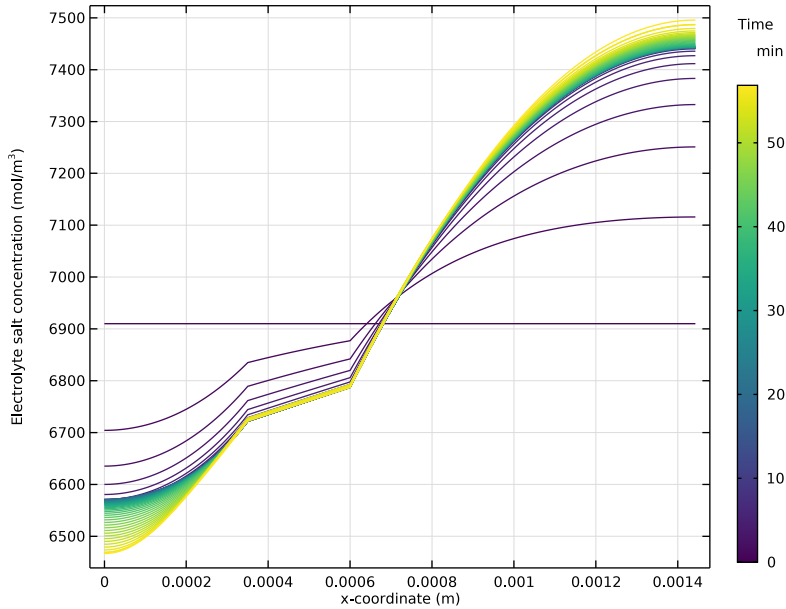


Figure 5: Electrolyte-phase concentration profiles at various times.

The concentration gradients are quite low and the cell experiences only minor concentration polarization due to electrolyte transport limitations.

Figure 6 shows that the local current density distribution varies during discharge. Initially it is evenly distributed, but toward the end of the discharge more of the current is

produced closer to the current collectors. This effect is more pronounced for the negative electrode.

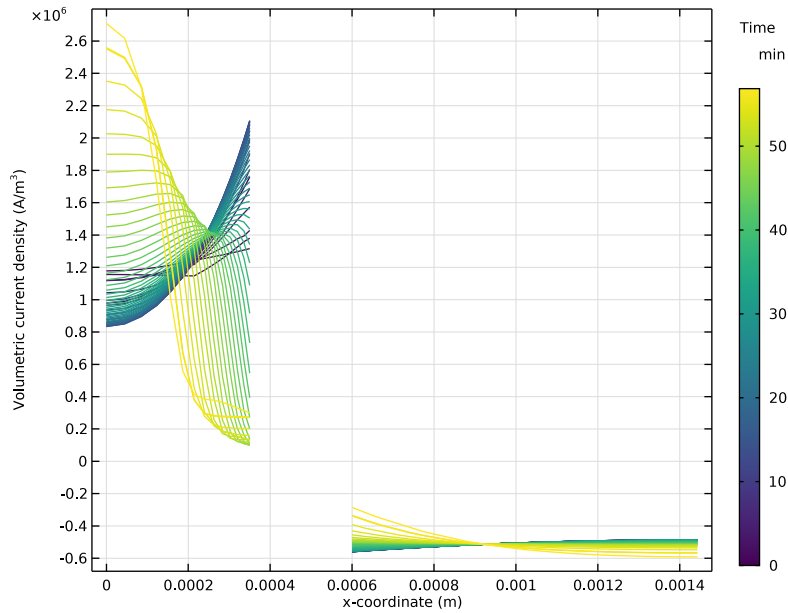


Figure 6: Local current-density distribution within the battery at various stages during the discharge.

The current density is related to the concentration in the solid phase at the surface of the particles. [Figure 7](#) depicts the distribution of the concentration in the solid-phase particles. At the end of discharge most of the concentration of intercalating material is depleted close

to the separator at the negative electrode. This explains the lower current densities in this region of the battery, as was shown in [Figure 6](#).

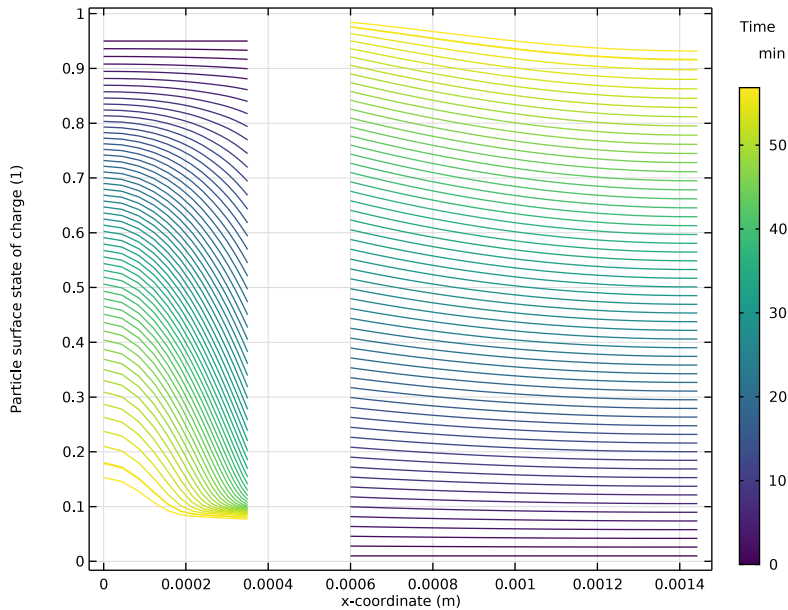


Figure 7: Concentration distribution of intercalated hydrogen in the solid particles during the discharge phase.

As the surface concentration changes, the equilibrium voltage also varies, causing a lower reaction overpotential and a decrease in the local current density. This effect tends to even out the local charge transfer current density to some extent but results in a larger overall voltage loss in the battery.

The difference between the concentration at the surface and at the center of the particles is small throughout the discharge cycle, indicating that the transport of intercalated material within the active particles is not a limiting factor for the performance of the battery at this discharge current density.

References

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1. B. Paxton and J. Newman, “Modeling of Nickel/Metal Hydride Batteries,” *J. Electrochem. Soc.*, vol. 144, no. 11, pp. 3818–3831, 1997.


2. P. Albertus, J. Christensen, and J. Newman, “Modeling Side Reactions and Nonisothermal Effects in Nickel Metal-Hydride Batteries,” *J. Electrochem. Soc.*, vol. 155, no. 1, pp. A48–A60, 2008.

Application Library path: Battery_Design_Module/Batteries,_General/nimh_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  **ID**.
- 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

Parameters 1

- 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 `nimh_battery_1d_parameters.txt`.

GEOMETRY I

Interval I (il)

- 1 In the **Model Builder** window, under **Component I (comp1)** right-click **Geometry I** 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_sep
L_pos

- 5 In the **Home** toolbar, click  **Build All**.


DEFINITIONS

Load the variables for this model from a text file.

Variables I

- 1 In the **Definitions** toolbar, click  **Local Variables**.
- 2 In the **Settings** window for **Variables**, locate the **Variables** section.
- 3 Click  **Load from File**.
- 4 Browse to the model's Application Libraries folder and double-click the file `nimh_battery_1d_variables.txt`.

Integration I (intop1)


- 1 In the **Definitions** toolbar, click  **Nonlocal Couplings** and choose **Integration**.
- 2 In the **Settings** window for **Integration**, locate the **Source Selection** section.
- 3 From the **Geometric entity level** list, choose **Boundary**.
- 4 Select Boundary 4 only.
- 5 In the **Operator name** text field, type `PositiveCC`.

MATERIALS

Load the materials from the material library.

ADD MATERIAL

- 1 In the **Materials** 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 Right-click and choose **Add to Component 1 (comp1)**.
- 5 In the tree, select **Battery > Electrodes > HxLiN5 (Negative, NiMH Battery)**.
- 6 Click the **Add to Component** button in the window toolbar.
- 7 In the tree, select **Battery > Electrodes > NiOHO-Hx (Positive discharge, NiMH Battery)**.
- 8 Click the **Add to Component** button in the window toolbar.
- 9 In the **Materials** toolbar, click  **Add Material** to close the **Add Material** window.


BATTERY WITH BINARY ELECTROLYTE (BATBE)

- 1 In the **Settings** window for **Battery with Binary Electrolyte**, locate the **Species** section.
- 2 In the M_{An-} text field, type M_{OH} .
- 3 In the M_{Cat+} text field, type M_K .
- 4 In the M_0 text field, type M_{H2O} .

Separator 1

- 1 In the **Model Builder** window, under **Component 1 (comp1) > Battery with Binary Electrolyte (batbe)** click **Separator 1**.
- 2 In the **Settings** window for **Separator**, locate the **Porous Matrix Properties** section.
- 3 In the ϵ_1 text field, type 1.

Porous Electrode 1

- 1 In the **Physics** toolbar, click  **Domains** and choose **Porous Electrode**.
- 2 Select Domain 1 only.
- 3 In the **Settings** window for **Porous Electrode**, locate the **Electrode Properties** section.
- 4 In the σ_s text field, type sigmas_neg .
- 5 Locate the **Porous Matrix Properties** section. In the ϵ_s text field, type eps_s_neg .
- 6 In the ϵ_1 text field, type eps_1_neg .


Particle Intercalation 1

- 1 In the **Model Builder** window, click **Particle Intercalation 1**.
- 2 In the **Settings** window for **Particle Intercalation**, locate the **Material** section.
- 3 From the **Particle material** list, choose **HxLiN5 (Negative, NiMH Battery) (mat2)**.
- 4 Locate the **Species Settings** section. In the $c_{s,init}$ text field, type cs_init_neg .
- 5 Locate the **Particle Transport Properties** section. In the r_p text field, type r_neg .

Porous Electrode Reaction 1

- 1 In the **Model Builder** window, click **Porous Electrode Reaction 1**.
- 2 In the **Settings** window for **Porous Electrode Reaction**, locate the **Material** section.
- 3 From the **Material** list, choose **HxLiN5 (Negative, NiMH Battery) (mat2)**.
- 4 Locate the **Electrode Kinetics** section. In the $i_{0,\text{ref}}(T)$ text field, type `i0_ref_neg`.
- 5 In the α_a text field, type `alpha_a_neg`.
- 6 In the α_c text field, type `alpha_c_neg`.
- 7 In the $c_{1,\text{ref}}$ text field, type `c1_ref`.
- 8 In the $c_{0,\text{ref}}$ text field, type `c0_ref`.

Porous Electrode 2

- 1 In the **Physics** toolbar, click  **Domains** and choose **Porous Electrode**.
- 2 Select Domain 3 only.
- 3 In the **Settings** window for **Porous Electrode**, locate the **Electrode Properties** section.
- 4 In the σ_s text field, type `sigmas_pos`.
- 5 Locate the **Porous Matrix Properties** section. In the ϵ_s text field, type `eps_s_pos`.
- 6 In the ϵ_l text field, type `eps_l_pos`.

Particle Intercalation 1

- 1 In the **Model Builder** window, click **Particle Intercalation 1**.
- 2 In the **Settings** window for **Particle Intercalation**, locate the **Material** section.
- 3 From the **Particle material** list, choose **NiOHO-Hx (Positive discharge, NiMH Battery) (mat3)**.
- 4 Locate the **Species Settings** section. In the $c_{s,\text{init}}$ text field, type `cs_init_pos`.
- 5 Locate the **Particle Transport Properties** section. In the r_p text field, type `r_pos`.

Porous Electrode Reaction 1


- 1 In the **Model Builder** window, click **Porous Electrode Reaction 1**.
- 2 In the **Settings** window for **Porous Electrode Reaction**, locate the **Material** section.
- 3 From the **Material** list, choose **NiOHO-Hx (Positive discharge, NiMH Battery) (mat3)**.
- 4 Locate the **Electrode Kinetics** section. In the $i_{0,\text{ref}}(T)$ text field, type `i0_ref_pos`.
- 5 In the α_a text field, type `alpha_a_pos`.
- 6 In the α_c text field, type `alpha_c_pos`.
- 7 In the $c_{1,\text{ref}}$ text field, type `c1_ref`.

8 In the $c_{0,\text{ref}}$ text field, type c_{0_ref} .

Electric Ground 1

- 1 In the **Physics** toolbar, click  **Boundaries** and choose **Electric Ground**.
- 2 Select Boundary 1 only.

Electrode Current Density 1

- 1 In the **Physics** toolbar, click  **Boundaries** and choose **Electrode Current Density**.
- 2 Select Boundary 4 only.
- 3 In the **Settings** window for **Electrode Current Density**, locate the **Electrode Current Density** section.
- 4 In the $i_{n,s}$ text field, type $-C1/10$.

Initial Values 1

Set up the initial value for the electrolyte concentration. The initial values for the potentials, corresponding to the initial state of charge values for the electrodes, will be calculated automatically in the Current Distribution Initialization study step.

- 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_l text field, type c_{l_init} .

GLOBAL DEFINITIONS

Default Model Inputs

Set up the temperature value used in the entire model.

- 1 In the **Model Builder** window, under **Global Definitions** click **Default Model Inputs**.
- 2 In the **Settings** window for **Default Model Inputs**, locate the **Browse Model Inputs** section.
- 3 In the tree, select **General > Temperature (K) - minput.T**.
- 4 Find the **Expression for remaining selection** subsection. In the **Temperature** text field, type T .

STUDY 1


First, set up a solver to solve for the specified discharge rate.

Step 2: Time Dependent

- 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 In the **Output times** text field, type range (0,600,36000).

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 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**.
- 6 In the table, enter the following settings:

Stop expression	Stop if	Active	Description
comp1.PositiveCC(comp1.phis)<0.99	True (>=1)	<input checked="" type="checkbox"/>	Stop expression 1

Specify that the solution is to be stored both before and after the stop condition is reached.

- 7 Locate the **Output at Stop** section. From the **Add solution** list, choose **Steps before and after stop**.
- 8 Clear the **Add information** checkbox.
- 9 In the **Study** toolbar, click  **Compute**.

RESULTS

Follow these instructions to set up the discharge curve plot shown in [Figure 3](#):

Cell voltage

- 1 In the **Settings** window for **ID Plot Group**, type **Cell voltage** in the **Label** text field.
- 2 Click to expand the **Title** section. From the **Title type** list, choose **Manual**.
- 3 In the **Title** text area, type **Cell voltages for different discharge rates**.
- 4 Locate the **Plot Settings** section.
- 5 Select the **x-axis label** checkbox. In the associated text field, type **Utilization**.
- 6 Select the **y-axis label** checkbox. In the associated text field, type **Cell voltage (V)**.
- 7 Locate the **Legend** section. Select the **Show legends** checkbox.

Point Graph 1

- 1 In the **Model Builder** window, expand the **Cell voltage** node, then click **Point Graph 1**.
- 2 In the **Settings** window for **Point Graph**, locate the **x-Axis Data** section.

- 3 From the **Parameter** list, choose **Expression**.
- 4 In the **Expression** text field, type $t/36000$.
- 5 Click to expand the **Legends** section. From the **Legends** list, choose **Manual**.
- 6 In the table, enter the following settings:

Legends

C/10

BATTERY WITH BINARY ELECTROLYTE (BATBE)

Now, modify the current density to study a different discharge rate, and create a new study to compare the results.

Electrode Current Density I

- 1 In the **Model Builder** window, under **Component 1 (comp1)** > **Battery with Binary Electrolyte (batbe)** click **Electrode Current Density I**.
- 2 In the **Settings** window for **Electrode Current Density**, locate the **Electrode Current Density** section.
- 3 In the $i_{n,s}$ text field, type $-C1$.


STUDY 1

Make a copy of the solution and resolve the problem.

Solver Configurations

In the **Study** toolbar, click  **Create Solution Copy**.

Step 2: Time Dependent

- 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 In the **Output times** text field, type range (0, 60, 3600).
- 4 In the **Study** toolbar, click  **Compute**.

RESULTS

Now you can finish the discharge curve plot in [Figure 3](#).

Point Graph 2


In the **Model Builder** window, under **Results** > **Cell voltage** right-click **Point Graph 1** and choose **Duplicate**.

Point Graph 1

- 1 In the **Settings** window for **Point Graph**, locate the **x-Axis Data** section.
- 2 In the **Expression** text field, type $t/3600$.
- 3 Locate the **Legends** section. In the table, enter the following settings:


Legends
1C

Point Graph 2


- 1 In the **Model Builder** window, click **Point Graph 2**.
- 2 In the **Settings** window for **Point Graph**, locate the **Data** section.
- 3 From the **Dataset** list, choose **Study 1/Solution 1 - Copy 1 (sol3)**.
- 4 In the **Cell voltage** toolbar, click  **Plot**.

Average Electrode State of Charge (batbe)

The remaining instructions reproduce, in turn, the plots shown in [Figure 4](#) through [Figure 7](#).

- 1 In the **Model Builder** window, under **Results** click **Average Electrode State of Charge (batbe)**.
- 2 In the **Settings** window for **ID Plot Group**, locate the **Title** section.
- 3 From the **Title type** list, choose **Label**.
- 4 In the **Average Electrode State of Charge (batbe)** toolbar, click  **Plot**.

ID Plot Group 7

- 1 In the **Home** toolbar, click  **Add Plot Group** and choose **ID Plot Group**.
- 2 In the **Settings** window for **ID Plot Group**, locate the **Data** section.
- 3 From the **Time selection** list, choose **From list**.
- 4 In the **Times (s)** list box, select **600**.
- 5 Locate the **Title** section. From the **Title type** list, choose **Manual**.
- 6 In the **Title** text area, type Comparison of voltage losses at $t=600$ s.
- 7 Locate the **Plot Settings** section.
- 8 Select the **x-axis label** checkbox. In the associated text field, type x (m).
- 9 Select the **y-axis label** checkbox. In the associated text field, type Voltage (V).

Line Graph 1

- 1 Right-click **ID Plot Group 7** 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 to expand the **Legends** section. Select the **Show legends** checkbox.
- 5 From the **Legends** list, choose **Manual**.
- 6 In the table, enter the following settings:


Legends
Electrolyte potential -0.91 V

- 7 Locate the **y-Axis Data** section. In the **Expression** text field, type `phi1-0.91`.

Line Graph 2

- 1 In the **Model Builder** window, right-click **ID Plot Group 7** 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 Locate the **y-Axis Data** section. In the **Expression** text field, type `batbe.eta_per1`.
- 5 Locate the **Legends** section. Select the **Show legends** checkbox.
- 6 From the **Legends** list, choose **Manual**.
- 7 In the table, enter the following settings:

Legends
Overpotential

- 8 In the **ID Plot Group 7** toolbar, click  **Plot**.

Voltage losses

- 1 In the **Model Builder** window, under **Results** click **ID Plot Group 7**.
- 2 In the **Settings** window for **ID Plot Group**, type `Voltage losses` in the **Label** text field.