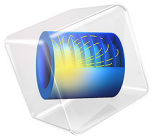


Model created in COMSOL Multiphysics 6.4

Voltage Hysteresis in a Lithium Iron Phosphate (LFP) Electrode

Introduction

Lithium iron phosphate (LFP) is a common positive electrode material in lithium-ion batteries. Specific for the LFP electrode material is that its equilibrium (open circuit) potential, when defined as a function of the lithiation state, features a large flat plateau with a more or less constant potential. The plateau also exhibits voltage hysteresis; that is, a difference in the plateau potential between lithiation and delithiation cycling, also referred to as a zero-current voltage gap.

This tutorial demonstrates a simplified model to include voltage hysteresis in a porous LFP electrode.

Model Definition

ORIGIN OF THE VOLTAGE HYSTERESIS

The voltage hysteresis in an electrode material is commonly attributed (Ref. 1) to a nonmonotonic equilibrium potential (or Gibbs free energy) dependency with respect to the intercalated lithium concentration (state of lithiation). The solid blue line of Figure 1 shows an example of a nonmonotonic equilibrium potential of a single electrode particle as function of the state of lithiation. When lithiation starts in point 1, the equilibrium potential decreases until the inflection point 2 is reached, after which further lithiation results in an increase in potential, until the derivative changes sign again at a second inflection point.

The distance between the two inflection points (the "miscibility" gap) is believed to decrease with the particle size, and the magnitude of the voltage offset between them is also assumed to vary with size (Ref. 2), based on experimental observations (Ref. 3).

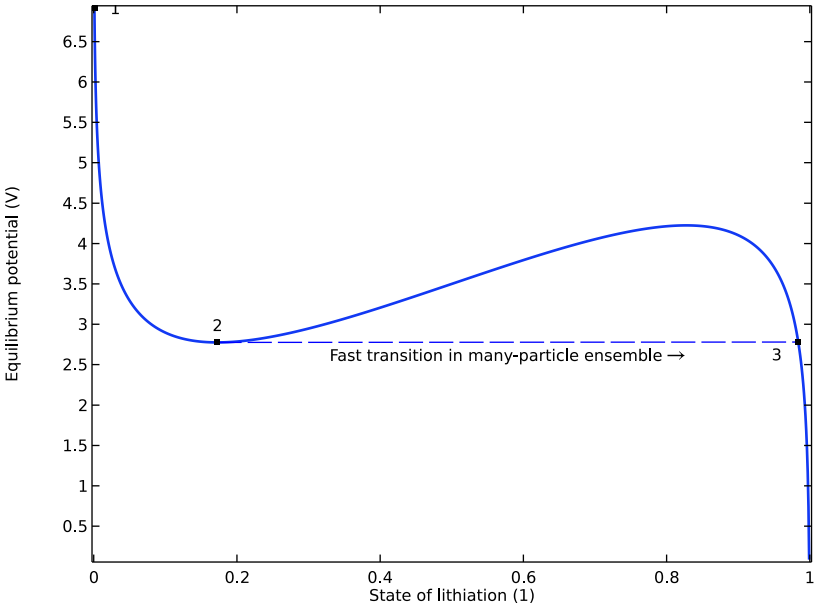


Figure 1: Schematic representation of the lithiation process in a particle subject to a nonmonotonic equilibrium potential function. Lithiation starts in point 1, proceeding via the inflection point 2 to point 3. Note: The voltage scale is arbitrary and only serves as an example.

The solid blue line in Figure 1 is however seldom observed experimentally, and the reason for this is related to the difficulties of recording the equilibrium potential of a single electrode particle. For electrodes comprising multiple particles, material inhomogeneities will result in the equilibrium potential exhibiting a different shape, which can be understood by considering an ensemble of many similar, but not identical, particles subject to a constant reduction current as follows: When lithiation starts in point 1 for the ensemble, all particles are initially at the same potential. However, as lithiation continues, small differences in particle properties result in one of the particles reaching point 2 first, and as this particle passes the inflection point, increasing cathodic overpotentials will favor a fast and accelerated continued reduction of this single particle up to the second inflection point, and then continued reduction until it reaches the same potential as the rest of the ensemble in point 3. During the process when the first particle gets reduced to point 3, all other particles in ensemble will remain at a position left of point 2, where they undergo slight oxidation in order to maintain the overall charge balance of the ensemble. Once the first particle has reached point 3, a subsequent particle will undergo the fast transition to point 3, and so on. During the fast transitions, the mixed potential of the ensemble will

stay close to the dashed line in Figure 1, and not until all particles have reached point 3 will the equilibrium potential proceed to decrease from the common equilibrium potential level of point 2 and 3.

The process described above is also referred to as a "mosaic" transition between lithium-poor and lithium-rich phases. For smaller ensembles of particles it should be possible to observe these transitions as voltage ripples using a high-precision potentiostat when operating at a constant current, but practically for any ordinary battery electrode, the continuum limit of the mosaic transitions results in a smooth voltage plateau.

Reversing the process with delithiation starting in point 4, as shown in Figure 2, results in a similar behavior, with a fast transition occurring between point 5 and 6. The difference in the equilibrium potential levels at the inflection points 2 (in Figure 1) and 5 (in Figure 2) results in voltage hysteresis.

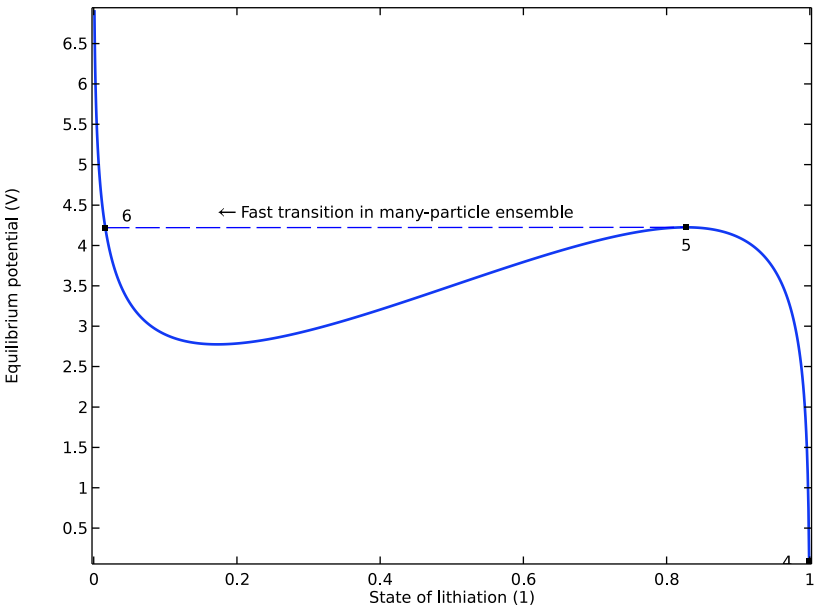


Figure 2: Schematic representation of the delithiation process in a particle subject to a nonmonotonic equilibrium potential function. Delithiation starts in point 4, proceeding via the inflection point 5 to point 6. Note: The voltage scale is arbitrary and only serves as an example.

LFP PARTICLE ENSEMBLE MODEL

The model defines an ensemble of particles by the usage of three dependent variables:

- The concentration of intercalated lithium in the lithium-rich phase, $c_{s,\mathrm{rich}}$ $(\mathrm{mol/m^3})$

- The concentration of intercalated lithium in the lithium-poor phase, $c_{\mathrm{s,\,poor}}$ $(\mathrm{mol/m^3})$
- The average concentration of lithium in the particle ensemble, $c_{\mathrm{s,avg}}$ $(\mathrm{mol/m^3})$

The three variables above are in turn used to define the volume fractions of the lithium-poor and lithium-rich phases, ϕ_{poor} (1) and ϕ_{rich} (1), using the relations

$$c_{s,\,\mathrm{avg}} = \theta_{\mathrm{poor}} c_{s,\,\mathrm{poor}} + \theta_{\mathrm{rich}} c_{s,\,\mathrm{rich}} \tag{1}$$

and

$$\theta_{\mathrm{poor}} + \theta_{\mathrm{rich}} = 1 \tag{2}$$

Diffusion is neglected within the ensemble. The material balances for the average intercalated concentration is defined as

$$\varepsilon_s \frac{\partial c_{s,\,\mathrm{avg}}}{\partial t} = -\frac{i_v}{F} \tag{3}$$

where ε_s (1) is the electrode volume fraction and i_v $(\mathrm{mol/m^3})$ the volumetric current density stemming from charge transfer reactions in the whole ensemble.

The volumetric charge transfer current densities at the electrolyte-electrode interface between the particle ensemble and the electrolyte from both the lithium-rich and lithium-poor phases are used to define i_v according to

$$i_v = \theta_{\mathrm{poor}} i_{v,\,\mathrm{poor}} + \theta_{\mathrm{rich}} i_{v,\,\mathrm{rich}} \tag{4}$$

where $i_{v,i}$ $(\mathrm{mol/m^3})$ is the volumetric current density of the respective phase. (In the following, the subscript index i refers to either the lithium-rich or the lithium-poor phase.)

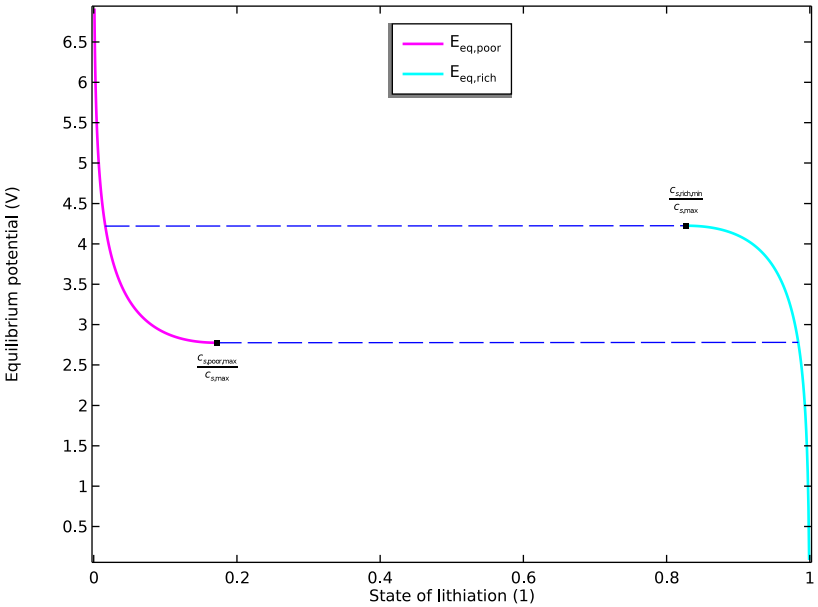


Figure 3: Schematic representation of the lithium-poor and lithium-rich equilibrium potential functions used by the ensemble model. Note: The voltage scale is arbitrary and only serves as an example.

Figure 3 shows a schematic plot of the equilibrium potential functions used for defining the overpotential (see Equation 11 below) of the lithium-rich and lithium-poor phases. Here the state of lithiation is defined as $c_s / c_{s,\max}$. In Figure 3 the locations of the two inflection points have also been indicated, which define the two concentration levels $c_{s,\text{poor,max}}$ (mol/m^3) and $c_{s,\text{rich,min}}$ (mol/m^3) in terms of $c_{s,\max}$.

For the lithium-poor phase concentration, any cathodic charge transfer current density is assumed to be counterbalanced by fast phase transitions whenever the concentration level exceeds the concentration level of the inflection point, $c_{s,\text{poor,max}}$ (mol/m^3), prohibiting further intercalation into the lithium-poor phase. The material balances for the lithium-poor phase concentration is hence defined as

$$\varepsilon_s \frac{\partial c_{s,\,\text{poor}}}{\partial t} = \begin{cases} 0 & \text{if } \eta_{\text{poor}} < 0 \text{ and } c_{s,\,\text{poor}} > c_{s,\,\text{poor,\,max}} \\ -\dfrac{i_{v,\,\text{poor}}}{F} & \text{otherwise} \end{cases} \tag{5}$$

Similarly, for the lithium-rich phase, the material balance is defined as

$$\varepsilon_s \frac{\partial c_{s,\,\mathrm{rich}}}{\partial t} = \begin{cases} 0 & \text{if } \eta_{\mathrm{rich}} > 0 \text{ and } c_{s,\,\mathrm{rich}} < c_{s,\,\mathrm{rich,\,min}} \\ -\dfrac{i_{v,\,\mathrm{rich}}}{F} & \text{otherwise} \end{cases} \tag{6}$$

The above way of conditionally adding the charge transfer current density to the phase concentration time derivatives implicitly defines the phase transition rate. This can be seen by differentiation with respect to time in Equation 1:

$$\frac{\partial c_{s,\,\mathrm{avg}}}{\partial t} = \theta_{\mathrm{poor}} \frac{\partial c_{s,\,\mathrm{poor}}}{\partial t} + \theta_{\mathrm{rich}} \frac{\partial c_{s,\,\mathrm{rich}}}{\partial t} + (c_{s,\,\mathrm{poor}} - c_{s,\,\mathrm{rich}}) \frac{\partial \theta_{\mathrm{poor}}}{\partial t} \tag{7}$$

which may be rearranged into

$$\frac{\partial \theta_{\mathrm{poor}}}{\partial t} = \frac{\dfrac{\partial c_{s,\,\mathrm{avg}}}{\partial t} - \theta_{\mathrm{poor}} \dfrac{\partial c_{s,\,\mathrm{poor}}}{\partial t} - \theta_{\mathrm{rich}} \dfrac{\partial c_{s,\,\mathrm{rich}}}{\partial t}}{c_{s,\,\mathrm{poor}} - c_{s,\,\mathrm{rich}}} \tag{8}$$

When any of the conditionals in Equation 5 or Equation 6 sets the time derivative of either $c_{\mathrm{s,rich}}$or $c_{\mathrm{s,rich}}$ to zero, respectively, this may result in a nonzero time derivative of ϕ_{poor}, which in turn results in changing the volume fractions of the lithium-rich and lithium-poor phases.

CHARGE TRANSFER KINETICS

For each phase, charge transfer occurs according to Butler–Volmer expressions defined as:

$$i_{v,\,i} = A_v i_{0,\,i} \left(e^{\frac{\eta_i F}{2RT}} - e^{-\frac{\eta_i F}{2RT}} \right) \tag{9}$$

where A_v ($\mathrm{m}^2/\mathrm{m}^3$) is the specific surface area of the electrolyte-electrode interface, $i_{0,i}$ is the exchange current density, and η_i (V) is the overpotential.

The exchange current density is defined as

$$i_{0,\,i} = 2 i_{0,\,\mathrm{ref}} \left(\frac{c_l}{c_{l,\,\mathrm{ref}}} \frac{c_{s,\,i}}{c_{s,\,\mathrm{max}}} \frac{c_{s,\,\mathrm{max}} - c_{s,\,i}}{c_{s,\,\mathrm{max}}} \right)^{0,5} \tag{10}$$

where c_l ($\mathrm{mol}/\mathrm{m}^3$) is the electrolyte ion concentration, $i_{0,\mathrm{ref}}$ is the exchange current density for a reference state corresponding to the reference conditions $c_l = c_{l,\mathrm{ref}}$ and $c_{s,\,\mathrm{ref}} = c_{s,\,\mathrm{max}}/2$, and $\mathrm{c_{s,max}}$ ($\mathrm{mol}/\mathrm{m}^3$) is the maximum intercalation concentration.

The overpotential is defined as

$$\eta_i = \phi_s - \phi_l - E_{\mathrm{eq},\,i}(c_{s,\,i}) \tag{11}$$

where ϕ_s (V) is the electrode phase potential, ϕ_l (V) the electrolyte phase potential, and $E_{\mathrm{eq},\,i}$ (V) the equilibrium potential as defined in Figure 4 below.

COMSOL IMPLEMENTATION

The **Lithium-Ion Battery** interface is used to define a half-cell model consisting of a Lithium-metal counter electrode, a separator, and a positive LFP porous electrode. The **Porous Electrode** > **Particle Intercalation** node, with the **No spatial gradients** option for defining the species concentration model, is used to define the $c_{s,\mathrm{avg}}$ variable.

The lithium-poor and lithium-rich equilibrium potential curves, as shown in Figure 4, and some additional modeling parameters, were taken from Ref. 4.

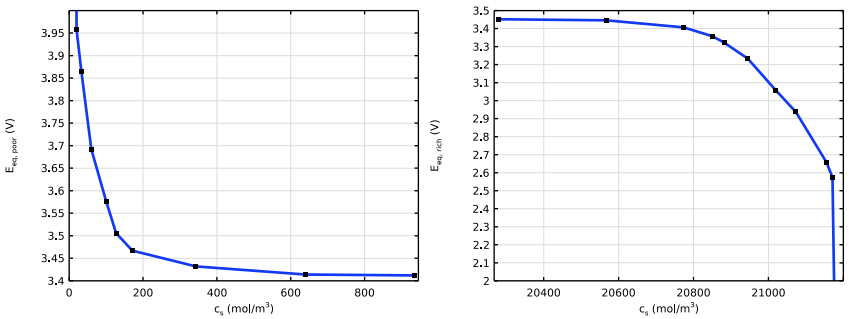


Figure 4: Equilibrium potential for the lithium-poor (left) and the lithium-rich (right) particles used in the simulation. (Based on experimental data from Ref. 4).

A **Domain ODEs and DAEs** interface is added to solve for $c_{s,\mathrm{poor}}$ and $c_{s,\mathrm{rich}}$ on the porous electrode domain.

To illustrate the hysteresis loop, the **Events** interface is used to define a load cycle using 1C lithiation/delithiation current pulses with 10 minute resting periods in between. The simulation starts from a lithiated electrode. The first current pulse delithiates the electrode to around 50%, followed by a rest, followed by another delithiation pulse to reach almost full delithiation. After yet another rest period, the current direction is reversed in order to lithiate the electrode to around 50%, followed by another 10-minute rest. Finally, the electrode is once again almost completely delithiated.

A **Global ODEs and DAEs** interface is added to integrate the current over time in order to compute the cycled capacity.

Figure 5 shows the cell voltage versus time during the load cycle. During each 10 minute rest period, a short rapid voltage relaxation, which stems from relaxation of gradients in the lithium-ion concentration in the cell, is followed by a longer plateau featuring a constant potential of either 3.452 V (after a delithiation pulse) or 3.412 V (after a lithiation pulse). These voltage levels correspond to the left-most data point of the lithium-rich particles, and the right-most data point of the lithium-poor particles in Figure 4, respectively.

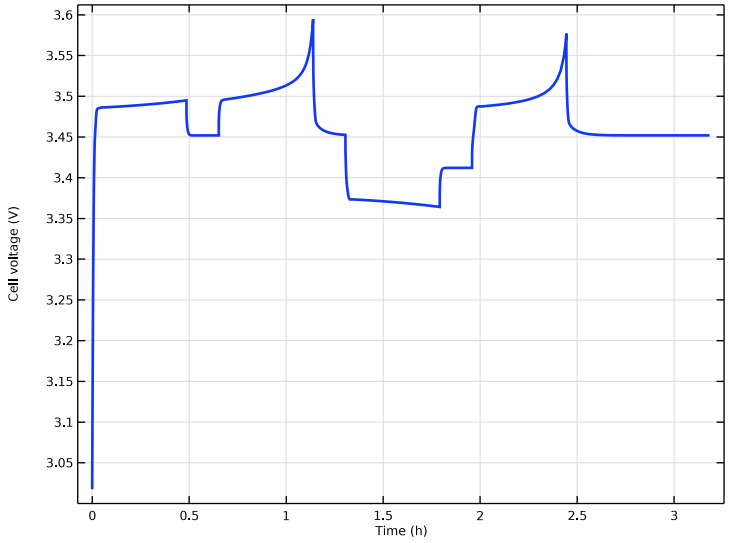


Figure 5: Cell voltage versus time.

Figure 6 shows a corresponding voltage versus capacity plot, where the different voltages at around 50% lithiation (0.88 mA/cm^2) illustrate the resulting voltage hysteresis at rest. A small hysteresis also in polarization is seen between the second and last delithiation step (above 0.92 mA/cm^2). This is an effect of the current distribution in the porous electrode, which predominantly will favor lithiation/delithiation in the region close to the separator in the beginning of a current pulse. The same behavior (qualitatively) is reported in Ref. 4.

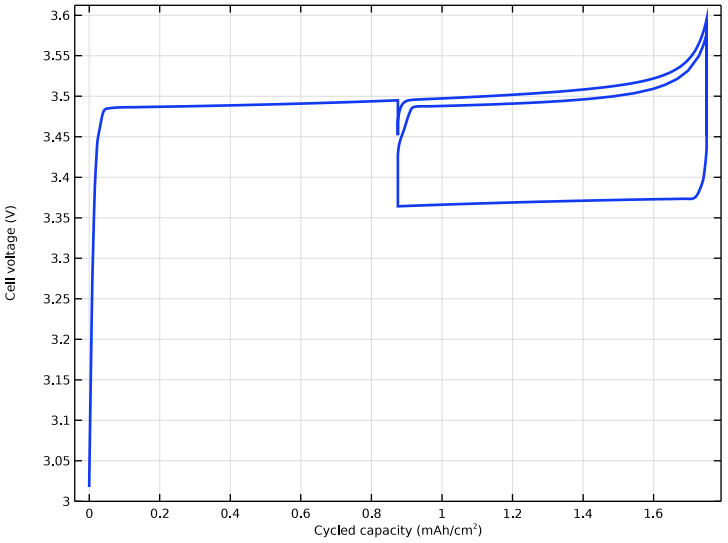


Figure 6: Cell voltage versus capacity for the delithiation-lithiation cycle.

References

1. W. Dreyer and others, "The thermodynamic origin of hysteresis in insertion batteries," *Nature Mater.*, vol. 9, pp. 448–453, 2010; doi.org/10.1038/nmat2730.

2. P. Ombrini and others, "Kinetically induced memory effect in Li-ion batteries," *EES Batteries*, vol. 1, no. 3, pp. 437–449, 2025; dx.doi.org/10.1039/D5EB00014A.

3. N. Meethong and others, "Size-Dependent Lithium Miscibility Gap in Nanoscale Li_{1-x} $FePO_4$," *Electrochem. Solid-State Lett.*, vol. 10, no. 5, A134, 2007; doi.org/10.1149/1.2710960.

4. V. Srinivasan and J. Newman, "Existence of Path-Dependence in the $LiFePO_4$ Electrode," *Electrochem. Solid-State Lett.*, vol. 9, no. 9, A110, 2006; doi.org/10.1149/1.2159299.

Application Library path: `Battery_Design_Module/Lithium-Ion_Batteries,_Performance/lfp_voltage_hysteresis`

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** > **Lithium-Ion Battery (liion)**.
3. Click **Add**.
4. In the **Select Physics** tree, select **Mathematics** > **ODE and DAE Interfaces** > **Global ODEs and DAEs (ge)**.
5. Click **Add**.
6. In the **Select Physics** tree, select **Mathematics** > **ODE and DAE Interfaces** > **Domain ODEs and DAEs (dode)**.
7. Click **Add**.
8. In the **Select Physics** tree, select **Mathematics** > **ODE and DAE Interfaces** > **Events (ev)**.
9. Click **Add**.
10. Click **Study**.
11. In the **Select Study** tree, select **Preset Studies for Selected Physics Interfaces** > **Lithium-Ion Battery** > **Time Dependent with Initialization**.
12. Click **Done**.

GLOBAL DEFINITIONS

Parameters 1

Add a list of parameter definitions from a text file as follows:

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 `lfp_voltage_hysteresis_parameters.txt`.

   Some definitions are highlighted in red, indicating missing operators. Add these next.

Interpolation - Eeq poor (lithiation from fully delithiated)

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

2 In the **Settings** window for **Interpolation**, type `Interpolation - Eeq poor (lithiation from fully delithiated)` in the **Label** text field.

3 Locate the **Definition** section. In the **Function name** text field, type `Eeq_poor`.

4 Click **Load from File**.

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

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

Function	Unit
Eeq_poor	V

7 In the **Argument** table, enter the following settings:

Argument	Unit
t	mol/m^3

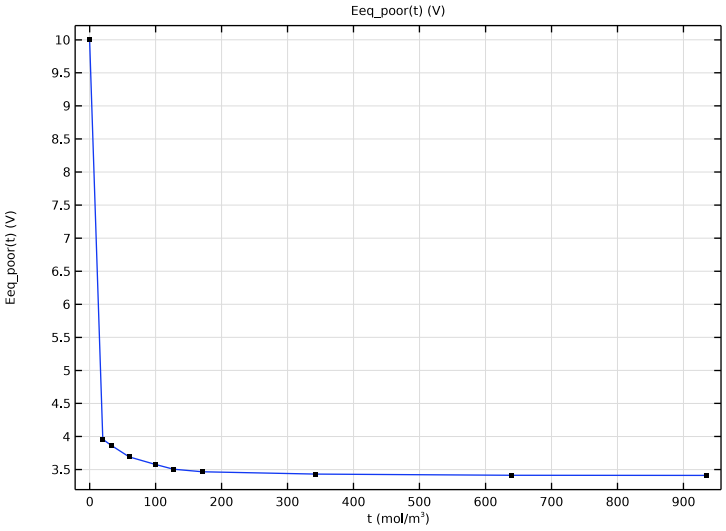
8 Click to expand the **Plot Parameters** section. Clear the **Include left extrapolation** checkbox.

9 Clear the **Include right extrapolation** checkbox.

10 Click to expand the **Related Functions** section. Select the **Define inverse function** checkbox.

11 In the **Inverse function name** text field, type `Eeq_poor_inv`.

12 Click **Plot**.



Interpolation - Eeq rich (delithiation from fully lithiated)

1 In the **Home** toolbar, click **Functions** and choose **Global** > **Interpolation**.

2 In the **Settings** window for **Interpolation**, type `Interpolation - Eeq rich (delithiation from fully lithiated)` in the **Label** text field.

3 Locate the **Definition** section. In the **Function name** text field, type `Eeq_rich`.

4 Click **Load from File**.

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

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

Function	Unit
Eeq_rich	V

7 In the **Argument** table, enter the following settings:

Argument	Unit
t	mol/m^3

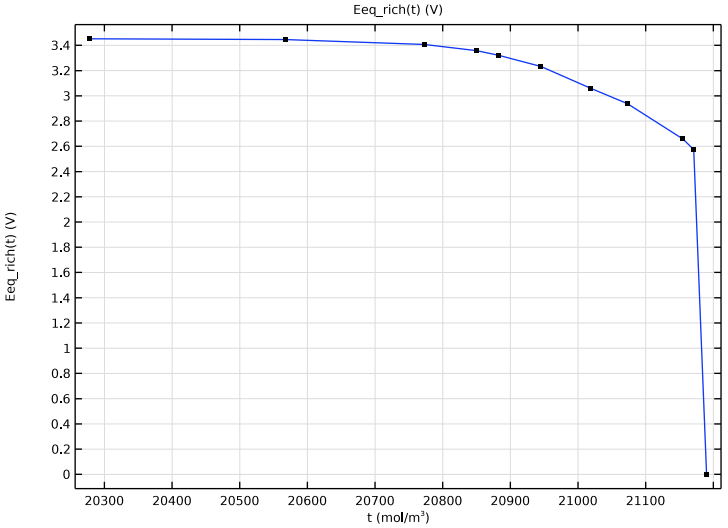
8 Click to expand the **Plot Parameters** section. Clear the **Include left extrapolation** checkbox.

9 Clear the **Include right extrapolation** checkbox.

10 Locate the **Related Functions** section. Select the **Define inverse function** checkbox.

11 In the **Inverse function name** text field, type `Eeq_rich_inv`.

12 Click **Plot**.



Analytic 1 (an1)

In the **Home** toolbar, click **Functions** and choose **Global** > **Analytic**.

Parameters 1

Check the parameter list again. The error indicators should now have vanished.

Analytic 1 - Eeq_avg

Also add a function for an averaged equilibrium potential function for the whole particle ensemble. This function is strictly not required in the model, but is convenient to have in order to assess a thermodynamically consistent equilibrium potential that can be used, for instance, to compute heat sources.

1 In the **Model Builder** window, under **Global Definitions** click **Analytic 1 (an1)**.

2 In the **Settings** window for **Analytic**, type `Analytic 1 - Eeq_avg` in the **Label** text field.

3 In the **Function name** text field, type `Eeq_avg`.

4 Locate the **Definition** section. In the **Expression** text field, type `if(cs<cs_poor_max, Eeq_poor(cs), if(cs>cs_rich_min, Eeq_rich(cs), Eeq_poor(cs_poor_max)+`

`(Eeq_rich(cs_rich_min)-Eeq_poor(cs_poor_max))*(cs-cs_poor_max)/(cs_rich_min-cs_poor_max))).`

5 In the **Arguments** text field, type `cs`.

6 Locate the **Units** section. In the **Function** text field, type `V`.

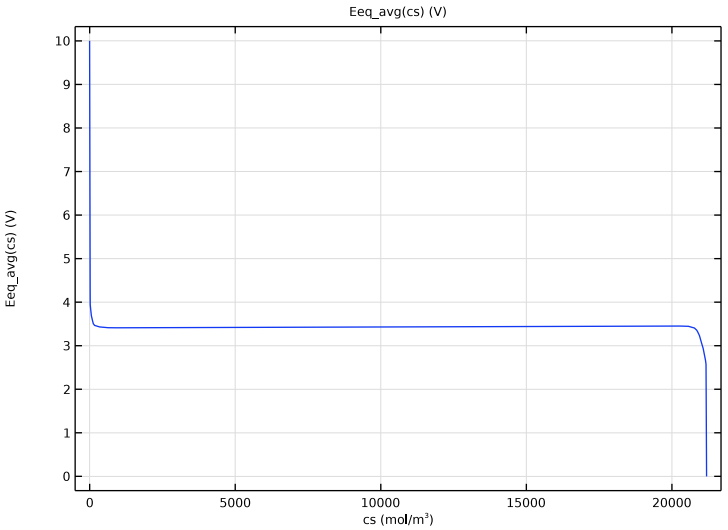
7 In the table, enter the following settings:

Argument	Unit
cs	mol/m^3

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

Plot	Argument	Lower limit	Upper limit	Fixed value	Unit
√	cs	0	csmax	0	mol/m^3

9 Click **Plot**.



GEOMETRY 1

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_sep
L_pos

5 Click **Build All Objects**.

ADD MATERIAL FROM LIBRARY

In the **Home** toolbar, click **Windows** and choose **Add Material from Library**.

ADD MATERIAL

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

2 In the tree, select **Battery** > **Electrodes** > **Lithium Metal, Li (Negative, Li-ion Battery)**.

3 Right-click and choose **Add to Component 1 (comp1)**.

4 In the tree, select **Battery** > **Electrolytes** > **LiPF6 in 1:1 EC:DEC (Liquid, Li-ion Battery)**.

5 Right-click and choose **Add to Component 1 (comp1)**.

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

MATERIALS

Lithium Metal, Li (Negative, Li-ion Battery) (mat1)

1 In the **Settings** window for **Material**, locate the **Geometric Entity Selection** section.

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

3 Select Boundary 1 only.

LiPF6 in 1:1 EC:DEC (Liquid, Li-ion Battery) (mat2)

1 In the **Model Builder** window, click **LiPF6 in 1:1 EC:DEC (Liquid, Li-ion Battery) (mat2)**.

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

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

DEFINITIONS

Define a number of variables for the positive porous electrode domain using a text file as follows:

Variables 1 - LFP 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 1 - LFP Electrode` in the **Label** text field.

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

4 Select Domain 2 only.

5 Click **Create Selection**.

6 In the **Create Selection** dialog, type `LFP Electrode` in the **Selection name** text field.

7 Click **OK**.

8 In the **Settings** window for **Variables**, locate the **Variables** section.

9 Click **Load from File**.

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

Here, a number of expressions are highlighted in yellow, indicating unknown variables. These will be corrected shortly.

Variables 2 - Global

Add a second, global, variable node to define an applied current density variable. The variable `C` will be defined later by the **Events** interface.

1 In the **Model Builder** window, right-click **Definitions** and choose **Variables**.

2 In the **Settings** window for **Variables**, type `Variables 2 - Global` in the **Label** text field.

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

Name	Expression	Unit	Description
`i_app`	`i1C*C`		`Applied current density`

LITHIUM-ION BATTERY (LIION)

Separator 1

1 In the **Model Builder** window, under **Component 1 (comp1)** > **Lithium-Ion Battery (liion)** click **Separator 1**.

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

3 In the ε_l text field, type `epsl_sep`.

Electrode Surface 1

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

2 Select Boundary 1 only.

Porous Electrode 1

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

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

3 From the **Selection** list, choose **LFP Electrode**.

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

5 In the ε_l text field, type `epsl`.

Particle Intercalation 1

1 In the **Model Builder** window, click **Particle Intercalation 1**.

2 In the **Settings** window for **Particle Intercalation**, locate the **Species Settings** section.

3 In the $c_{s,init}$ text field, type `cs_init`.

4 From the $c_{s,max}$ list, choose **User defined**. In the associated text field, type `csmax`.

5 Locate the **Particle Transport Properties** section. From the **Species concentration transport model** list, choose **No spatial gradients**.

6 In the r_p text field, type `rp`.

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 **Equilibrium Potential** section.

3 From the E_{eq} list, choose **User defined**. In the associated text field, type `Eeq_avg(cs_avg)`.

4 Locate the **Electrode Kinetics** section. From the $i_{loc,expr}$ list, choose **User defined**. In the associated text field, type `iloc`.

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

Electrode Current Density 1

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

2 Select Boundary 3 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 `i_app`.

GLOBAL ODES AND DAES - CYCLED CAPACITY

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

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

Global Equations 1 (ODE1)

1 In the **Model Builder** window, under **Component 1 (comp1)** > **Global ODEs and DAEs - Cycled capacity (ge)** click **Global Equations 1 (ODE1)**.

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

3 In the table, enter the following settings:

Name	f(u,ut,utt, t) (1)	Initial value (u_0) (1)	Initial value (ut_0) (1/s)	Description
q	qt-i_app	0	0	Cycled capacity

4 Locate the **Units** section. Click **Define Dependent Variable Unit**.

5 In the **Dependent variable quantity** table, enter the following settings:

Dependent variable quantity	Unit
Custom unit	C/m^2

6 Click **Define Source Term Unit**.

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

Source term quantity	Unit
Custom unit	A/m^2

DOMAIN ODES AND DAES - CS_POOR AND CS_RICH

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

2 In the **Settings** window for **Domain ODEs and DAEs**, type `Domain ODEs and DAEs - cs_poor and cs_rich` in the **Label** text field.

3 Locate the **Domain Selection** section. From the **Selection** list, choose **LFP Electrode**.

4 Locate the **Units** section. Click **Define Dependent Variable Unit**.

5 In the **Dependent variable quantity** table, enter the following settings:

Dependent variable quantity	Unit
Custom unit	mol/m^3

6 Click **Define Source Term Unit**.

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

Source term quantity	Unit
Custom unit	mol/m^3/s

8 Click to expand the **Discretization** section. From the **Element order** list, choose **Linear**.

9 Click to expand the **Dependent Variables** section. In the **Field name (mol/m³)** text field, type `cs`.

10 In the **Number of dependent variables** text field, type `2`.

11 In the **Dependent variables (mol/m³)** table, enter the following settings:

cs_poor
cs_rich

Distributed ODE 1

1 In the **Model Builder** window, under **Component 1 (comp1)** > **Domain ODEs and DAEs - cs_poor and cs_rich (dode)** click **Distributed ODE 1**.

2 In the **Settings** window for **Distributed ODE**, locate the **Source Term** section.

3 In the *f* text-field array, type `R_poor` on the first row.

4 In the f text-field array, type `R_rich` on the second row.

5 Locate the **Damping or Mass Coefficient** section. In the d_a text-field array, type `epss` in the first column of the first row.

6 In the d_a text-field array, type `epss` in the second column of the second row.

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 cs_{poor} text field, type `cs_poor_init`.

4 In the cs_{rich} text field, type `cs_rich_init`.

EVENTS- LOAD CYCLE

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

2 In the **Settings** window for **Events**, type `Events- Load Cycle` in the **Label** text field.

Explicit Event List 1

1 In the **Physics** toolbar, click **Global** and choose **Explicit Event List**.

2 In the **Settings** window for **Explicit Event List**, locate the **Discrete State** section.

3 In the u text field, type `C`.

4 In the **Description** text field, type `C rate`.

5 In the u_0 text field, type `1`.

6 Locate the **Explicit Events** section. Click **Clear Table**.

7 Click **Load from File**.

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

DEFINITIONS

Return to the **Variables** nodes and check that all warnings have vanished.

Point Probe 1 - Cell voltage

Before solving the model, add some probes. The probe values will be stored in a table for every time step computed by the solver.

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

2 In the **Settings** window for **Point Probe**, type `Point Probe 1 - Cell voltage` in the **Label** text field.

3 Locate the **Source Selection** section. Click **Clear Selection**.

4 Select Boundary 3 only.

5 Locate the **Expression** section. In the **Expression** text field, type `phis`.

6 Select the **Description** checkbox. In the associated text field, type `Cell voltage`.

Global Variable Probe 1 - Cycled capacity

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

2 In the **Settings** window for **Global Variable Probe**, type `Global Variable Probe 1 - Cycled capacity` in the **Label** text field.

3 Locate the **Expression** section. In the **Table and plot unit** field, type `mAh/cm^2`.

STUDY 1

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

4 In the **Output times** text field, type `0 3`.

Step 1: Current Distribution Initialization

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

2 In the **Settings** window for **Current Distribution Initialization**, locate the **Physics and Variables Selection** section.

3 In the **Solve for** column of the table, under **Component 1 (comp1)**, clear the checkboxes for **Global ODEs and DAEs - Cycled capacity (ge)** and **Domain ODEs and DAEs - cs_poor and cs_rich (dode)**.

Solution 1 (sol1)

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

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

Adding manual scales for the `cs_poor` and `cs_rich` variables improves convergence.

3 In the **Model Builder** window, expand the **Study 1** > **Solver Configurations** > **Solution 1 (sol1)** > **Dependent Variables 2** node, then click **Dependent Variable Cs_poor (comp1.cs_poor)**.

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 `10000`.

7 In the **Model Builder** window, under **Study 1** > **Solver Configurations** > **Solution 1 (sol1)** > **Dependent Variables 2** click **Dependent Variable Cs_rich (comp1.cs_rich)**.

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

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

10 In the **Scale** text field, type `10000`.

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

12 In the **Settings** window for **Study**, locate the **Study Settings** section.

13 Clear the **Generate default plots** checkbox.

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

RESULTS

Duplicate and modify the auto-generated probe plot as follows:

Cell Voltage vs Time

1 In the **Model Builder** window, right-click **Probe Plot Group 1** and choose **Duplicate**.

2 In the **Model Builder** window, click **Probe Plot Group 1.1**.

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

Probe Table Graph 1

1 In the **Model Builder** window, click **Probe Table Graph 1**.

2 In the **Settings** window for **Table Graph**, locate the **Data** section.

3 In the **Columns** list box, select **Cell voltage (V), Point Probe 1 - Cell voltage**.

4 Locate the **Coloring and Style** section. From the **Width** list, choose **2**.

Cell Voltage vs Time

1 In the **Model Builder** window, click **Cell Voltage vs Time**.

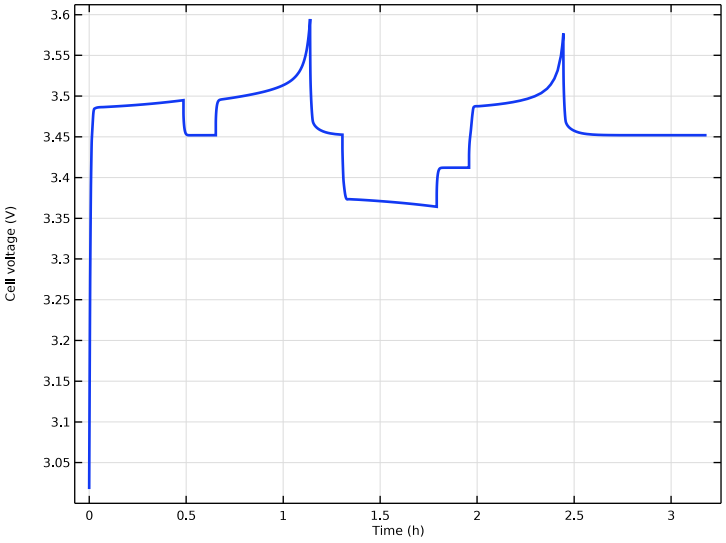
2 In the **Settings** window for **1D Plot Group**, locate the **Legend** section.

3 Clear the **Show legends** checkbox.

4 Locate the **Plot Settings** section.

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

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



Cell Voltage vs Capacity

1 Right-click **Cell Voltage vs Time** and choose **Duplicate**.

2 In the **Model Builder** window, click **Cell Voltage vs Time 1**.

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

Probe Table Graph 1

1 In the **Model Builder** window, click **Probe Table Graph 1**.

2 In the **Settings** window for **Table Graph**, locate the **Data** section.

3 From the **x-axis data** list, choose **Cycled capacity (mAh/cm^2)**.

Cell Voltage vs Capacity

1 In the **Model Builder** window, click **Cell Voltage vs Capacity**.

2 In the **Cell Voltage vs Capacity** toolbar, click **Plot**.