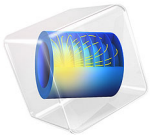

Silicon–Graphite-Blended Electrode with Thermodynamic Voltage Hysteresis

Introduction

Due to its high capacity, silicon (Si) is often added to graphite in the negative electrode of lithium-ion batteries.

Silicon-graphite blended electrodes may exhibit significant thermodynamic voltage hysteresis ("path dependence") because the equilibrium potential of the lithium–silicon intercalation reaction is dependent on the charge–discharge history of the electrode.

This example demonstrates how to add Si as an Additional Electrode Material in the Lithium-Ion Battery interface and how to define a memory variable for handling the voltage hysteresis using an additional Coefficient From PDE interface.

Model Definition

The model solves for a half cell with the following components:

- Blended porous electrode with graphite (Li_xC_6, MCMB) and silicon (Li_xSi), where the thickness depends on the graphite:silicon ratio; see below
- Separator (25 μm thick)
- Negative lithium-metal counter electrode
- Electrolyte, 1.0 M $LiPF_6$ in EC:EMC (3:7 by weight)

The potential of the blended electrode is defined versus a reference electrode positioned at the boundary between the blended electrode and the separator.

Similar processes are accounted for as in the Lithium-Ion Battery with Multiple Intercalating Electrode Materials example, but with some exceptions: The cell has a lithium metal counter electrode instead of a negative porous electrode that provides lithium-ion flux during charge-discharge. A memory variable is used to handle the voltage hysteresis of silicon material in the blended electrode.

ELECTRODE MATERIAL HYSTERESIS

The hysteresis, or path dependence, of the silicon electrode material is depicted in Figure 1. Here, the equilibrium (rest) potentials of the individual silicon and graphite materials are plotted as a function of the degree of lithiation (x_{Gr} for graphite and x_{Si} for silicon).

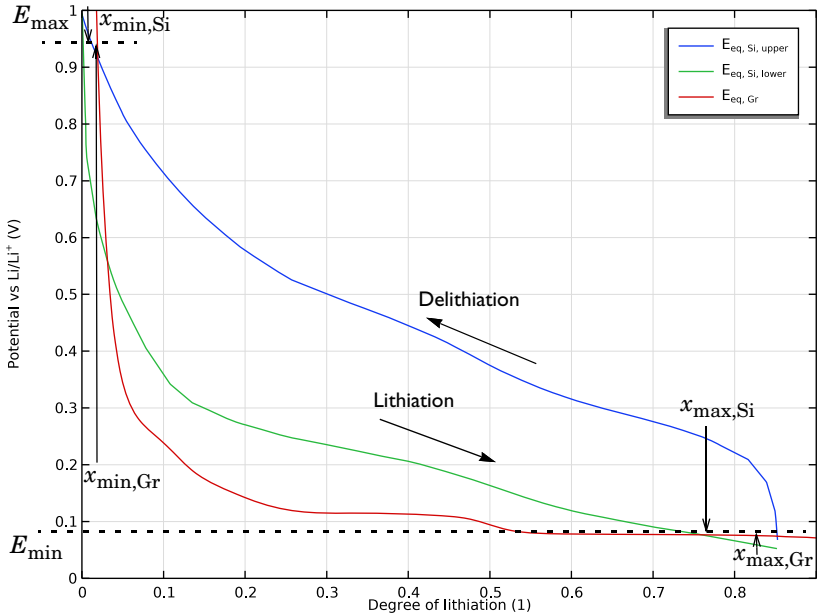

Figure 1: Equilibrium potentials defined as functions of the degree of lithiation. Current-direction dependent potential curve for silicon (upper/delithiation and lower/lithiation). Maximum and minimum lithiation degrees, x_{min} and x_{max}, correspond to the potential limits, E_{min} and E_{max}, of the blended electrode.

For silicon, the equilibrium potential exhibits hysteresis and depends on the charging direction. Graphite does not exhibit voltage hysteresis to the same degree, and in the model the potential is only dependent on the degree of lithiation.

The potential equilibrium curve for graphite is added from the Material library and used in a Porous Electrode Reaction node on the blended porous electrode domain. In the same domain, an Additional Porous Electrode Material node is also added, defining the silicon material.

The silicon potential equilibrium is defined using a user-defined expression according to (Ref. 1)

$$E_{eq,Si} = U_{avg} + S \cdot U_{offset}$$

with

$$U_{\text{avg}} = \frac{E_{\text{eq,Si,upper}}(x_{\text{Si}}) + E_{\text{eq,Si,lower}}(x_{\text{Si}})}{2}$$

and

$$U_{\text{offset}} = \frac{E_{\text{eq,Si,upper}}(x_{\text{Si}}) - E_{\text{eq,Si,lower}}(x_{\text{Si}})}{2}$$

Here S is a memory variable that is set up in a Coefficient Form PDE interface in which the following equation is solved

$$\frac{dS}{dt} = \left(-K\left|\frac{dx_{\text{Si}}}{dt}\right|\left(\text{sign}\left(\frac{dx_{\text{Si}}}{dt}\right) + S\right)\right)$$

In this way, S approaches 1 during delithiation and –1 during lithiation.

The intercalation rate is defined as

$$\frac{dx_{\text{Si}}}{dt} = \frac{i_{\text{v, Si}}}{F\varepsilon_{s,\text{ Si}}c_{s,\text{ max,Si}}}$$

where i_{v} denotes the volumetric electrochemical reaction current, ε_s the active electrode material volume fraction, and $c_{\text{s,max}}$ the maximum (host) capacity for lithium intercalation in mol/m^3.

ELECTRODE BALANCING

The blended porous electrode thickness, L_{cl}, depends on the areal capacity, Q_{cl}, set to 20 Ah/m^2 and the chosen potential limits for 0 and 100% state of charge (SOC) using the formulation

$$L_{\text{el}} = \frac{\text{Q}_{\text{el}}}{F(\varepsilon_{s,\text{ Gr}}(x_{\text{max,Gr}} - x_{\text{min,Gr}})c_{s,\text{ max,Gr}} + \varepsilon_{s,\text{ Si}}(x_{\text{max,Si}} - x_{\text{min,Si}})c_{s,\text{ max,Si}})}$$

where x_{max} and x_{min} for the materials are defined from the maximum and minimum cutoff voltages (versus the reference electrode), E_{max} and E_{min} (Figure 1)

$$E_{\text{eq,Gr}}(x_{\text{max,Gr}}) = E_{\text{eq,Si,lower}}(x_{\text{max,Si}}) = E_{\text{min}} = 0.075\text{ V}$$

$$E_{\text{eq,Gr}}(x_{\text{min,Gr}}) = E_{\text{eq,Si,lower}}(x_{\text{min,Si}}) = E_{\text{max}} = 0.95\text{ V}$$

ENERGY DENSITY

The accumulated energy required for lithiation and delithiation, E_{lith} and E_{delith} (Wh/m^2), is computed in a Global ODEs and DAEs interface using the expressions

$$E_{\text{lith}} = -\int_0^{t_{\text{lith}}} i_{\text{app}}(E_{\text{vs ref}} - E_{\text{max}})\,\text{d}t$$

$$E_{\text{delith}} = \int_{t_{\text{lith}}}^{t_{\text{end}}} i_{\text{app}}(E_{\text{vs ref}} - E_{\text{max}})\,\text{d}t$$

where $E_{\text{vs ref}}$ is the potential of the blended electrode versus the reference electrode during the cycle.

The energy densities, e (Wh/m^3), are obtained by dividing the accumulated energies with the electrode thickness:

$$e = \frac{E}{L_{\text{el}}}$$

Note that, as a result of the electrode balancing, the electrode thickness decreases when the Si fraction increases.

The energies are also used to compute the delithiation-to-lithiation energy efficiency

$$\text{eff} = \frac{E_{\text{delith}}}{E_{\text{lith}}}$$

Results and Discussion

The cell is simulated for a full lithiation–delithiation cycle for three different electrode blends, and two different charge–discharging C-rates. The results of the potential change

with lithiation and current direction in Figure 2 demonstrate how the hysteresis becomes more prominent with a larger fraction of silicon, and at lower SOCs.

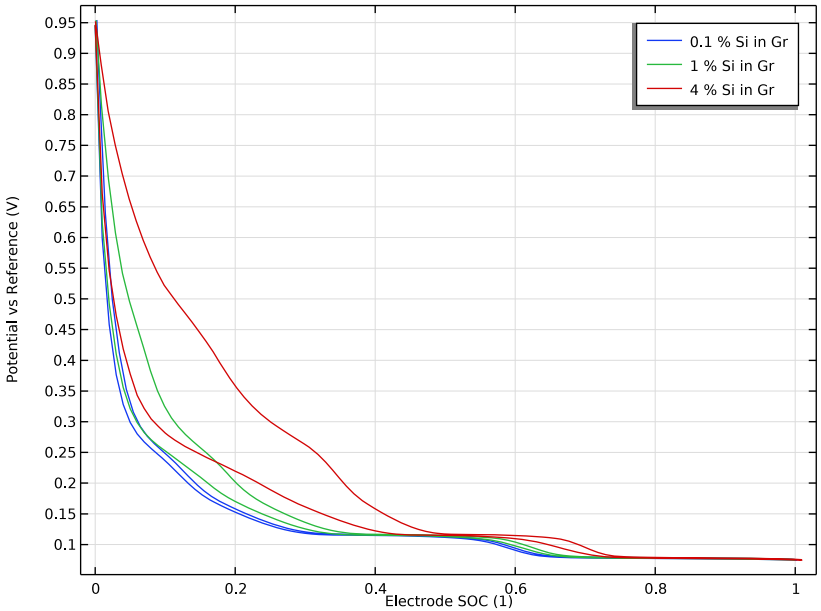

Figure 2: Blended electrode potential versus the reference electrode for three different blends for a C/10 lithiation-delithiation rate.

As shown in Figure 3, for the 1C rate, the hysteresis is more severe. For the 4% silicon-in-graphite blend it is present over the whole SOC interval.

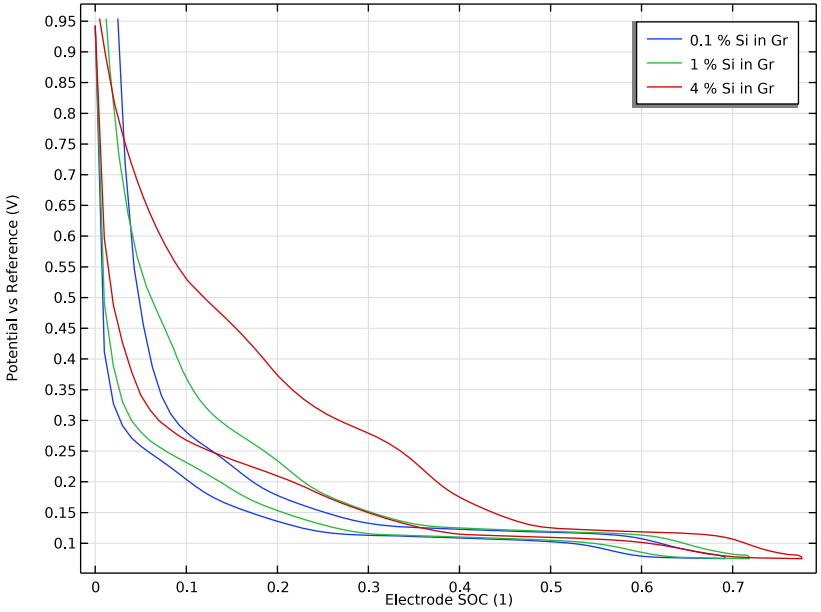

Figure 3: Blended electrode potential versus the reference electrode for three different blends for a 1C lithiation-delithiation rate.

From the average material lithiation levels in Figure 4, it can be seen that the silicon is intercalated first when starting a charging cycle, and that graphite intercalation dominates

toward the end of the charging and at the start of the discharge (at around 10 h). This is directly related to the individual equilibrium potential curves of the two materials.

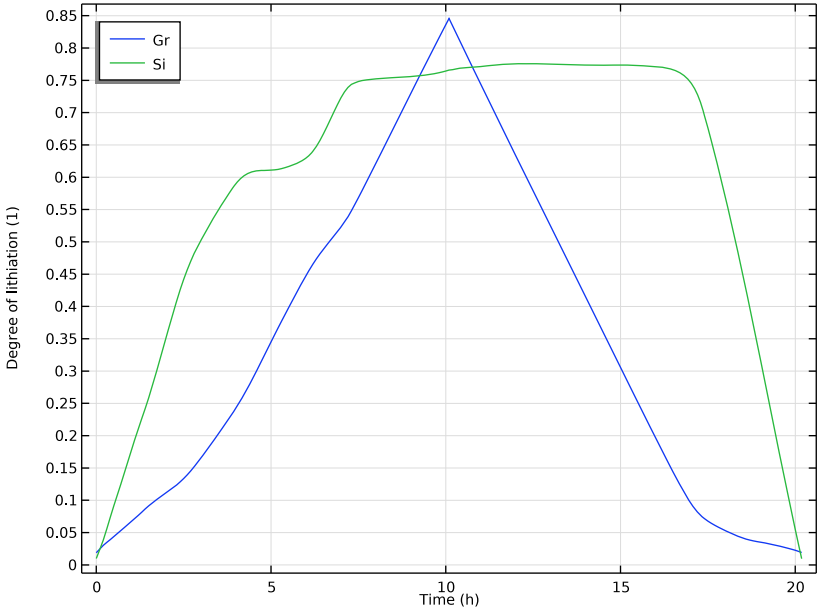

Figure 4: Average material lithiation levels for a 0.1C cycle and 4% silicon-in-graphite blend.

For the higher charge-discharge rate in Figure 5, it is seen that the relative silicon utilization increases over the whole cycle.

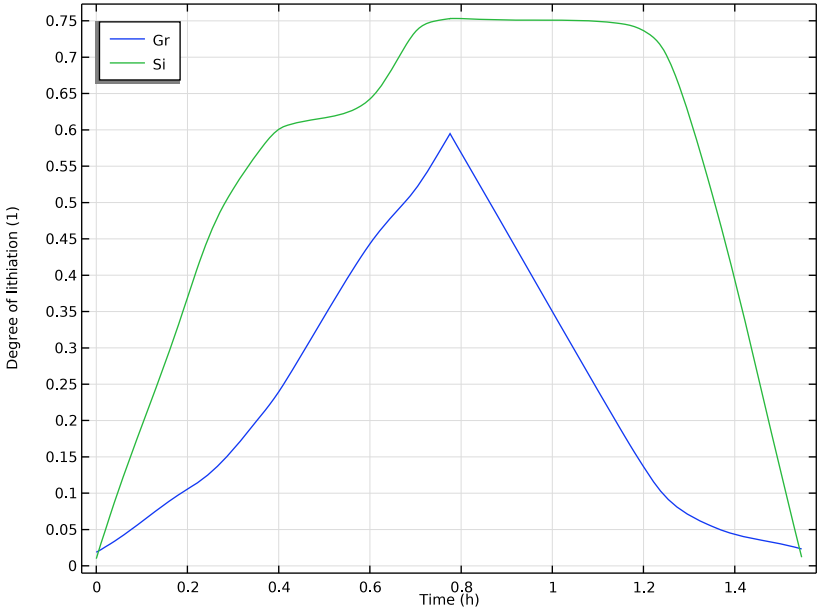

Figure 5: Average material lithiation levels for 1C cycle and 4% silicon-in-graphite blend.

In Figure 6, the hysteresis memory variable variation for the 1C cycle is displayed. A noteworthy difference in the dynamics of the memory variable between lithiation and

delithiation is seen. It also shows that the path dependence can differ along the electrode thickness. The latter phenomena is primarily observed during the delithiation.

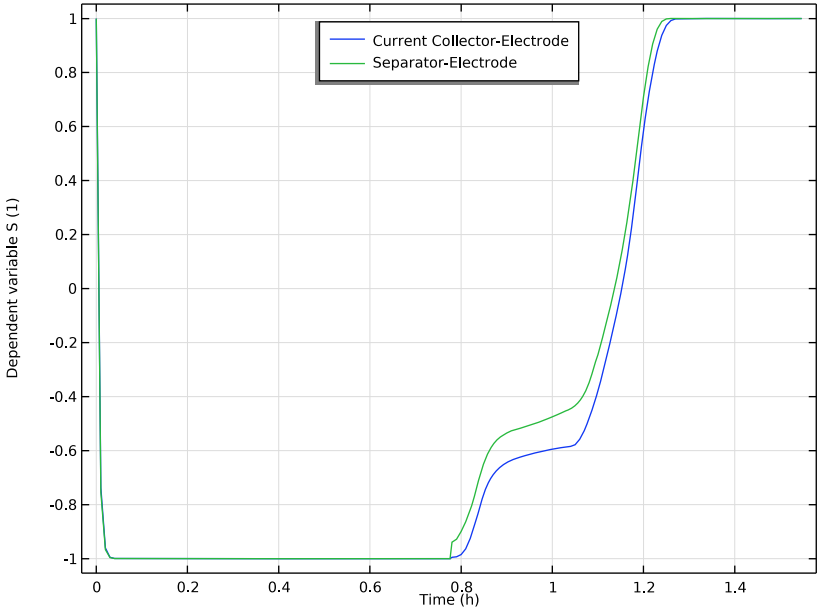

Figure 6: Hysteresis memory variable during 1C lithiation-delithiation for 4% silicon-in-graphite blend at two electrode locations.

Figure 7 shows that the delithiation energy density increases with the silicon content regardless of C-rate.

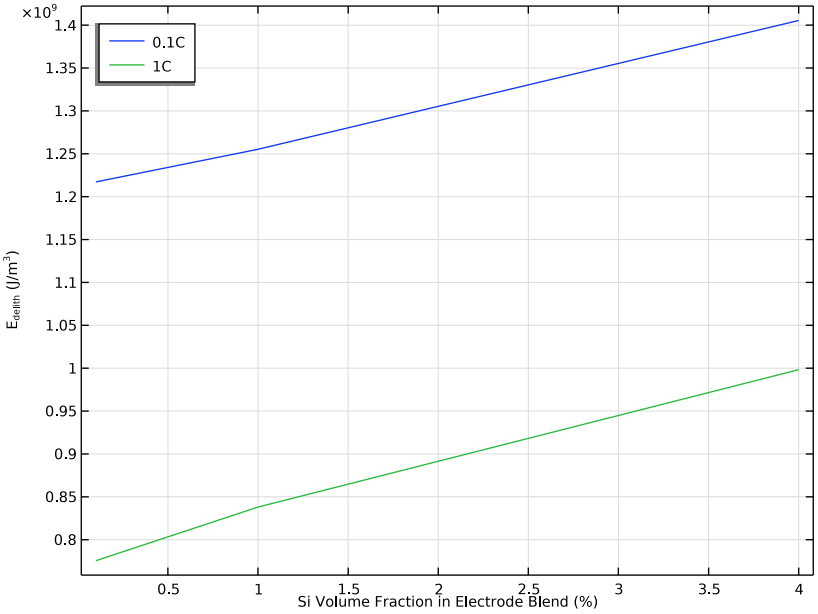

Figure 7: Energy density for 0.1C and 1C delithiation.

In contrast, Figure 8 displays lower delithiation-to-lithiation energy efficiency with increased silicon content.This is related to the increasing hysteresis voltage differences at higher silicon levels.

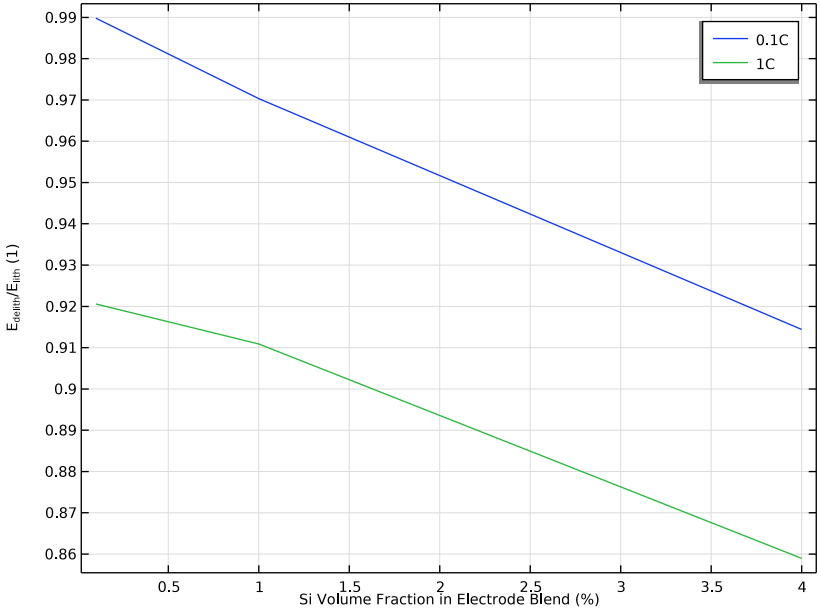

Figure 8: Delithiation-to-lithiation energy efficiencies for 0.1C and 1C cycles.

Reference

1. D.R. Baker, M.W. Verbrugge, and X. Xiao, "An approach to characterize and clarify hysteresis phenomena of lithium-silicon electrodes,"*J. Appl. Phys.*, vol. 122, p. 165105, 2017.

Application Library path: `Battery_Design_Module/Batteries,_Lithium-Ion/li_battery_sigr_hysteresis`

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>Lithium-Ion Battery (liion)**.

3 Click **Add**.

4 Click **Study**.

5 In the **Select Study** tree, select **General Studies>Time Dependent**.

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 `li_battery_sigr_hysteresis_parameters.txt`.

Some expressions will render warnings, indicating missing definitions. This is expected at this stage and will be resolved as soon as the materials are defined.

Add all materials except for LixSi (silicon) from the Material Library.

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>Graphite, LixC6 MCMB (Negative, Li-ion Battery)**.

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

4 In the tree, select **Battery>Electrolytes>LiPF6 in 3:7 EC:EMC (Liquid, Li-ion Battery)**.

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

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

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

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

DEFINITIONS

Import the LixSi (silicon) equilibrium potential curves using Interpolation functions. Two curves are required to model the hysteresis; one for the delithiation (upper) and another for the lithiation (lower).

Interpolation - Eeq Si Upper

1. In the **Home** toolbar, click f(x) **Functions** and choose **Local>Interpolation**.
2. In the **Settings** window for **Interpolation**, type `Interpolation - Eeq Si Upper` in the **Label** text field.
3. Locate the **Definition** section. In the **Function name** text field, type `Eeq_Si_upper`.
4. Click **Load from File**.
5. Browse to the model's Application Libraries folder and double-click the file `li_battery_sigr_hysteresis_Eeq_Si_upper.txt`.
6. Locate the **Interpolation and Extrapolation** section. From the **Extrapolation** list, choose **Linear**.
7. Locate the **Units** section. In the **Function** table, enter the following settings:

Function	Unit
Eeq_Si_upper	V

8. Click to expand the **Related Functions** section. Select the **Define inverse function** check box.
9. In the **Inverse function name** text field, type `Eeq_Si_upper_inv`.
10. Click to collapse the **Related Functions** section.

Interpolation - Eeq Si Lower

1. In the **Home** toolbar, click f(x) **Functions** and choose **Local>Interpolation**.
2. In the **Settings** window for **Interpolation**, type `Interpolation - Eeq Si Lower` in the **Label** text field.
3. Locate the **Definition** section. In the **Function name** text field, type `Eeq_Si_lower`.
4. Click **Load from File**.
5. Browse to the model's Application Libraries folder and double-click the file `li_battery_sigr_hysteresis_Eeq_Si_lower.txt`.
6. Locate the **Interpolation and Extrapolation** section. From the **Extrapolation** list, choose **Linear**.

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

Function	Unit
Eeq_Si_lower	V

8 Click to expand the **Related Functions** section. Select the **Define inverse function** check box.

9 In the **Inverse function name** text field, type `Eeq_Si_lower_inv`.

10 Click to collapse the **Related Functions** section.

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_el
L_sep

5 Click **Build All Objects**.

MATERIALS

Graphite, LixC6 MCMB (Negative, Li-ion Battery) (mat1)

1 In the **Model Builder** window, under **Component 1 (comp1)>Materials** click **Graphite, LixC6 MCMB (Negative, Li-ion Battery) (mat1)**.

2 Select Domain 1 only.

LiPF6 in 3:7 EC:EMC (Liquid, Li-ion Battery) (mat2)

1 In the **Model Builder** window, click **LiPF6 in 3:7 EC:EMC (Liquid, Li-ion Battery) (mat2)**.

2 Select Domain 2 only.

Lithium Metal, Li (Negative, Li-ion Battery) (mat3)

1 In the **Model Builder** window, click **Lithium Metal, Li (Negative, Li-ion Battery) (mat3)**.

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

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

4 Select Boundary 3 only.

DEFINITIONS

Define integration operators at the location of the reference electrode, and the current collector of the blended electrode, to allow for local variables to be accessed globally.

Integration - Reference

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

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

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

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

5 Select Boundary 2 only.

Integration - Current Collector

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

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

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

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

5 Select Boundary 1 only.

Import variables. Some expressions will render warnings, indicating missing definitions. This is expected at this stage and will be resolved as soon as the interfaces have been fully set up. The Electrode variables include the silicon equilibrium potential and relevant definitions related to the hysteresis.

Variables - Electrode

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

2 In the **Settings** window for **Variables**, type `Variables - 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. Click **Load from File**.

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

Variables - Global

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

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

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

Name	Expression	Unit	Description
`i_app`	`i_1C*C_rate*CurrentDirection`		`Applied current density`
`E_vs_ref`	`intop_cc(phis)-intop_ref(phil)`	`V`	`Electrode potential vs reference`
`SOC`	`Cap/Q_el`		`Electrode SOC`

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`.

Define the graphite material properties of the blended porous electrode in a **Porous Electrode** node.

Porous Electrode 1 - Graphite

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

2 In the **Settings** window for **Porous Electrode**, type `Porous Electrode 1 - Graphite` in the **Label** text field.

3 Select Domain 1 only.

4 Locate the **Electrolyte Properties** section. From the **Electrolyte material** list, choose **LiPF6 in 3:7 EC:EMC (Liquid, Li-ion Battery) (mat2)**.

5 Locate the **Electrode Properties** section. In the σ_s text field, type `sigma_s`.

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

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

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_Gr_init`.

4 Locate the **Material** section. From the **Particle material** list, choose **Graphite, LixC6 MCMB (Negative, Li-ion Battery) (mat1)**.

5 Locate the **Particle Transport Properties** section. In the r_p text field, type `rp_Gr`.

6 Click to expand the **Operational SOCs for Initial Cell Charge Distribution** section. From the soc_{min} list, choose **User defined**. From the soc_{max} list, choose **User defined**.

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 **Graphite, LixC6 MCMB (Negative, Li-ion Battery) (mat1)**.

4 Locate the **Electrode Kinetics** section. In the $i_{0,ref}(T)$ text field, type `i0_ref_Gr`.

Define the Silicon material properties of the blended porous electrode using an **Additional Porous Electrode Material** node.

Additional Porous Electrode Material 1 - Silicon

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

2 In the **Settings** window for **Additional Porous Electrode Material**, type `Additional Porous Electrode Material 1 - Silicon` in the **Label** text field.

3 Select Domain 1 only.

4 Locate the **Volume Fraction** section. In the ε_s text field, type `epss_Si`.

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_Si_init`.

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

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_Si`.

7 Click to expand the **Operational SOCs for Initial Cell Charge Distribution** section. From the soc_{min} list, choose **User defined**. From the soc_{max} list, choose **User defined**.

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_Si`.

4 Locate the **Electrode Kinetics** section. In the $i_{0,ref}(T)$ text field, type `i0_ref_Si`.

Electrode Surface 1 - Lithium Metal

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

2 In the **Settings** window for **Electrode Surface**, type `Electrode Surface 1 - Lithium Metal` in the **Label** text field.

3 Select Boundary 3 only.

Electrode Current Density 1

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

2 Select Boundary 1 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`.

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 *phis* text field, type `E_init_el`.

ADD PHYSICS

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

Add a **Coefficient Form PDE** to compute the memory variable, `S`.

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

3 In the tree, select **Mathematics>PDE Interfaces>Coefficient Form PDE (c)**.

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

COEFFICIENT FORM PDE - MEMORY VARIABLE

1 In the **Settings** window for **Coefficient Form PDE**, type `Coefficient Form PDE - Memory Variable` in the **Label** text field.

2 Select Domain 1 only.

3 Click to expand the **Dependent Variables** section. In the **Field name (1)** text field, type `S`.

4 In the **Dependent variables (1)** table, enter the following settings:

S

Coefficient Form PDE 1

1 In the **Model Builder** window, under **Component 1 (comp1)>Coefficient Form PDE - Memory Variable (c)** click **Coefficient Form PDE 1**.

2 In the **Settings** window for **Coefficient Form PDE**, locate the **Diffusion Coefficient** section.

3 In the *c* text field, type `0`.

4 Locate the **Source Term** section. In the *f* text field, type `dSdt`.

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 *S* text field, type `S_init`.

ADD PHYSICS

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

2 In the tree, select **Mathematics>ODE and DAE Interfaces>Events (ev)**.

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

EVENTS - CHARGE-DISCHARGE CONTROL

Add an **Events** interface to cycle the blended electrode between the voltage limits and keep track of the current direction.

1 In the **Settings** window for **Events**, type `Events - Charge-Discharge Control` in the **Label** text field.

Discrete States 1

1 Right-click **Component 1 (comp1)>Events - Charge-Discharge Control** and choose **Discrete States**.

2 In the **Settings** window for **Discrete States**, locate the **Discrete States** section.

3 In the table, enter the following settings:

Name	Initial value (u0)	Description
`CurrentDirection`	`-1`	`Direction of current`

Indicator States 1

1 In the **Physics** toolbar, click **Global** and choose **Indicator States**.

2 In the **Settings** window for **Indicator States**, locate the **Indicator Variables** section.

3 In the table, enter the following settings:

Name	g(v,vt,vtt,t)	Initial value (u0)	Description
switch	-(E_vs_ref-E_switch)	0	
end	E_vs_ref-E_end	0	

Implicit Event 1

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

2 In the **Settings** window for **Implicit Event**, locate the **Event Conditions** section.

3 In the **Condition** text field, type `switch>0`.

4 Locate the **Reinitialization** section. In the table, enter the following settings:

Variable	Expression
CurrentDirection	1

Implicit Event 2

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

2 In the **Settings** window for **Implicit Event**, locate the **Event Conditions** section.

3 In the **Condition** text field, type `end>0`.

ADD PHYSICS

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

2 In the tree, select **Mathematics>ODE and DAE Interfaces>Global ODEs and DAEs (ge)**.

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

GLOBAL ODES AND DAES - CHARGE INTEGRATION

Define global **Global ODEs and DAEs** interfaces to compute cumulative variables.

1 In the **Settings** window for **Global ODEs and DAEs**, type `Global ODEs and DAEs - Charge Integration` in the **Label** text field.

Global Equations 1 (ODE1)

1 In the **Model Builder** window, under **Component 1 (comp1)>Global ODEs and DAEs - Charge Integration (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 (u_t0) (1/s)	Description
Cap	d(Cap, t)+ i_app	0	0	Cumulative charge

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

ADD PHYSICS

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

2 In the tree, select **Mathematics>ODE and DAE Interfaces>Global ODEs and DAEs (ge)**.

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

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

GLOBAL ODES AND DAES - ENERGY INTEGRATION

In the **Settings** window for **Global ODEs and DAEs**, type `Global ODEs and DAEs - Energy Integration` in the **Label** text field.

Global Equations 1 (ODE2)

1 In the **Model Builder** window, under **Component 1 (comp1)>Global ODEs and DAEs - Energy Integration (ge2)** click **Global Equations 1 (ODE2)**.

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 (u_t0) (1/s)	Description
E_lith	d(E_lith,t)-if(CurrentDirection==-1, i_app*(E_vs_ref-E_max_el),0)	0	0	Cumulative lithiation energy
E_delith	d(E_delith,t)-if(CurrentDirection==1, -i_app*(E_vs_ref-E_max_el),0)	0	0	Cumulative delithiation energy

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	J/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	W/m^2

STUDY 1

Set up a parametric sweep to simulate the half cell for different C-rates and blended electrode compositions.

Parametric Sweep

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

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

3 Click **Add**.

4 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
C_rate (Lithiation/delithiation rate)	0.1 1	

5 Click **Add**.

6 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
Si_f (Fraction of Si in electrode blend)	`0.1 1 4`	%

7 From the **Sweep type** list, choose **All combinations**.

Step 1: Time Dependent

1 In the **Model Builder** window, click **Step 1: 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(0,0.01/C_rate,2.1/C_rate)`.

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 **Study 1>Solver Configurations> Solution 1 (sol1)>Time-Dependent Solver 1** node.

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

5 In the **Settings** window for **Stop Condition**, locate the **Stop Events** section.

6 In the table, select the **Active** check box for **Events - Charge-Discharge Control (ev)/ Implicit Event 2**.

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

8 Clear the **Add warning** check box.

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

The following steps reproduce the model figures.

RESULTS

0.1 C Electrode Voltage vs SOC

1 In the **Settings** window for **1D Plot Group**, type `0.1 C Electrode Voltage vs SOC` in the **Label** text field.

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

3 In the **Parameter values (C_rate)** list, select **0.1**.

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

5 Locate the **Plot Settings** section.

6 Select the **y-axis label** check box. In the associated text field, type `Potential vs Reference (V)`.

Point Graph 1

1 In the **Model Builder** window, expand the **0.1 C Electrode Voltage vs SOC** node, then click **Point Graph 1**.

2 In the **Settings** window for **Point Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)> Definitions>Variables>E_vs_ref - Electrode potential vs reference - V**.

3 Locate the **x-Axis Data** section. From the **Axis source data** list, choose **Inner solutions**.

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

5 Click **Replace Expression** in the upper-right corner of the **x-Axis Data** section. From the menu, choose **Component 1 (comp1)>Definitions>Variables>SOC - Electrode SOC - 1**.

6 Click to expand the **Legends** section. Select the **Show legends** check box.

7 Find the **Include** subsection. Clear the **Point** check box.

8 Clear the **Solution** check box.

9 Find the **Prefix and suffix** subsection. In the **Prefix** text field, type `eval(Si_f*100) % Si in Gr`.

10 In the **0.1 C Electrode Voltage vs SOC** toolbar, click **Plot**.

0.1 C Electrode Voltage vs SOC

In the **Model Builder** window, right-click **0.1 C Electrode Voltage vs SOC** and choose **Duplicate**.

1 C Electrode Voltage vs SOC

1 In the **Model Builder** window, under **Results** click **0.1 C Electrode Voltage vs SOC 1**.

2 In the **Settings** window for **1D Plot Group**, type `1 C Electrode Voltage vs SOC` in the **Label** text field.

3 Locate the **Data** section. In the **Parameter values (C_rate)** list, select **1**.

4 In the **1 C Electrode Voltage vs SOC** toolbar, click **Plot**.

0.1 C Average Material Lithiation Levels

1 In the **Model Builder** window, under **Results** click **Average Electrode State of Charge (liion)**.

2 In the **Settings** window for **1D Plot Group**, type `0.1 C Average Material Lithiation Levels` in the **Label** text field.

3 Locate the **Data** section. From the **Parameter selection (C_rate)** list, choose **From list**.

4 In the **Parameter values (C_rate)** list, select **0.1**.

5 From the **Parameter selection (Si_f)** list, choose **From list**.

6 In the **Parameter values (Si_f (%))** list, select **4**.

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

8 Locate the **Plot Settings** section.

9 Select the **y-axis label** check box. In the associated text field, type `Degree of lithiation (1)`.

10 Locate the **Legend** section. From the **Position** list, choose **Upper left**.

Global 1

1 In the **Model Builder** window, expand the **0.1 C Average Material Lithiation Levels** node, then click **Global 1**.

2 In the **Settings** window for **Global**, click **Add Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)>Lithium-Ion Battery> Particle intercalation>liion.soc_average_addm1 - Average SOC, Additional Porous Electrode Material 1 - Silicon - 1**.

3 Click to expand the **Legends** section. From the **Legends** list, choose **Manual**.

4 In the table, enter the following settings:

Legends
Gr
Si

5 In the **0.1 C Average Material Lithiation Levels** toolbar, click **Plot**.

0.1 C Average Material Lithiation Levels

In the **Model Builder** window, right-click **0.1 C Average Material Lithiation Levels** and choose **Duplicate**.

1 C Average Material Lithiation Levels

1 In the **Model Builder** window, under **Results** click **0.1 C Average Material Lithiation Levels 1**.

2 In the **Settings** window for **1D Plot Group**, type `1 C Average Material Lithiation Levels` in the **Label** text field.

3 Locate the **Data** section. In the **Parameter values (C_rate)** list, select **1**.

4 In the **1 C Average Material Lithiation Levels** toolbar, click **Plot**.

Hysteresis Memory Variable

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

2 In the **Settings** window for **1D Plot Group**, type `Hysteresis Memory Variable` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Study 1/ Parametric Solutions 1 (sol2)**.

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

5 In the **Parameter values (C_rate)** list, select **1**.

6 From the **Parameter selection (Si_f)** list, choose **From list**.

7 In the **Parameter values (Si_f (%))** list, select **4**.

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

9 Locate the **Legend** section. From the **Position** list, choose **Upper middle**.

Point Graph 1

1 Right-click **Hysteresis Memory Variable** and choose **Point Graph**.

2 Select Boundaries 1 and 2 only.

3 In the **Settings** window for **Point Graph**, locate the **y-Axis Data** section.

4 In the **Expression** text field, type `S`.

5 Locate the **Legends** section. Select the **Show legends** check box.

6 From the **Legends** list, choose **Manual**.

7 In the table, enter the following settings:

Legends
`Current Collector-Electrode`
`Separator-Electrode`

8 In the **Hysteresis Memory Variable** toolbar, click **Plot**.

Delithiation Energy Densities

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

2 In the **Settings** window for **1D Plot Group**, type `Delithiation Energy Densities` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **None**.

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

5 Locate the **Plot Settings** section.

6 Select the **x-axis label** check box. In the associated text field, type `Si Volume Fraction in Electrode Blend (%)`.

7 Select the **y-axis label** check box. In the associated text field, type `E<sub>delith</sub> (J/m<sup>3</sup>)`.

8 Locate the **Legend** section. From the **Position** list, choose **Upper left**.

Global 1

1 Right-click **Delithiation Energy Densities** and choose **Global**.

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

3 From the **Dataset** list, choose **Study 1/Parametric Solutions 1 (sol2)**.

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

5 In the **Parameter values (C_rate)** list, select **0.1**.

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

7 Locate the **y-Axis Data** section. Click  **Clear Table**.

8 In the table, enter the following settings:

Expression	Unit	Description
`E_delith/L_el`	`J/m^3`	

9 Locate the **Legends** section. From the **Legends** list, choose **Manual**.

10 In the table, enter the following settings:

Legends
`0.1C`

11 Locate the **x-Axis Data** section. From the **Axis source data** list, choose **Outer solutions**.

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

13 Click **Replace Expression** in the upper-right corner of the **x-Axis Data** section. From the menu, choose **Global definitions>Parameters>Si_f - Fraction of Si in electrode blend - 1**.

14 Locate the **x-Axis Data** section. From the **Unit** list, choose **%**.

15 Right-click **Global 1** and choose **Duplicate**.

Global 2

1 In the **Model Builder** window, click **Global 2**.

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

3 In the **Parameter values (C_rate)** list, select **1**.

4 Locate the **Legends** section. In the table, enter the following settings:

Legends
1C

5 In the **Delithiation Energy Densities** toolbar, click **Plot**.

Delithiation Energy Densities

In the **Model Builder** window, right-click **Delithiation Energy Densities** and choose **Duplicate**.

Lithiation/Delithiation Energy Efficiencies

1 In the **Model Builder** window, under **Results** click **Delithiation Energy Densities 1**.

2 In the **Settings** window for **1D Plot Group**, type `Lithiation/Delithiation Energy Efficiencies` in the **Label** text field.

3 Locate the **Plot Settings** section. In the **y-axis label** text field, type `E<sub>delith</sub>/E<sub>lith</sub> (1)`.

4 Locate the **Legend** section. From the **Position** list, choose **Upper right**.

Global 1

1 In the **Model Builder** window, expand the **Lithiation/Delithiation Energy Efficiencies** node, then click **Global 1**.

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

3 In the table, enter the following settings:

Expression	Unit	Description
`E_delith/E_lith`	1	

Global 2

1 In the **Model Builder** window, click **Global 2**.

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

3 In the table, enter the following settings:

Expression	Unit	Description
`E_delith/E_lith`	1	

4 In the **Lithiation/Delithiation Energy Efficiencies** toolbar, click **Plot**.

DEFINITIONS (COMP1)

Interpolation - Eeq Si Upper (Eeq_Si_upper, Eeq_Si_upper_inv)

1. In the **Model Builder** window, under **Component 1 (comp1)>Definitions** click **Interpolation - Eeq Si Upper (Eeq_Si_upper, Eeq_Si_upper_inv)**.
2. In the **Settings** window for **Interpolation**, click **Create Plot**.

RESULTS

Equilibrium Potentials vs Lithiation

1. In the **Settings** window for **1D Plot Group**, type `Equilibrium Potentials vs Lithiation` in the **Label** text field.
2. Locate the **Data** section. From the **Dataset** list, choose **None**.
3. Locate the **Title** section. From the **Title type** list, choose **None**.
4. Locate the **Plot Settings** section.
5. Select the **x-axis label** check box. In the associated text field, type `Degree of lithiation (1)`.
6. In the **y-axis label** text field, type `Potential vs Li/Li<sup>+</sup> (V)`.
7. Locate the **Axis** section. Select the **Manual axis limits** check box.
8. In the **x minimum** text field, type `0`.
9. In the **x maximum** text field, type `0.9`.
10. In the **y minimum** text field, type `0`.
11. In the **y maximum** text field, type `1`.

Function 1

1. In the **Model Builder** window, expand the **Equilibrium Potentials vs Lithiation** node, then click **Function 1**.
2. In the **Settings** window for **Function**, locate the **Data** section.
3. From the **Dataset** list, choose **Grid 1D 1**.
4. Locate the **y-Axis Data** section. Clear the **Description** check box.
5. Locate the **Output** section. From the **Display** list, choose **Line**.
6. From the **Extrapolation** list, choose **None**.
7. Click to expand the **Legends** section. Select the **Show legends** check box.
8. From the **Legends** list, choose **Manual**.

9 In the table, enter the following settings:

Legends
E<sub>eq, Si, upper</sup>

DEFINITIONS (COMP1)

Interpolation - Eeq Si Lower (Eeq_Si_lower, Eeq_Si_lower_inv)

1 In the **Model Builder** window, under **Component 1 (comp1)>Definitions** click **Interpolation - Eeq Si Lower (Eeq_Si_lower, Eeq_Si_lower_inv)**.

2 In the **Settings** window for **Interpolation**, click **Create Plot**.

RESULTS

Function 1

In the **Model Builder** window, expand the **1D Plot Group 15** node, then click **Function 1**.

Function 2

1 Drag and drop below **Equilibrium Potentials vs Lithiation>Function 1**.

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

3 From the **Dataset** list, choose **Grid 1D 1a**.

4 Locate the **y-Axis Data** section. Clear the **Description** check box.

5 Locate the **Output** section. From the **Display** list, choose **Line**.

6 From the **Extrapolation** list, choose **None**.

7 Locate the **Legends** section. Select the **Show legends** check box.

8 From the **Legends** list, choose **Manual**.

9 In the table, enter the following settings:

Legends
E<sub>eq, Si, lower</sup>

MATERIALS

Graphite, LixC6 MCMB (Negative, Li-ion Battery) (mat1)

In the **Model Builder** window, expand the **Component 1 (comp1)>Materials>Graphite, LixC6 MCMB (Negative, Li-ion Battery) (mat1)** node.

Interpolation 1 (Eeq_int1, Eeq_inv)

1 In the **Model Builder** window, expand the **Component 1 (comp1)>Materials>Graphite, LixC6 MCMB (Negative, Li-ion Battery) (mat1)>Equilibrium potential (elpot)** node, then click **Interpolation 1 (Eeq_int1, Eeq_inv)**.

2 In the **Settings** window for **Interpolation**, click **Create Plot**.

RESULTS

Function 1

In the **Model Builder** window, expand the **1D Plot Group 16** node, then click **Function 1**.

Function 3

1 Drag and drop below **Equilibrium Potentials vs Lithiation>Function 2**.

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

3 From the **Dataset** list, choose **Grid 1D 2**.

4 Locate the **y-Axis Data** section. Clear the **Description** check box.

5 Locate the **Legends** section. Select the **Show legends** check box.

6 From the **Legends** list, choose **Manual**.

7 In the table, enter the following settings:

Legends
E<sub>eq, Gr</sup>

8 In the **Equilibrium Potentials vs Lithiation** toolbar, click **Plot**.

1D Plot Group 15, 1D Plot Group 16, 1D Plot Group 7, 1D Plot Group 8, Coefficient Form PDE - Memory Variable, Electrode Potential with Respect to Ground (liion), Electrolyte Potential (liion), Electrolyte Salt Concentration (liion)

1 In the **Model Builder** window, under **Results**, Ctrl-click to select **Electrolyte Potential (liion)**, **Electrode Potential with Respect to Ground (liion)**, **Electrolyte Salt Concentration (liion)**, **Coefficient Form PDE - Memory Variable**, **1D Plot Group 7**, **1D Plot Group 8**, **1D Plot Group 15**, and **1D Plot Group 16**.

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

1 C Electrode Voltage vs SOC

1 In the **Model Builder** window, click **1 C Electrode Voltage vs SOC**.

2 Drag and drop below **0.1 C Electrode Voltage vs SOC**.