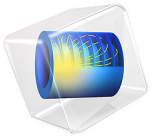

Modeling Impedance in the Lithium-Ion Battery

Introduction

Electrochemical impedance spectroscopy (EIS) is a valuable method to investigate electrochemical systems such as batteries. For a battery, where potential perturbations of varying frequency are applied on an electrode, the impedance response gives insight into several battery properties and processes. At high frequencies, short time-scale processes such as capacitance, electrochemical reactions, and local resistances affect the impedance. On the other hand, at low frequencies, diffusion in the electrolyte and active material particles (that is, large time-scale processes) contribute to the impedance.

This example simulates the impedance of a full lithium-ion battery cell using the Lithium-Ion Battery interface with an AC Impedance Stationary study. The model also reproduces to the results by Abraham et al. (Ref. 1) for sinusoidal potential perturbations between 10 mHz to 1 kHz after model fitting using the Optimization interface.

Note: This tutorial model requires the Optimization Module.

Model Definition

The model consists of the following components:

- Negative porous electrode: LTO ($Li_4Ti_5O_{12}$) active material, electronic conductor, and filler.
- Separator: Celgard 2325
- Positive porous electrode: NCA ($LiNi_{0.08}Co_{0.15}Al_{0.05}O_2$) active material, electronic conductor, and filler.
- Electrolyte: 1.2 M $LiPF_6$ in EC:EMC (3:7 by weight)

A 1D model with three domains of different thickness is used: a 115 µm negative electrode, a 50 µm separator, and a 35 µm positive electrode. The model is set up in a similar fashion as the 1D Isothermal Lithium-Ion Battery, but with double-layer capacitances on the active electrode materials and on the electronic conductor in the positive electrode. The model approach using an additional double-layer at the electronic conductor has, for example, been used by Brown et al. (Ref. 2) to describe experimental EIS spectra measured between 1 mHz and 1 kHz on NCA electrodes.

An AC Stationary Impedance study is used to solve the problem, implying that all variables are shifted from being time dependent to frequency dependent, as illustrated with the following expression:

$$n = n_0 + \mathrm{Re}\{\tilde{n} \cdot e^{2\pi f \cdot it}\}$$

where n is the variable, and subscript 0 denotes the initial value around which the perturbation takes place and tilde the complex perturbation. i is the imaginary unit, f the frequency in Hz, and t the time.

The boundary of the positive electrode current-collector is set to a sinusoidal perturbation with a 10 mV amplitude and the boundary of the negative electrode current-collector fixed to 0 V, that is, ground.

The cell impedance, Z (SI unit: $\Omega \cdot m^2$), is calculated at the boundary of the positive electrode current-collector as follows:

$$\tilde{Z} = \tilde{\phi}_s / (\mathbf{n} \cdot \tilde{\mathbf{I}}_s)$$

where ϕ_s (SI unit: V) is the potential, $\mathbf{n}$ the boundary normal and $\mathbf{I}_s$ (SI unit: Am^{-2}) the current density in the solid. (Note that the `lindev` operator is used in the model file in order to use the perturbing values of the variables in the evaluation.)

Subtracting the reference electrode potential from the solid potential in the numerator enables the analysis of the impedance of the NCA positive electrode versus the reference electrode, thus separating the contribution of each electrode to the impedance. The LTO impedance versus the reference is consequently given by the difference between the cell impedance and NCA impedance versus the reference.

The model is computed for frequencies between 10 mHz and 1 kHz. This range is common in EIS to minimize any errors from experimental interference (e.g. Ref. 2).

OPTIMIZATION

The model is initially solved for the presented experimental set-up (Ref. 1) with the aid of parameters given in Ref. 2. However, since the simulated impedance deviates to a large extent from the experiments, an optimization is performed using the Global Least-Squares Objective feature in the Optimization interface. This feature is set to minimize the least-squares error between the simulated and measured NCA impedance versus the reference

electrode through variation of some control parameters. These parameters are given in Table 1.

TABLE 1: CONTROL PARAMETERS WITH BOUNDS FOR A CELL VOLTAGE OF 2.30V.

Control Parameters	Initial value	Bounds
Exchange current density NCA	1 Am^{-2}	Lower: 1 Am^{-2} Upper: 6 Am^{-2}
Double-layer capacitance NCA	$5 \cdot 10^{-1}$ Fm^{-2}	Lower: $1 \cdot 10^{-1}$ Fm^{-2} Upper: $9 \cdot 10^{-1}$ Fm^{-2}
Film resistance NCA	$1 \cdot 10^{-3}$ Ωm^2	Lower: $1 \cdot 10^{-6}$ Ωm^2 Upper: $5 \cdot 10^{-3}$ Ωm^2
Volumetric double-layer capacitance positive electronic conductor	$5 \cdot 10^{5}$ Fm^{-3}	Lower: $1 \cdot 10^{5}$ Fm^{-3} Upper: $1 \cdot 10^{6}$ Fm^{-3}

The first three parameters have bounds selected as anticipated by the information given by Abraham et al. (Ref. 1). The last parameter depend on the size of the electronic conductor particles. It is also common to run parametric sweeps before selecting control parameters and to narrow down the bounds. Normally the optimization time is reduced and the optimization accuracy is improved when few control parameters and narrow bound intervals are selected.

STUDY SETTINGS

The problem is solved with an AC Impedance, Initial Values study. The optimization solver is set up by adding an Optimization node to the study and selecting the SNOPT method with the numeric gradient method.

Results and Discussion

Simulated and experimental Nyquist spectra from the LTO/NCA cell at 2.30 V are displayed in Figure 1. The simulation utilizes the parameters from Ref. 2. Characteristic semi-circles and low-frequency tails are seen. The largest contribution to the cell impedance is in the positive NCA electrode. The difference between the experimental and simulated impedance spectra of the NCA electrode versus reference is evident: The

simulation shows one large semi-circle and an indication of another semi-circle at high frequencies. The experimental spectrum has a smaller depressed (elongated) semi-circle.

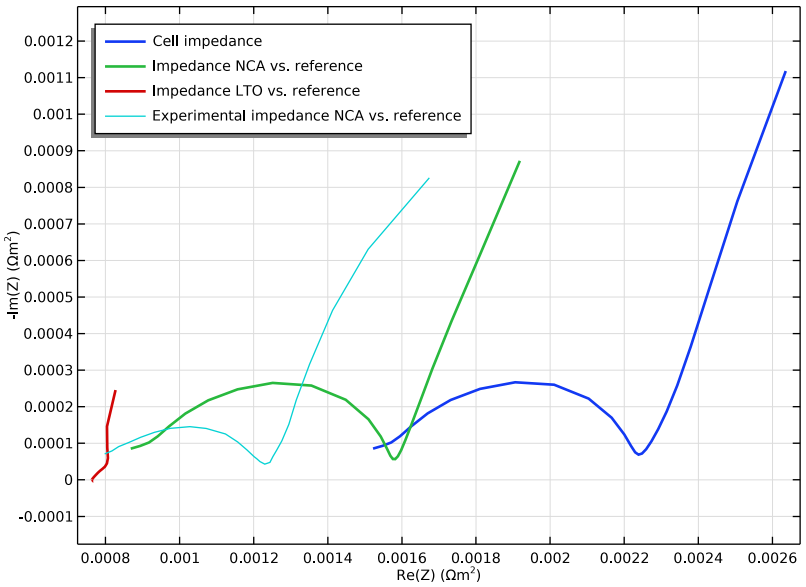

Figure 1: Simulated and experimental Nyquist spectra for 10 mHz to 1 kHz. Parameters taken from Ref. 2.

Since the difference is most prominent in the semi-circle frequency region (that is, mid-high frequencies) mainly the parameters describing short time-scale processes do not fit

the experiments. Four of these parameters are investigated with a parametric sweep to determine their impact on the impedance. The sweep is shown in Figure 2.

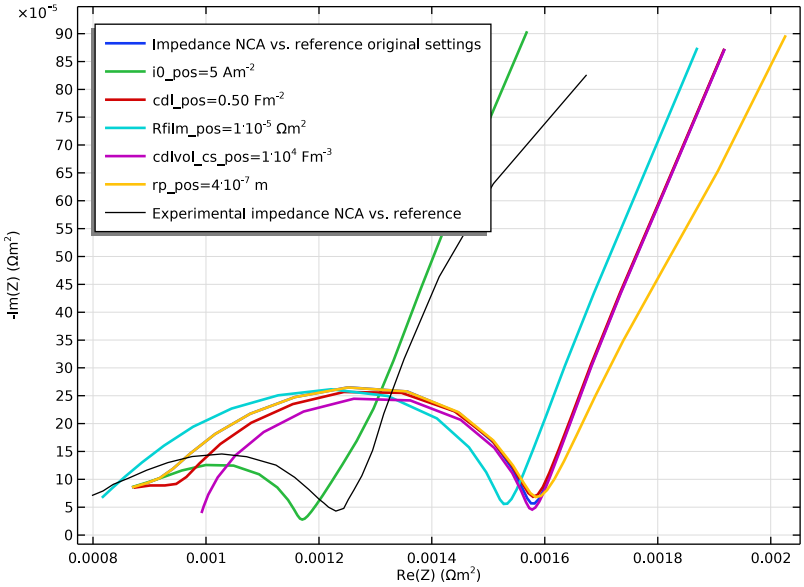

Figure 2: Nyquist plots when testing the impact of five parameters for 10 mHz to 1 kHz.

As a comparison, the sweep also includes variation of the radius of the positive electrode material particles, mainly affecting the large time-scale process of diffusion in the particles. Its impact is therefore more evident at lower frequencies. This is seen in Figure 2, where both the angle and shape of the low-frequency tail change. The results also show that the parameters describing large time-scale processes seem to be quite accurate in the model.

These findings are consistent with the observations by Abraham et al. (Ref. 1) indicating that the electrochemical reaction is less limited in their electrodes. With this input Table 1 is set up and the optimization is run. The resulting spectra are shown in Figure 3.

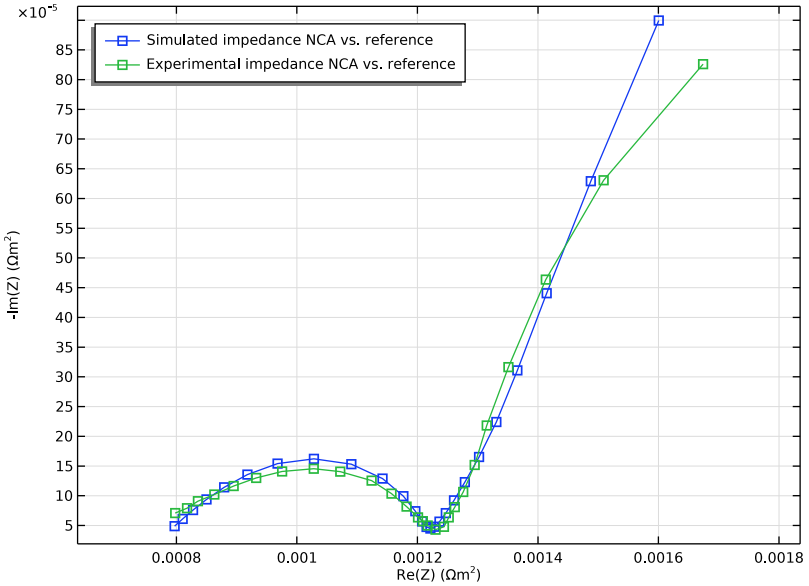

Figure 3: Nyquist spectra with optimized parameters for 10 mHz to 1 kHz. Squares denote the data points used in the optimization.

The simulated and experimental spectra for NCA versus reference are now seen to overlap well. The optimized control parameters are tabulated in Table 2.

TABLE 2: CHANGE OF CONTROL PARAMETERS AFTER OPTIMIZATION.

Control Parameters	**Optimized Value**
Exchange current density NCA	2.5 Am^{-2}
Double-layer capacitance NCA	$4.1 \cdot 10^{-1}$ Fm^{-2}
Film resistance NCA	$1 \cdot 10^{-6}$ Ωm^2
Volumetric double-layer capacitance positive electronic conductor	$5.6 \cdot 10^{5}$ Fm^{-3}

References

1. D.P. Abraham, S. Kawauchi, and D.W. Dees, "Modeling the impedance versus voltage characteristics of $LiNi_{0.08}Co_{0.15}Al_{0.05}O_2$," *Electrochim. Acta*, vol. 53, pp. 2121–2129, 2008.

2. S. Brown, N. Mellgren, M. Vynnycky, and G. Lindbergh, "Impedance as a Tool for Investigating Aging in Lithium-Ion Porous Electrodes. II. Positive Electrode Examination," *J. Electrochem. Soc*, vol. 155, p. A320, 2008.

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

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>Lithium-Ion Battery (liion)**.

3 Click **Add**.

4 Click **Study**.

5 In the **Select Study** tree, select **Preset Studies for Selected Physics Interfaces> AC Impedance, Initial Values**.

6 Click **Done**.

GLOBAL DEFINITIONS

Load parameters from a text file

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_impedance_parameters.txt`.

DEFINITIONS

The impedance is calculated using variables defined in a text file. It is defined at the rightmost boundary versus ground (at the leftmost boundary) or a reference electrode. The `lindev` operator explicitly evaluates the deviation from the stationary solution in the perturbed solution.

Variables 1

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Definitions** and choose **Variables**.

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

3 Click **Load from File**.

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

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 In the table, enter the following settings:

Coordinates (m)
0
L_neg

Interval 2 (i2)

1 In the **Model Builder** window, 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 **Left endpoint** text field, type `L_neg`.

5 In the table, enter the following settings:

Lengths (m)
L_sep

Interval 3 (i3)

1 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 **Left endpoint** text field, type `L_neg+L_sep`.

5 In the table, enter the following settings:

Lengths (m)
L_pos

6 Click **Build Selected**.

7 Click the **Zoom Extents** button in the **Graphics** toolbar.

ADD MATERIAL

The cell materials are available in the Battery Material Library.

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

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

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

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

5 In the tree, select **Battery>Electrodes>LTO Electrode, Li4Ti5O12 (Negative, Li-ion Battery)**.

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

7 In the tree, select **Battery>Electrodes>NCA Electrode, LiNi0.8Co0.15Al0.05O2 (Positive, Li-ion Battery)**.

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

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

DEFINITIONS

Use a domain point probe to retrieve the potential in the middle of the separator where the reference electrode is located.

Reference Electrode (RE) Probe

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

2 In the **Settings** window for **Domain Point Probe**, type `Reference Electrode (RE) Probe` in the **Label** text field.

3 Locate the **Point Selection** section. In row **Coordinate**, set **x** to `L_neg+L_sep/2`.

Point Probe Expression 1 (ppb1)

1 In the **Model Builder** window, expand the **Reference Electrode (RE) Probe** node, then click **Point Probe Expression 1 (ppb1)**.

2 In the **Settings** window for **Point Probe Expression**, type `RE_phi` in the **Variable name** text field.

Integration 1 (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.

LITHIUM-ION BATTERY (LIION)

Set up the model with a negative and a positive porous electrode with a separator in between. Double layers exist on both active materials.

Porous Electrode 1

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Lithium-Ion Battery (liion)** and choose **Porous Electrode**.

2 Select Domain 1 only.

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

4 From the **Electrode material** list, choose **LTO Electrode, Li4Ti5O12 (Negative, Li-ion Battery) (mat2)**.

5 Click to expand the **Film Resistance** section. From the **Film resistance** list, choose **Surface resistance**.

6 In the R_{film} text field, type `Rfilm_neg`.

7 Locate the **Porous Matrix Properties** section. In the ε_s text field, type `epss_neg`.

8 In the ε_l text field, type `epsl_neg`.

9 Locate the **Effective Transport Parameter Correction** section. From the **Electrolyte conductivity** list, choose **User defined**. In the f_l text field, type `epsl_neg^brugl_neg`.

10 From the **Diffusion** list, choose **User defined**. In the f_{Dl} text field, type `epsl_neg^brugl_neg`.

Particle Intercalation 1

1 In the **Model Builder** window, expand the **Porous Electrode 1** node, then click **Particle Intercalation 1**.

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

3 From the **Particle material** list, choose **LTO Electrode, Li4Ti5O12 (Negative, Li-ion Battery) (mat2)**.

4 Locate the **Species Settings** section. In the $c_{s,init}$ text field, type `mat2.elpot.cEeqref*soc0_neg`.

5 Locate the **Particle Transport Properties** section. In the r_p text field, type `rp_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 **LTO Electrode, Li4Ti5O12 (Negative, Li-ion Battery) (mat2)**.

4 Locate the **Electrode Kinetics** section. In the $i_{0,ref}(T)$ text field, type `i0ref_neg`.

Porous Electrode 1

In the **Model Builder** window, click **Porous Electrode 1**.

Porous Matrix Double Layer Capacitance 1

1 In the **Physics** toolbar, click **Attributes** and choose **Porous Matrix Double Layer Capacitance**.

2 In the **Settings** window for **Porous Matrix Double Layer Capacitance**, locate the **Porous Matrix Double Layer Capacitance** section.

3 In the C_{dl} text field, type `cdl_neg`.

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 From the **Electrode material** list, choose **NCA Electrode, LiNi0.8Co0.15Al0.05O2 (Positive, Li-ion Battery) (mat3)**.

5 Locate the **Film Resistance** section. From the **Film resistance** list, choose **Surface resistance**.

6 In the R_{film} text field, type `Rfilm_pos`.

7 Locate the **Porous Matrix Properties** section. In the ε_s text field, type `epss_pos`.

8 In the ε_l text field, type `epsl_pos`.

9 Locate the **Effective Transport Parameter Correction** section. From the **Electrolyte conductivity** list, choose **User defined**. In the f_l text field, type `epsl_pos^brugl_pos`.

10 From the **Diffusion** list, choose **User defined**. In the f_{Dl} text field, type `epsl_pos^brugl_pos`.

Particle Intercalation 1

1 In the **Model Builder** window, expand the **Porous Electrode 2** node, then click **Particle Intercalation 1**.

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

3 From the **Particle material** list, choose **NCA Electrode, LiNi0.8Co0.15Al0.05O2 (Positive, Li-ion Battery) (mat3)**.

4 Locate the **Species Settings** section. In the $c_{s,init}$ text field, type `mat3.elpot.cEeqref*soc0_pos`.

5 Locate the **Particle Transport Properties** section. In the r_p text field, type `rp_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 **NCA Electrode, LiNi0.8Co0.15Al0.05O2 (Positive, Li-ion Battery) (mat3)**.

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

5 In the i_0 text field, type `i0_pos`.

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

Porous Electrode 2

In the **Model Builder** window, click **Porous Electrode 2**.

Porous Matrix Double Layer Capacitance 1

1 In the **Physics** toolbar, click **Attributes** and choose **Porous Matrix Double Layer Capacitance**.

2 In the **Settings** window for **Porous Matrix Double Layer Capacitance**, locate the **Porous Matrix Double Layer Capacitance** section.

3 In the C_{dl} text field, type `cdl_pos`.

4 From the **Double layer area** list, choose **User defined**. In the $a_{v,dl}$ text field, type `as_pos`.

Separator 1

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

2 Select Domain 2 only.

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

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

5 Locate the **Effective Transport Parameter Correction** section. From the **Electrolyte conductivity** list, choose **User defined**. In the f_l text field, type `epsl_sep^brugl_sep`.

6 From the **Diffusion** list, choose **User defined**. In the f_{Dl} text field, type `epsl_sep^brugl_sep`.

Initial Values 1

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

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

3 In the list, select **3**.

4 Locate the **Initial Values** section. In the *phil* text field, type `-mat2.elpot.Eeq_int1(soc0_neg)`.

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

Initial Values 2

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

2 Select Domain 3 only.

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

4 In the *phil* text field, type `-mat2.elpot.Eeq_int1(soc0_neg)`.

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

6 In the *phis* text field, type `mat3.elpot.Eeq_int1(soc0_pos)-mat2.elpot.Eeq_int1(soc0_neg)`.

Electric Ground 1

Select ground on the current collector of the negative LTO electrode. Set a 10 mV perturbation around the cell voltage of 2.30 V.

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

2 Select Boundary 1 only.

Electric Potential 1

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

2 Select Boundary 4 only.

3 In the **Settings** window for **Electric Potential**, locate the **Electric Potential** section.

4 In the $\phi_{s,bnd}$ text field, type `E_cell_init`.

Harmonic Perturbation 1

1 In the **Physics** toolbar, click **Attributes** and choose **Harmonic Perturbation**.

2 In the **Settings** window for **Harmonic Perturbation**, locate the **Harmonic Perturbation** section.

3 In the $\Delta\phi_s$ text field, type `E_pert`.

Additional Porous Electrode Material 1

Add an Additional Porous Electrode Material feature to model the electronic conductor in NCA.

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

2 Select Domain 3 only.

3 In the **Settings** window for **Additional Porous Electrode Material**, locate the **Particle Properties** section.

4 From the list, choose **Nonintercalating particles**.

Porous Electrode Reaction 1

No electrochemical reaction takes place on the electronic conductor, but a double layer capacitance exists.

1 In the **Model Builder** window, expand the **Additional Porous Electrode Material 1** node.

2 Right-click **Porous Electrode Reaction 1** and choose **Disable**.

Additional Porous Electrode Material 1

In the **Model Builder** window, click **Additional Porous Electrode Material 1**.

Porous Matrix Double Layer Capacitance 1

1 In the **Physics** toolbar, click **Attributes** and choose **Porous Matrix Double Layer Capacitance**.

2 In the **Settings** window for **Porous Matrix Double Layer Capacitance**, locate the **Porous Matrix Double Layer Capacitance** section.

3 In the C_{dl} text field, type `1[F/m^2]`.

4 From the **Double layer area** list, choose **User defined**. In the $a_{v,dl}$ text field, type `cdlvol_cs_pos/1[F/m^2]`.

MESH 1

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

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

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

Size

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

2 In the **Settings** window for **Size**, locate the **Element Size** section.

3 Click the **Custom** button.

4 Locate the **Element Size Parameters** section. In the **Maximum element size** text field, type `1e-5`.

Size 1

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

2 Select Domains 2 and 3 only.

3 In the **Settings** window for **Size**, locate the **Element Size** section.

4 Click the **Custom** button.

5 Locate the **Element Size Parameters** section. Select the **Maximum element size** check box.

6 In the associated text field, type `1e-6`.

Size 2

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

2 Select Boundaries 2–4 only.

3 In the **Settings** window for **Size**, locate the **Element Size** section.

4 Click the **Custom** button.

5 Locate the **Element Size Parameters** section. Select the **Maximum element size** check box.

6 In the associated text field, type `5E-7`.

STUDY 1

Solve the model for frequencies between 10 mHz and 1 kHz.

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

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

3 Clear the **Generate default plots** check box.

4 Clear the **Generate convergence plots** check box.

Step 1: Frequency Domain Perturbation

1 In the **Model Builder** window, under **Study 1** click **Step 1: Frequency Domain Perturbation**.

2 In the **Settings** window for **Frequency Domain Perturbation**, locate the **Study Settings** section.

3 In the **Frequencies** text field, type `10^{range(-2,0.2,3)}`.

4 In the **Home** toolbar, click **Compute**.

STUDY 1

Solution 1 (sol1)

Save the solution of the nonoptimized impedance results.

1 In the **Model Builder** window, under **Study 1>Solver Configurations** right-click **Solution 1 (sol1)** and choose **Solution>Copy**.

2 Expand the **Solution 1 (sol1)** node.

Not optimized

1 In the **Model Builder** window, expand the **Study 1>Solver Configurations>Solution 1 (sol1)>Stationary Solver 1** node, then click **Study 1>Solver Configurations>Solution 1 - Copy 1 (sol2)**.

2 In the **Settings** window for **Solution**, type `Not optimized` in the **Label** text field.

RESULTS

Follow these steps to generate Figure 1:

Start by loading experimental data of real and imaginary impedance into a table for plotting purposes. Organize the tables by naming them.

Experimental Impedance Table

1 In the **Results** toolbar, click **Table**.

2 In the **Settings** window for **Table**, type `Experimental Impedance Table` in the **Label** text field.

3 Locate the **Data** section. Click **Import**.

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

Reference Electrode (RE) Probe Table

1 In the **Model Builder** window, under **Results>Tables** click **Probe Table 1**.

2 In the **Settings** window for **Table**, type `Reference Electrode (RE) Probe Table` in the **Label** text field.

Reference Electrode (RE) Potential Probe Plot

1 In the **Model Builder** window, under **Results** click **Probe Plot Group 1**.

2 In the **Settings** window for **1D Plot Group**, type `Reference Electrode (RE) Potential Probe Plot` in the **Label** text field.

Nyquist plots

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

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

3 Click to expand the **Title** section. Locate the **Data** section. From the **Dataset** list, choose **Study 1/Not optimized (sol2)**.

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

5 Locate the **Plot Settings** section. Select the **x-axis label** check box.

6 In the associated text field, type `Re(Z) ([Omega]m<sup>2</sup>)`.

7 Select the **y-axis label** check box.

8 In the associated text field, type `-Im(Z) ([Omega]m<sup>2</sup>)`.

Cell impedance

1 Right-click **Nyquist plots** and choose **Point Graph**.

2 In the **Settings** window for **Point Graph**, type `Cell impedance` in the **Label** text field.

3 Select Boundary 4 only.

4 Locate the **y-Axis Data** section. In the **Expression** text field, type `-imag(Z_ground)`.

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

6 In the **Expression** text field, type `real(Z_ground)`.

7 Click to expand the **Coloring and Style** section. In the **Width** text field, type `2`.

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

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

10 In the table, enter the following settings:

Legends
Cell impedance

Impedance NCA vs. reference

1 Right-click **Cell impedance** and choose **Duplicate**.

2 In the **Settings** window for **Point Graph**, type `Impedance NCA vs. reference` in the **Label** text field.

3 Locate the **y-Axis Data** section. In the **Expression** text field, type `-imag(Z_ref_NCA)`.

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

5 Locate the **x-Axis Data** section. In the **Expression** text field, type `real(Z_ref_NCA)`.

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

Legends
`Impedance NCA vs. reference`

Impedance LTO vs. reference

1 Right-click **Impedance NCA vs. reference** and choose **Duplicate**.

2 In the **Settings** window for **Point Graph**, type `Impedance LTO vs. reference` in the **Label** text field.

3 Locate the **y-Axis Data** section. In the **Expression** text field, type `-imag(Z_ref_LTO)`.

4 Locate the **x-Axis Data** section. In the **Expression** text field, type `real(Z_ref_LTO)`.

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

Legends
`Impedance LTO vs. reference`

Experimental impedance NCA vs. reference

1 In the **Model Builder** window, right-click **Nyquist plots** and choose **Table Graph**.

The Table Graph plots the experimental data that was imported into the Experimental Impedance Table.

2 In the **Settings** window for **Table Graph**, type `Experimental impedance NCA vs. reference` in the **Label** text field.

3 Locate the **Data** section. From the **Table** list, choose **Experimental Impedance Table**.

4 From the **x-axis data** list, choose **Column 2**.

5 From the **Plot columns** list, choose **Manual**.

6 In the **Columns** list, select **Column 3**.

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
`Experimental impedance NCA vs. reference`

Nyquist plots

1 In the **Model Builder** window, click **Nyquist plots**.

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

3 From the **Position** list, choose **Upper left**.

4 Locate the **Axis** section. Select the **Preserve aspect ratio** check box.

5 In the **Nyquist plots** toolbar, click **Plot**.

6 Click the **Zoom Extents** button in the **Graphics** toolbar.

STUDY 1

Add a parametric sweep to investigate the impact four key parameters have on the impedance of NCA versus the reference and how it relates to the experimental measurements.

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 **Load from File**.

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

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

Parametric sweep

1 In the **Model Builder** window, under **Study 1>Solver Configurations** click **Parametric Solutions 1 (sol3)**.

2 In the **Settings** window for **Solution**, type `Parametric sweep` in the **Label** text field.

RESULTS

Nyquist plots parametric sweep

1 In the **Model Builder** window, right-click **Nyquist plots** and choose **Duplicate**.

Rename the solution for the parametric sweep.

2 In the **Settings** window for **1D Plot Group**, type `Nyquist plots parametric sweep` in the **Label** text field.

Follow these steps to generate Figure 2:

Impedance NCA vs. reference

1 In the **Model Builder** window, expand the **Nyquist plots parametric sweep** node, then click **Impedance NCA vs. reference**.

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

3 From the **Dataset** list, choose **Study 1/Parametric sweep (sol3)**.

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

Legends
`Impedance NCA vs. reference original settings`
`i0_pos=5 Am<sup>-2</sup>`
`cdl_pos=0.50 Fm<sup>-2</sup>`
Rfilm_pos=1[.]10⁻⁵ Ωm²
`cdlvol_cs_pos=1<sup>.</sup>10<sup>4</sup> Fm<sup>-3</sup>`
`rp_pos=4<sup>.</sup>10<sup>-7</sup> m`

Cell impedance

In the **Model Builder** window, right-click **Cell impedance** and choose **Disable**.

Impedance LTO vs. reference

In the **Model Builder** window, right-click **Impedance LTO vs. reference** and choose **Disable**.

Nyquist plots parametric sweep

1 In the **Model Builder** window, click **Nyquist plots parametric sweep**.

2 In the **Nyquist plots parametric sweep** toolbar, click **Plot**.

3 Click the **Zoom Extents** button in the **Graphics** toolbar.

COMPONENT 1 (COMP1)

Now use Optimization to fit the model to experimental data.

ADD PHYSICS

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

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

3 In the tree, select **Mathematics>Optimization and Sensitivity>General Optimization (opt)**.

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

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

GENERAL OPTIMIZATION (OPT)

Global Least-Squares Objective 1

Select the optimization of global parameters using the least squares method.

1 Right-click **Component 1 (comp1)>General Optimization (opt)** and choose **Global Least-Squares Objective**.

Import the experimental data in `csv` format for the impedance of the NCA electrode versus the reference.

2 In the **Settings** window for **Global Least-Squares Objective**, locate the **Experimental Data** section.

3 Click **Browse**.

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

Parameter Column 1

The first column of the experimental data contains the global parameter frequency.

1 In the **Physics** toolbar, click **Attributes** and choose **Parameter Column**.

2 In the **Settings** window for **Parameter Column**, locate the **Parameter Column** section.

3 In the **Parameter name** text field, type `freq`.

Global Least-Squares Objective 1

The second column of the experimental data contains the global value real impedance.

In the **Model Builder** window, click **Global Least-Squares Objective 1**.

Value Column 1

1 In the **Physics** toolbar, click **Attributes** and choose **Value Column**.

2 In the **Settings** window for **Value Column**, locate the **Value Column** section.

3 In the **Expression** text field, type `intop1(real(Z_ref_NCA))`.

4 In the **Variable name** text field, type `Real_impedance`.

5 In the **Column contribution weight** text field, type `1e6`.

Global Least-Squares Objective 1

The third column of the experimental data contains the global value imaginary impedance.

In the **Model Builder** window, click **Global Least-Squares Objective 1**.

Value Column 2

1 In the **Physics** toolbar, click **Attributes** and choose **Value Column**.

2 In the **Settings** window for **Value Column**, locate the **Value Column** section.

3 In the **Expression** text field, type `-intop1(imag(Z_ref_NCA))`.

4 In the **Variable name** text field, type `Imaginary_impedance`.

5 In the **Column contribution weight** text field, type `1e6`.

ROOT

Add a second AC impedance Initial Values study and include the Optimization feature.

ADD STUDY

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

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

3 Find the **Studies** subsection. In the **Select Study** tree, select **Preset Studies for Selected Physics Interfaces>Lithium-Ion Battery>AC Impedance, Initial Values**.

4 Click **Add Study** in the window toolbar.

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

STUDY 2

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

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

3 Clear the **Generate default plots** check box.

4 Clear the **Generate convergence plots** check box.

Optimization

Select `iO_pos`, `Rfilm_pos`, `cdl_pos`, and `cslvol_cs_pos` as the four parameters to be optimized. The Optimization tolerance is set to `1e-4`.

1 In the **Study** toolbar, click **Optimization**.

The SNOPT method allows the use of lower and upper bounds.

2 In the **Settings** window for **Optimization**, locate the **Optimization Solver** section.

3 From the **Method** list, choose **SNOPT**.

4 In the **Optimality tolerance** text field, type `1E-4`.

5 Find the **Solver settings** subsection. From the **Least-squares time/parameter method** list, choose **From least-squares objective**.

6 Locate the **Control Variables and Parameters** section. Click **Add**.

7 In the table, enter the following settings:

Parameter name	Initial value	Scale	Lower bound	Upper bound
i0_pos (Exchange current density positive electrode)	1[A/m^2]	1	1	6

8 Click **Add**.

9 In the table, enter the following settings:

Parameter name	Initial value	Scale	Lower bound	Upper bound
Rfilm_pos (Film resistance positive electrode)	1e-3[m^2/S]	1e-3	1e-6	5e-3

10 Click **Add**.

11 In the table, enter the following settings:

Parameter name	Initial value	Scale	Lower bound	Upper bound
cdl_pos (Double layer capacitance positive electrode material)	0.5[F/m^2]	1	0.10	0.90

12 Click **Add**.

13 In the table, enter the following settings:

Parameter name	Initial value	Scale	Lower bound	Upper bound
cdlvol_cs_pos (Volumetric capacitance of electronic conductor in positive electrode)	5e5[F/m^3]	1e5	1e5	1e6

14 Locate the **Output While Solving** section. Select the **Plot** check box.

15 From the **Plot group** list, choose **Default**.

Solution 10 (sol10)

Choose the numeric gradient method.

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

2 In the **Model Builder** window, expand the **Solution 10 (sol10)** node, then click **Optimization Solver 1**.

3 In the **Settings** window for **Optimization Solver**, locate the **Optimization Solver** section.

4 From the **Gradient method** list, choose **Numeric**.

5 In the **Difference interval** text field, type `5e-4`.

6 In the **Central difference interval** text field, type `5e-3`.

RESULTS

It is common to monitor the optimization, especially if the optimization is time-consuming. This makes it possible to stop the optimization if the fit seems adequate or if the optimization settings need to be improved.

The optimized parameters can be monitored using Global Probes.

First, a table is generated that collects the parameters during the optimization.

Optimized Parameters Table

1 In the **Results** toolbar, click  **Table**.

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

DEFINITIONS (COMPI)

Thereafter, the global probes are made.

Exchange current density NCA

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

2 In the **Settings** window for **Global Variable Probe**, type `Exchange current density NCA` in the **Label** text field.

3 Locate the **Expression** section. In the **Expression** text field, type `linpoint(iO_pos)`.

4 Click to expand the **Table and Window Settings** section. From the **Output table** list, choose **Optimized Parameters Table**.

Double-layer capacitance NCA

1 Right-click **Exchange current density NCA** and choose **Duplicate**.

2 In the **Settings** window for **Global Variable Probe**, type `Double-layer capacitance NCA` in the **Label** text field.

3 Locate the **Expression** section. In the **Expression** text field, type `linpoint(cdl_pos)`.

Film resistance NCA

1 Right-click **Double-layer capacitance NCA** and choose **Duplicate**.

2 In the **Settings** window for **Global Variable Probe**, type `Film resistance NCA` in the **Label** text field.

3 Locate the **Expression** section. In the **Expression** text field, type `linpoint(Rfilm_pos)`.

Vol. double-layer cap. pos. electronic conductor

1 Right-click **Film resistance NCA** and choose **Duplicate**.

2 In the **Settings** window for **Global Variable Probe**, type `Vol. double-layer cap. pos. electronic conductor` in the **Label** text field.

3 Locate the **Expression** section. In the **Expression** text field, type `linpoint(cdlvol_cs_pos)`.

RESULTS

Follow these steps to set up a plot group that also enables graphical monitoring of optimization:

Nyquist plots optimization

1 In the **Model Builder** window, right-click **Nyquist plots parametric sweep** and choose **Duplicate**.

2 In the **Settings** window for **1D Plot Group**, type `Nyquist plots optimization` in the **Label** text field.

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

Impedance NCA vs. reference

1 In the **Model Builder** window, expand the **Nyquist plots optimization** node, then click **Impedance NCA vs. reference**.

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

3 From the **Dataset** list, choose **Study 2/Solution 10 (sol10)**.

4 Locate the **Coloring and Style** section. In the **Width** text field, type `1`.

5 Find the **Line markers** subsection. From the **Marker** list, choose **Square**.

6 From the **Positioning** list, choose **In data points**.

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

Legends
`Simulated impedance NCA vs. reference`

8 Click the  **Zoom Extents** button in the **Graphics** toolbar.

9 In the **Nyquist plots optimization** toolbar, click  **Plot**.

Experimental impedance NCA vs. reference

1 In the **Model Builder** window, click **Experimental impedance NCA vs. reference**.

2 In the **Settings** window for **Table Graph**, locate the **Coloring and Style** section.

3 Find the **Line markers** subsection. From the **Marker** list, choose **Square**.

4 From the **Positioning** list, choose **In data points**.

5 Click the  **Zoom Extents** button in the **Graphics** toolbar.

6 In the **Nyquist plots optimization** toolbar, click  **Plot**.

STUDY 2

Thereafter, select the plot group and table you want to monitor in the Optimization study step and compute.

Optimization

1 In the **Model Builder** window, under **Study 2** click **Optimization**.

2 In the **Settings** window for **Optimization**, locate the **Output While Solving** section.

3 From the **Plot group** list, choose **Nyquist plots optimization**.

4 In the **Home** toolbar, click  **Compute**.

Optimized

Rename the solution of the optimization.

1 In the **Model Builder** window, under **Study 2>Solver Configurations** click **Solution 10 (sol10)**.

2 In the **Settings** window for **Solution**, type `Optimized` in the **Label** text field.

RESULTS

Nyquist plots optimization

1 In the **Model Builder** window, under **Results** click **Nyquist plots optimization**.

2 In the **Nyquist plots optimization** toolbar, click  **Plot**.

3 Click the  **Zoom Extents** button in the **Graphics** toolbar.

To control the parameters in the last iteration, consult the Optimized Parameters Table that gives you the optimized parameters.