Lecture 15

Modelling of lithium-ion batteries in COMSOL Multiphysics using Lithium-ion battery Interface

Goal of the Lecture

The goal of this lecture is to familiarize students with the numerical modelling of lithium-ion batteries (LIBs) using COMSOL Multiphysics' dedicated ***Lithium-Ion Battery Interface****. Students will learn how to simulate charge–discharge cycles, material transport in porous electrodes and solid particles, Butler–Volmer kinetics, and concentration-dependent material properties. The lecture emphasizes how modelling is used to investigate design parameters, performance limits, and degradation-related behavior in modern Li-ion cells.*

Lecture Objectives

By the end of this lecture, students will be able to:

1. ***Describe*** *the structure of a 1D LIB model including porous electrodes, separator, electrolyte, and active particles.*
2. ***Explain*** *the role of electronic conduction, ionic conduction, solid-state diffusion, and concentration-dependent properties in LIB simulations.*
3. ***Apply*** *Butler–Volmer kinetics and Fickian diffusion in spherical active-material particles within COMSOL Multiphysics.*
4. ***Simulate*** *galvanostatic discharge and charge cycles and analyze voltage losses (activation, ohmic, concentration).*
5. ***Evaluate*** *how model parameters (material choice, electrode thickness, particle size) influence battery capacity and rate performance.*

This example demonstrates the Lithium-Ion Battery interface for studying the discharge and charge of a lithium-ion battery for a given set of material properties.

The model includes the following processes:

- Electronic current conduction in the electrodes
- Ionic charge transport in the electrodes and electrolyte/separator
- Material transport in the electrolyte, allowing for the introduction of the effects of concentration on ionic conductivity and concentration overpotential, which in this case are obtained from experimental data

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

The geometry is in one dimension (1D) and the model is isothermal. Battery developers can use the model to investigate the influence of various design parameters such as the choice of materials, dimensions, and the particle sizes of the active materials, in this case carbon material in the negative electrode and lithium manganese oxide ($LiMn_2O_4$ spinel) in the positive electrode. You can also benefit from simulating battery performance under different operating conditions and in different devices, for example, cell phones or laptop computers.

The example treats a detailed model of a discharge-recharge cycle for a lithium-ion battery. The model is based on a study by J. Newman and others [1].

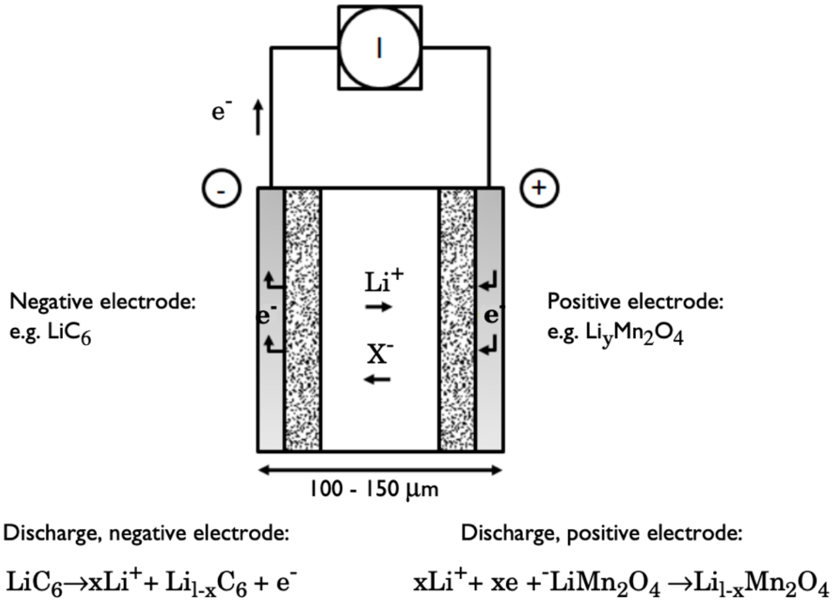

Figure 1. Cross section of a lithium-ion battery showing the electrochemical processes that occur during operation.

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

- Negative porous electrode: 100 μm
- Polymer electrolyte: 52 μm

- Positive porous electrode: 183 μm
- Fickian diffusion describes the transport in the spherical particles. The diffusion equation is expressed in spherical coordinates for the material balance of lithium in the particles.
- Butler-Volmer electrode kinetics describes the local charge transfer current density in the electrodes. The Butler-Volmer expressions are introduced as source or sink terms in the charge balances and material balances.

The ionic charge balances and material balances are modeled according to the equations for binary 1:1 electrolytes [1]. The material parameters for the electrolyte refer to a plasticized EC/DMC electrolyte residing in a polymer matrix, and the electrolyte volume fraction specified in the model hence refer to the sum of the liquid electrolyte and polymer matrix volume fractions.

The material properties are those of a typical lithium-ion battery. The electrolyte consists of 2 M $LiPF_6$ salt in 1:2 EC:DMC (by volume) solvent and p(VDF-HFP). The electrode materials are carbon-based material for the negative electrode and $Li_yMn_2O_4$ for the positive electrode.

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

The battery is initially at a fully charged state. A first modeling approach is to simulate discharge at various current densities and then display the discharge curves. The results show the capacity of the battery at different discharge rates. This model defines end-of-discharge as the time when the cell voltage drops below 3 V. The nominal discharge current density, corresponding to case 1C below (a current density corresponding to a theoretical full discharge in one hour), is 17.5 A/m^2.

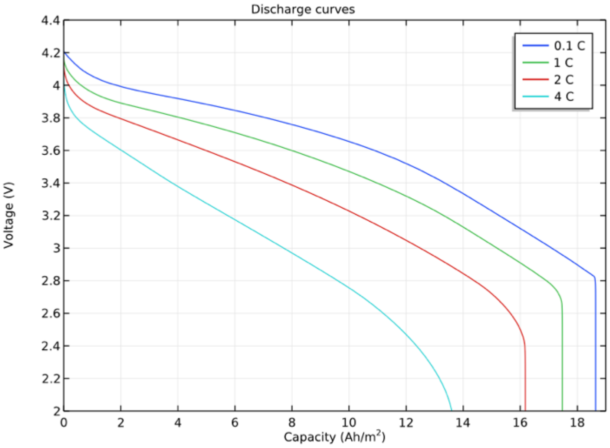

Figure 2. Discharge curves for various discharge rates.

Figure 2 shows that the maximum discharge capacity of 17.5 Ah/m^2 is obtained for a current density of 1.75 A/m^2 (0.1 C). It can also be seen that the 3 V discharge capacity decreases slightly when applying a 1C discharge current and dramatically when going above that. At 4C, the battery delivers approximately 50% of the theoretical capacity before it reaches a cell voltage of 3 V. The discharge curves are identical to those presented in [2].

Figure 3 depicts the discharge-charge cycle applied in the next step of the simulation. The cycle applies 2000 s of discharge at nominal current density (case 1C above), 300 s at open circuit, then 2000 s of charge at nominal current density, and finally open-circuit conditions.

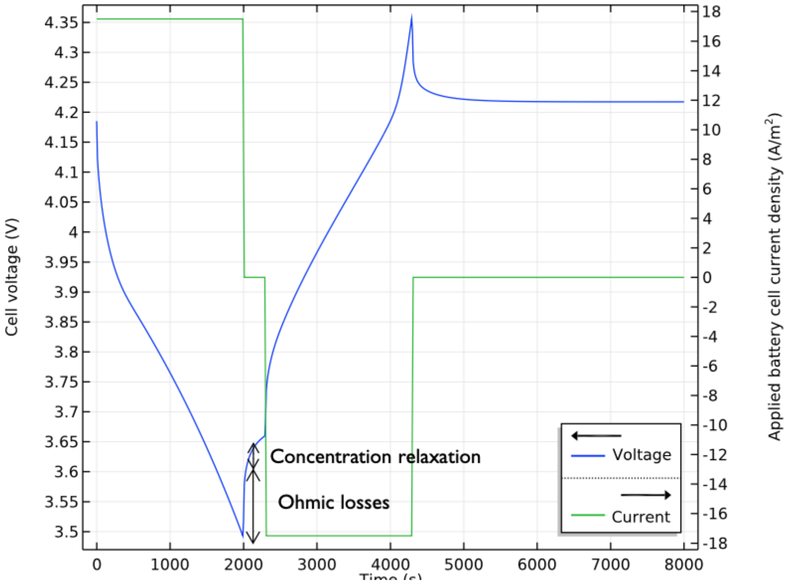

Figure 3. Cell voltage and current during the applied cycle.

During both discharge and charge, the cell voltage experiences ohmic losses of approximately 100 mV and a concentration overpotential of about 50 mV. These losses are clearly visible in the plot when the current is set to 0, where you can see an immediate relaxation of the voltage due to the relaxation of ohmic losses followed by a slower relaxation of the concentration overpotential.

Questions for Self-Examination

1. What assumptions justify using a 1D through-thickness model for LIB simulation?
2. Why must transport within spherical active particles be modeled using Fick's diffusion equation in spherical coordinates?
3. What concentration-dependent material properties strongly influence LIB voltage curves?
4. Explain why the equilibrium potential of both electrodes varies with lithium composition.
5. How does increasing particle size influence diffusion limitations?
6. Why do high discharge rates lead to reduced delivered capacity?
7. What causes the immediate voltage relaxation when current switches from non-zero to zero?
8. Explain the difference between ohmic and concentration overpotential.
9. Why is Butler–Volmer kinetics appropriate for LIB electrode reactions?

Self-Study Assignment

Assignment Title:

Simulation of Charge–Discharge Cycling and Rate Performance in a Lithium-Ion Battery Using COMSOL's Lithium-Ion Battery Interface

Objective:
To model a full charge–discharge cycle of an LIB cell, evaluate the influence of discharge rate on capacity, and study internal variables such as electrolyte concentration, solid-state lithium diffusion, and overpotentials.

Tasks

1. Geometry and Physics Initialization

Use COMSOL's **Lithium-Ion Battery Interface** with:

- Negative porous electrode (e.g., graphite or carbon-based active material)
- Polymer electrolyte/separator
- Positive porous electrode (e.g., $LiMn_2O_4$ spinel)

Include:

- Charge conservation in solid phase
- Charge conservation in electrolyte
- Nernst–Planck material transport
- Solid-state diffusion in spherical particles
- Butler–Volmer kinetics for both electrodes

2. Electrode and Electrolyte Properties

Implement composition-dependent material properties:

- Electrolyte conductivity vs. concentration
- Electrolyte diffusion coefficient vs. concentration
- Equilibrium potentials of anode and cathode as functions of stoichiometry
- Particle diffusion coefficients for negative and positive active materials

Use experimental tables or COMSOL's material library.

3. Discharge Rate Simulation

Simulate discharge at multiple current densities:

- 0.1 C
- 1 C
- 4 C

For each simulation, extract:

- Discharge curves (V vs t)
- Extracted capacity at 3 V cut-off
- Overpotential contributions (activation, ohmic, concentration)

4. Charge–Discharge Cycle Simulation
Implement a full cycle identical to Figure 3:

- 2000 s discharge at 1C
- 300 s open-circuit
- 2000 s charge at 1C
- Open-circuit relaxation

Plot:

- Voltage vs. time
- Current vs. time
- Relaxation behavior after discharge and charge

5. Internal Variable Analysis
Extract and interpret:

- Lithium concentration profile inside battery thickness
- Lithium intercalation gradients inside solid particles
- Ionic potential and electronic potential distributions
- Separator concentration gradients

Explain how internal gradients cause observed macroscopic overpotentials.

6. Design Parameter Sensitivity (Optional Advanced Task)
Perform parametric sweeps for:

- Electrode thickness (±50%)
- Particle size (1–10 µm)
- Electrolyte conductivity

Evaluate influence on:

- Delivered capacity
- Overpotential
- Rate capability

7. Report (3–4 pages)
Include:

- Description of model

- Voltage curves and internal-variable plots
- Comparison to literature (e.g., Newman's model predictions)
- Discussion of capacity limitations at high rates
- Design recommendations for improved performance

Learning Outcomes

Learning Outcome (LO)	**Indicator of Achievement (ID)**	**Description**
LO 4: Describe the key structures and performance criteria of chemical and electrochemical energy storage systems.	**ID 4.4:** Apply numerical tools to model the charge/discharge behavior of lithium-ion batteries.	Students will construct and evaluate numerical LIB models using COMSOL's Lithium-Ion Battery Interface.

References

1. M. Doyle, J. Newman, A.S. Gozdz, C.N. Schmutz, and J.M. Tarascon, "Comparison of Modeling Predictions with Experimental Data from Plastic Lithium Ion Cells," J. Electrochem. Soc., vol. 143, no. 6, pp. 1890–1903, 1996.
2. COMSOL Multiphysics. Application Library path: Batteries_and_Fuel_Cells_Module/Batteries,_Lithium-Ion/li_battery_1d