Electrochemomechanical simulations of 3D-resolved solid-state lithium-ion battery cells

Giulia Blanco

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Gemmate Technologies

Buttigliera Alta (Turin), Italy

www.gemmate-technologies.com

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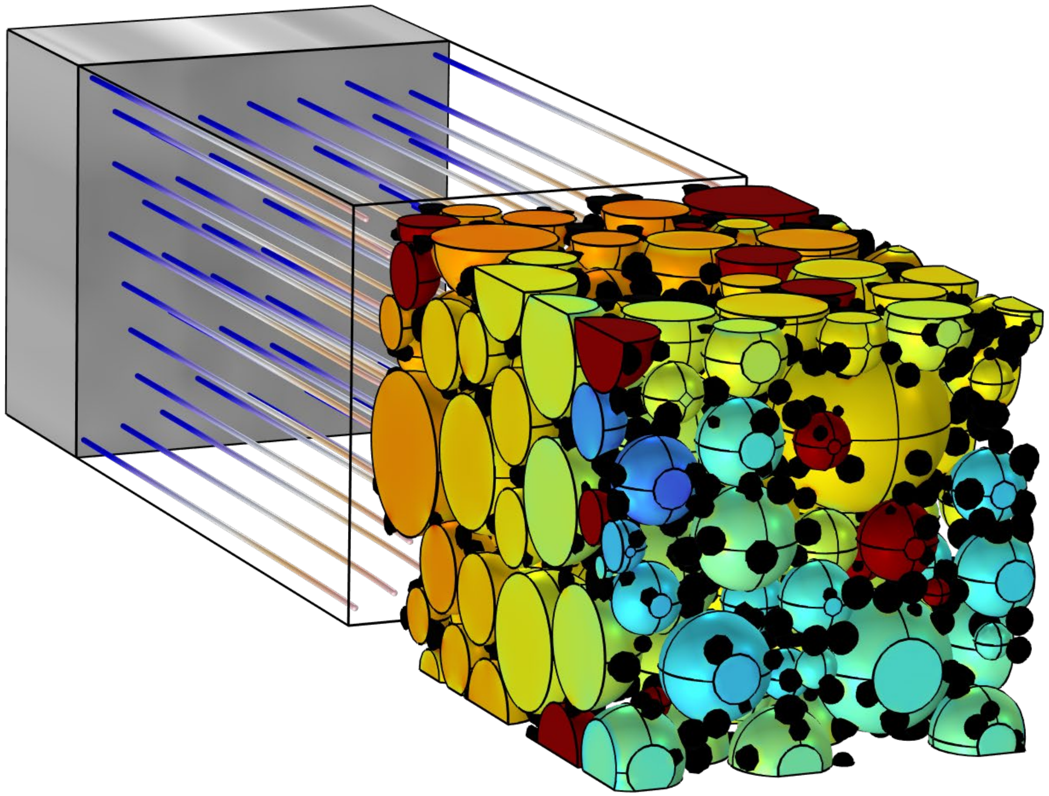
Outline

1. Introduction
2. Simulation set up and model comparison
3. Microstructure and mechanical properties
4. Cell performances evaluation
5. Conclusion



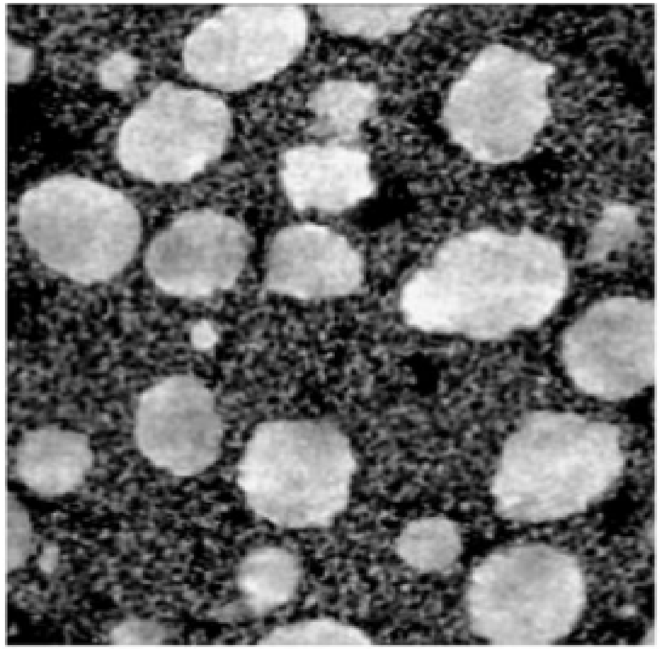
Introduction

- **WHAT?** 3D microstructure-resolved electrochemo-mechanical model of high fidelity
- **WHY?** Li-B affected by microstructural heterogeneities and mechanical interaction
- **HOW?** Comparison between models to assess the better performance representation

Optimize design at the microstructure level

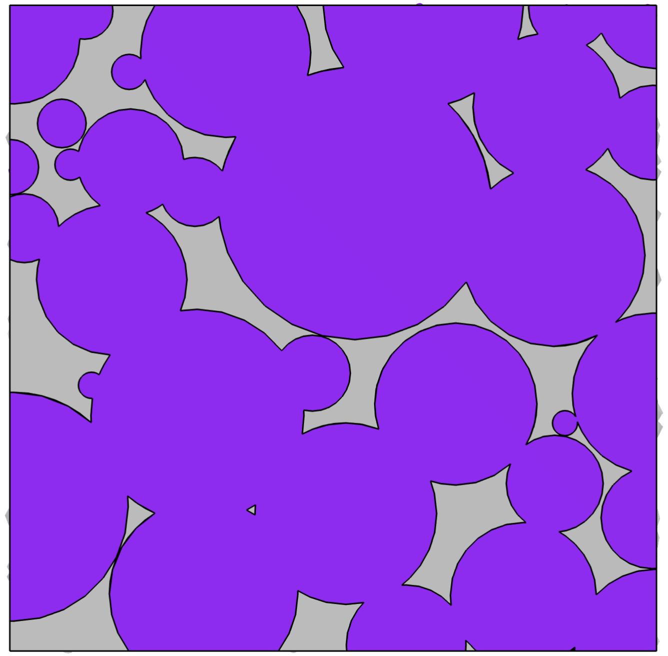
Cathode geometry

FIB-SEM images:
High computational cost



Novel design approach

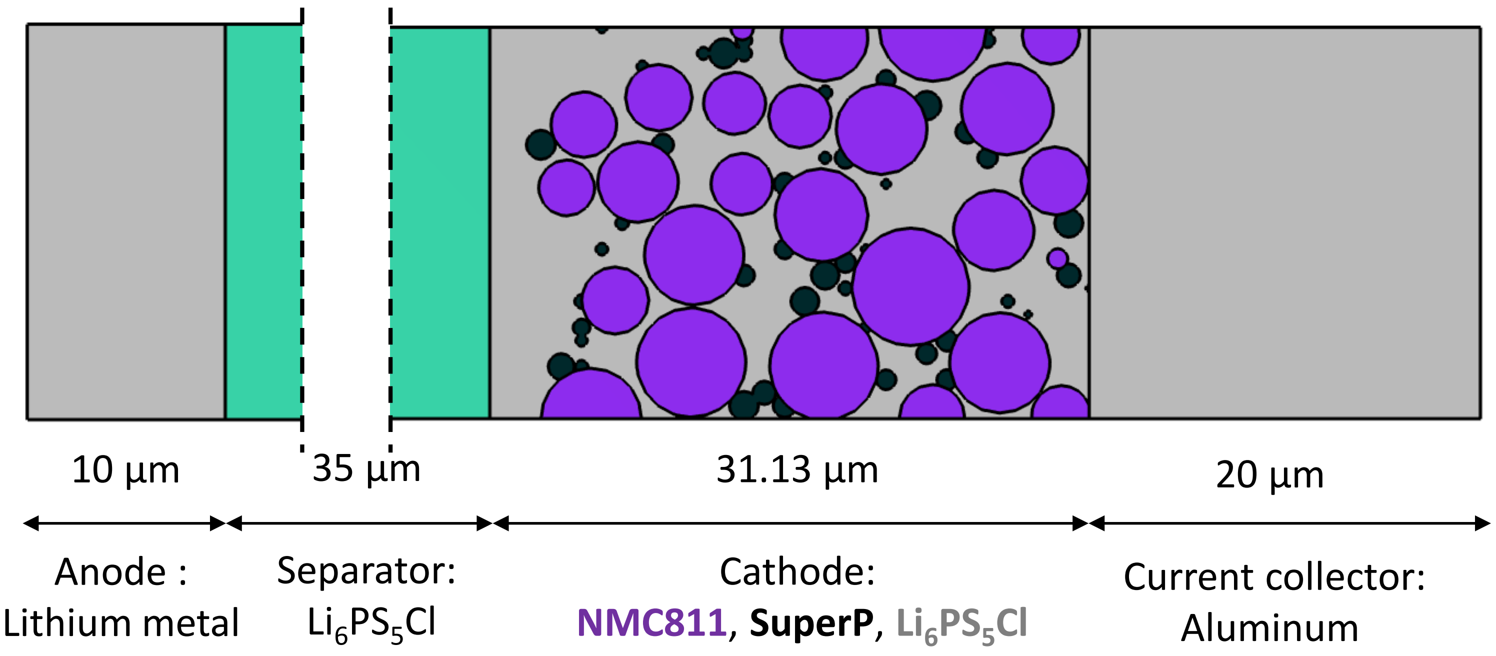
Standard model:
Inadequate transport phenomena



Simulation setup

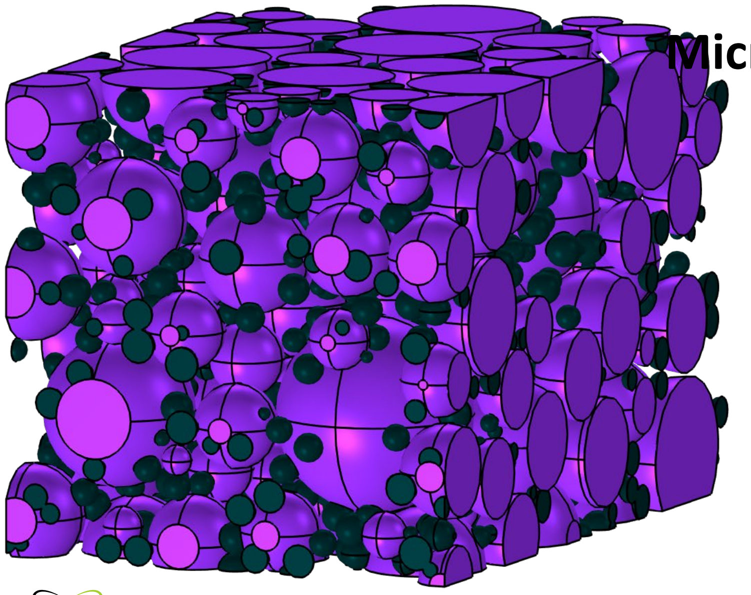
The cell is reconstruct considering:

- Experimental parameters
- Volume fraction
- Particle size distribution



Configuration comparison

Novel configuration		Standard configuration
Avoided	NMC overlap	Allowed
Explicit aggregates	Carbon black	Homogeneously dispersed
Homogeneous	Electrolyte domain	Conductive porous
Coupled	Electrochemistry-mechanics	Decoupled



Microstructural detail and coupled physical phenomena

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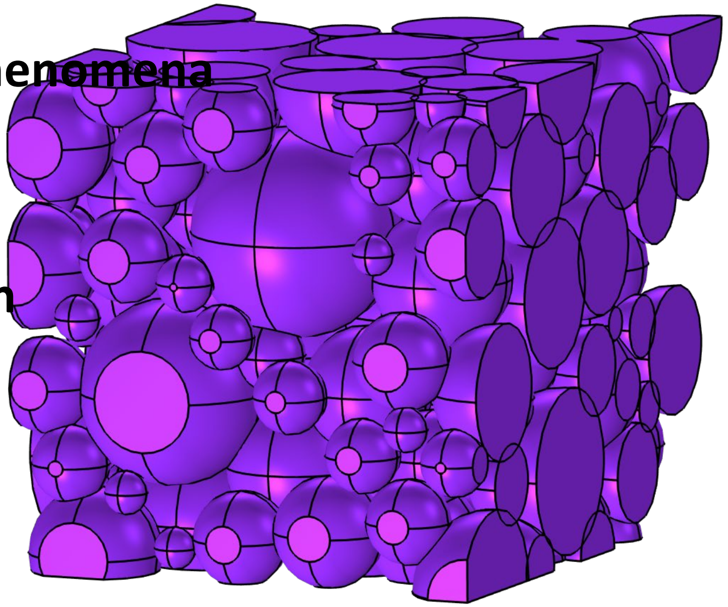
Li concentration and stresses distribution

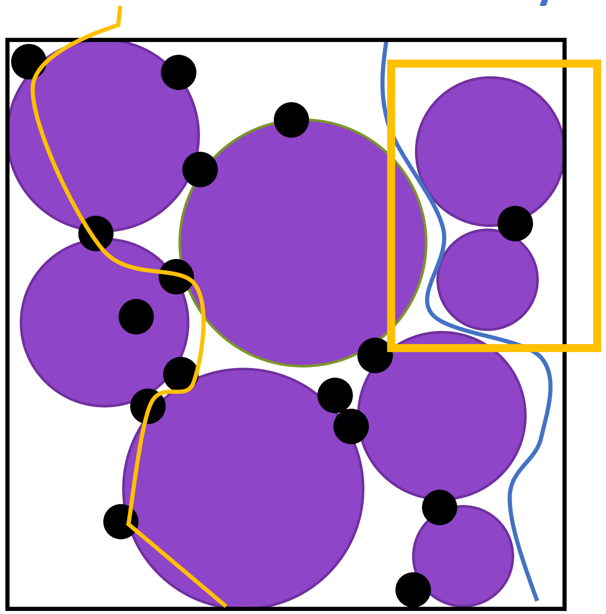


Microstructure properties

Novel configuration

Electrical conductivity

Tortuosity



Conductivity Domain:

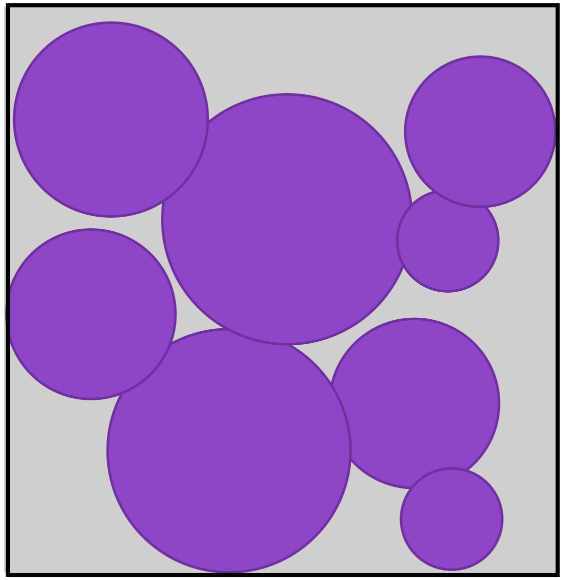
NMC-CB network

Tortuosity Domain:

Homogenous Electrolyte

Standard configuration

The transport properties corrected whit CB volume fraction



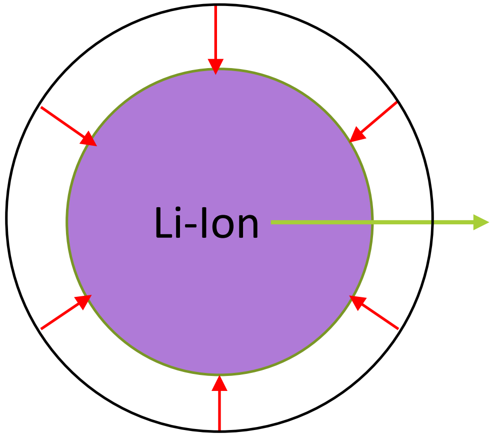
Conductivity Domain:

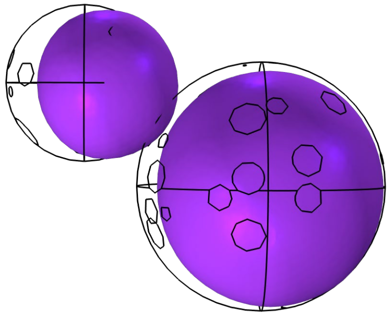
NMC-Porous Electrolyte

Tortuosity Domain:

Porous Electrolyte

Mechanical interaction





The **volumetric deformation** due to the Li intercalation generates a **field of stresses**

The gradient of the stress field facilitates Li transport

Mechanical interaction affect the electrochemical behavior:

1. Modifying the equilibrium potentials $$V = V_0 + \frac{\Omega \sigma_h}{F}$$

   Local hydrostatic stress $\boldsymbol{\sigma_h}$

   Partial molar volume $\boldsymbol{\Omega}$

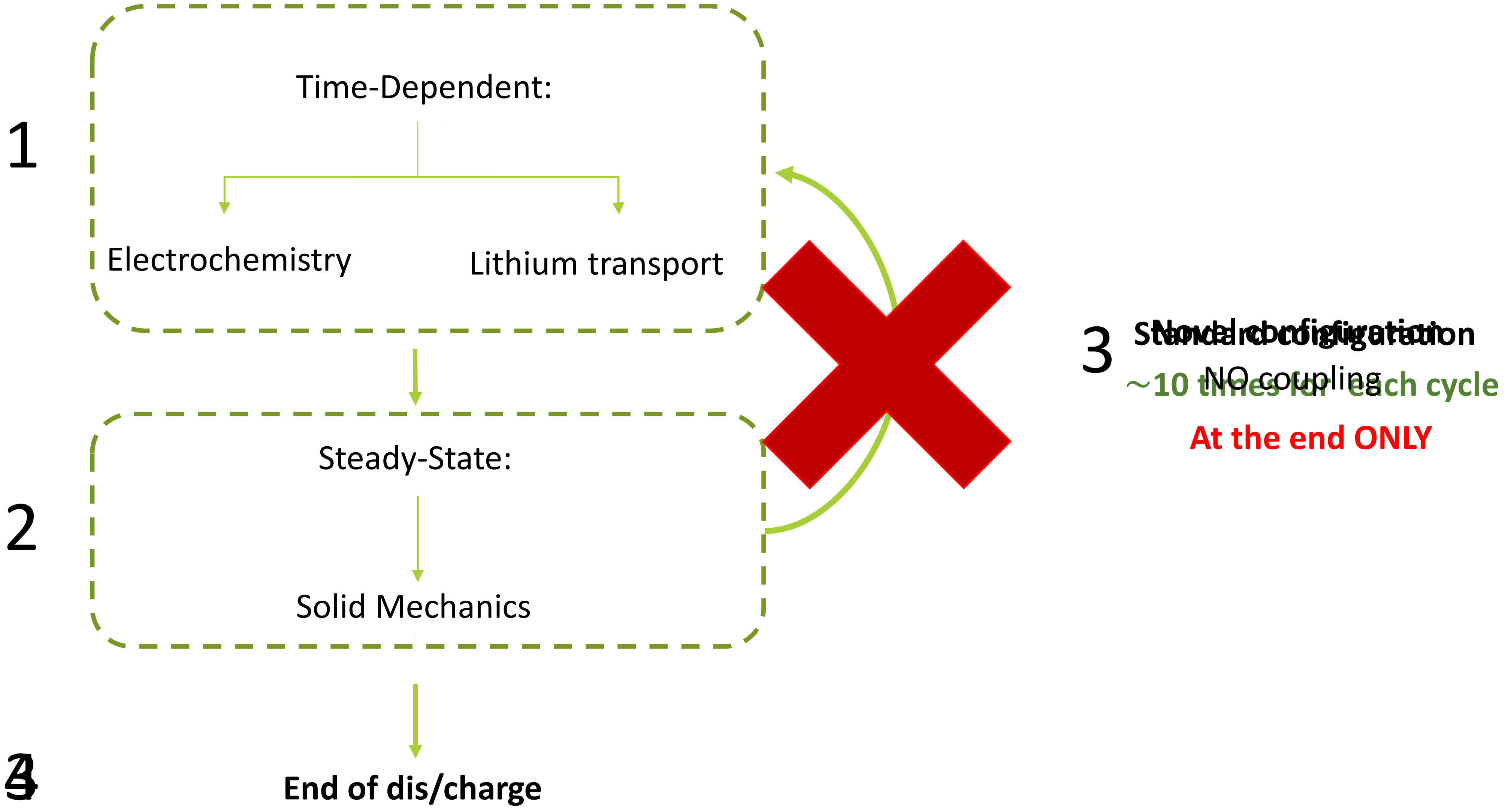
2. Introducing a convective term in the transport equation $$\frac{\partial c}{\partial t} + \nabla \cdot (-D\nabla c + \boldsymbol{\beta} c) = 0$$

   $$\boldsymbol{\beta = \frac{D\Omega(c)}{RT} \nabla \sigma_h}$$

   convection coefficient

Solver setup

Method script to run the simulations



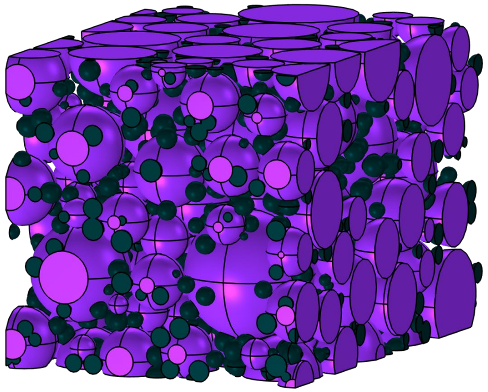
Simulation results

How the different assumptions affect cell performance?

- Tortuosity and electrical conductivity
- Electrochemical potential and charge transfer
- State of lithiation and Li-ion transport
- Overpotential
- Mechanical stresses

Microstructure results

Novel configuration



Tortuosity: **1.53**

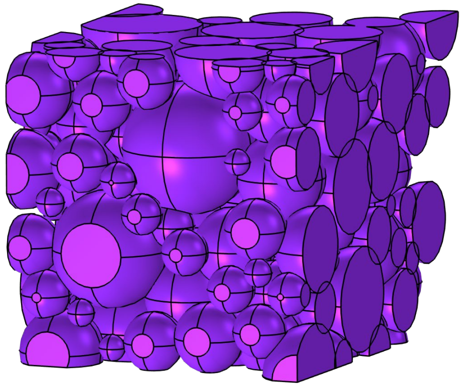
Low affected by CB aggregates

Theoretical value of Bruggeman theory

Electrical conductivity : **1.4 S/cm**

Experimental values of similar electrodes

Standard configuration



Tortuosity: **3.98**

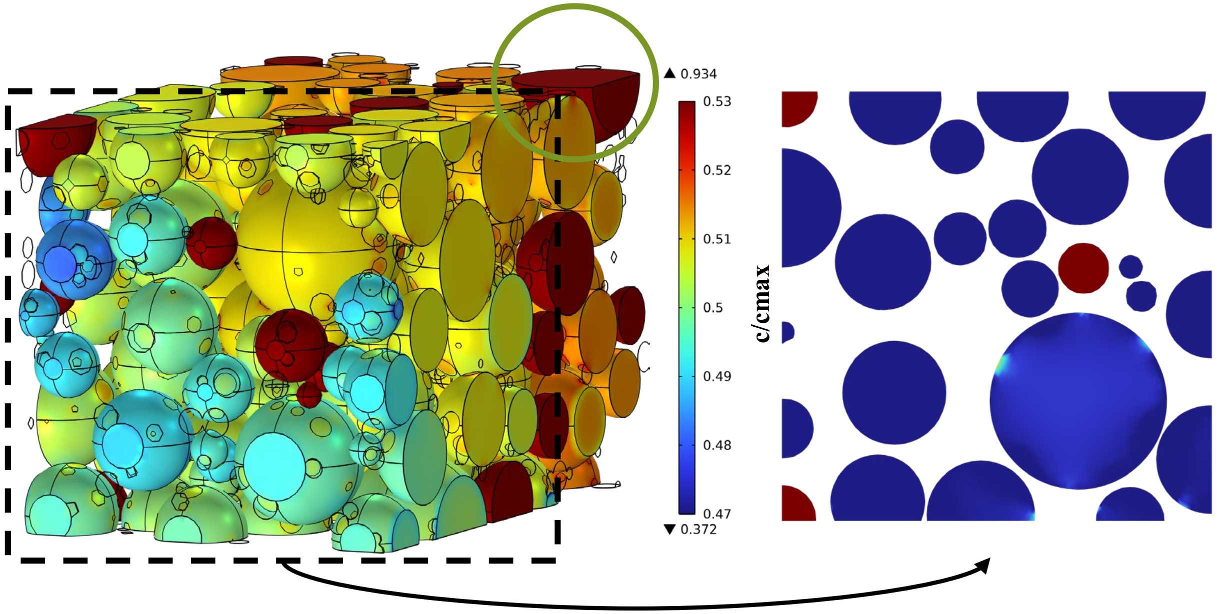
Mostly affected by NMC overlap

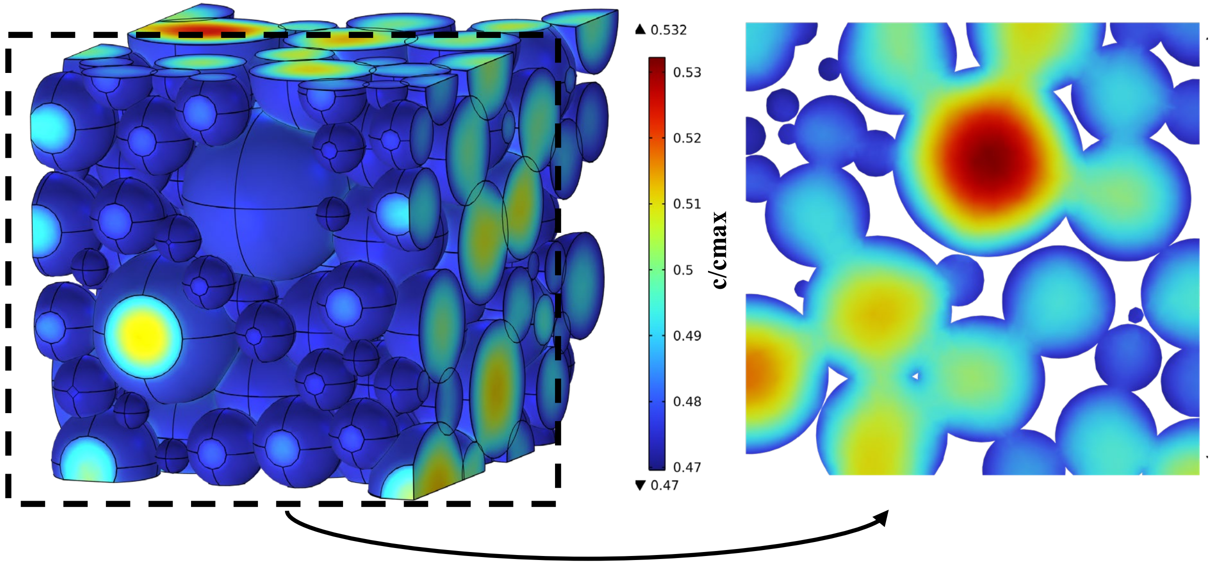
Electrical conductivity : **33.0 S/cm**

Results closer to real cells with proposed approach

State of lithiation and Li-ion transport

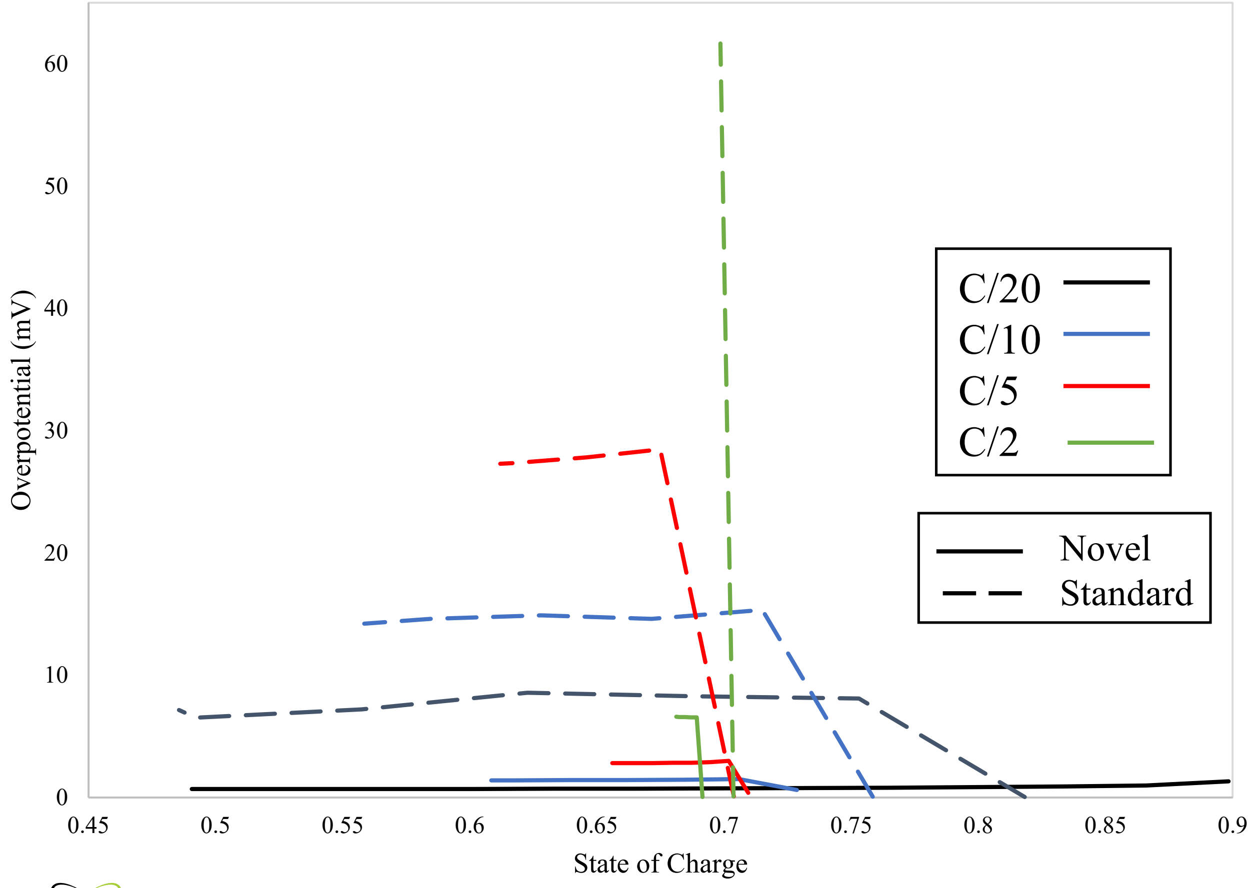
Novel configuration		Standard configuration
Non-uniform	Utilization of active material	Uniform
Non-uniform	Lithiation along the thickness direction	Uniform
Homogeneous	Internal Li- distribution	Non-homogeneous





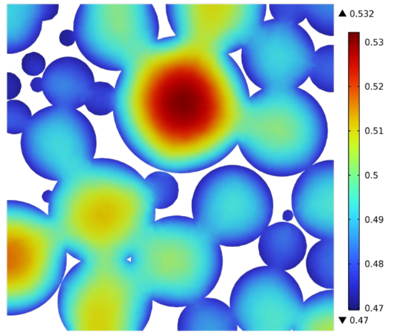
Overpotential

The stress at the particle surface modifies the overpotential



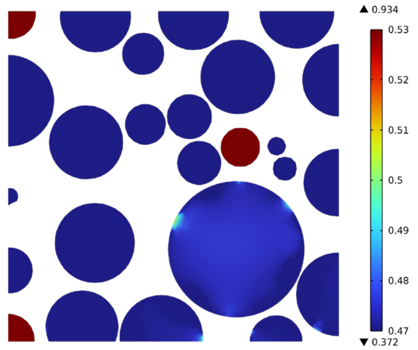
Higher concentration gradients within the NMC particles

High values of overpotential



Lower concentration gradients within the NMC particles

Low values of overpotential



Tends to limit the losses due to concentration polarization

Von Mises Stresses

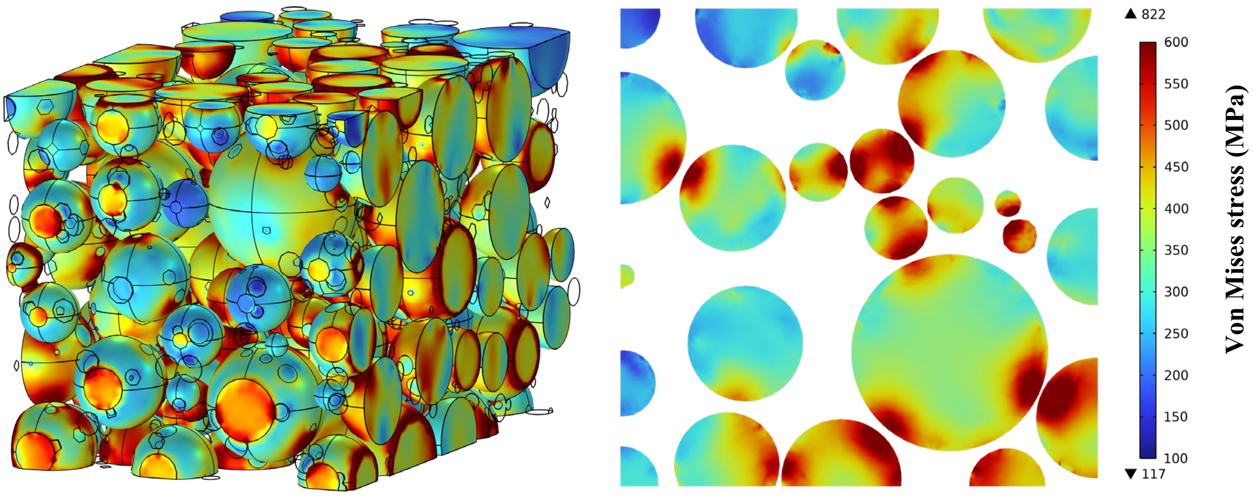
Novel configuration

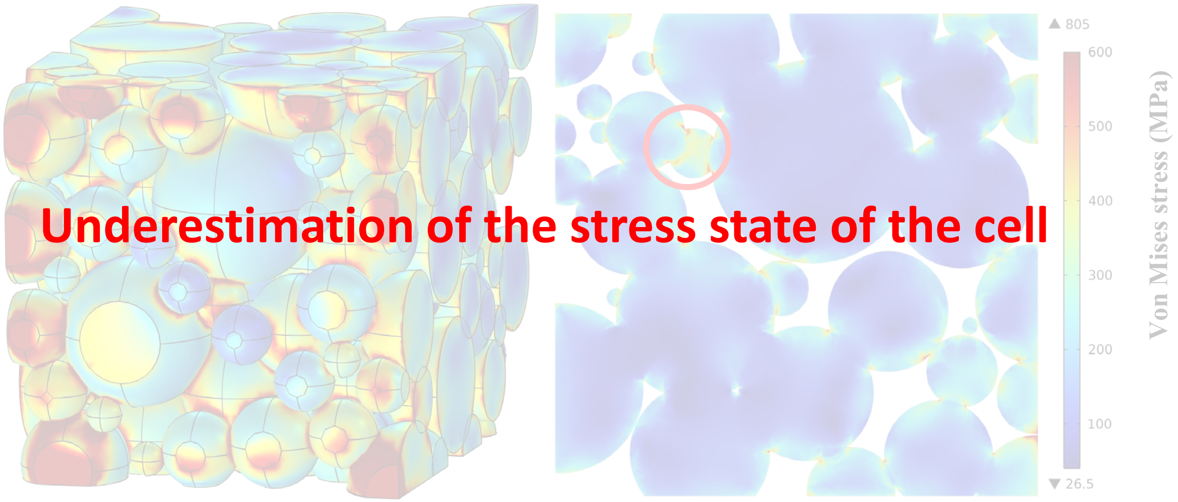
Higher
Distributed through particles
Particles in close proximity

Standard configuration

Average stresses
Arrangement
Higher values

Lower
Peaks where particles in contact
Particles in contact to CC





Underestimation of the stress state of the cell

Conclusion

Comparison between Solid-state Li-ion battery

Balancing accuracy and simplicity the proposed approach provide a more accurate model

3D microstructural-resolved electrochemo-mechanical model

Microstructure heterogeneities

Electrochemo-mechanical interaction

Particle utilisation

State of lithiation

Charge transfer

Lithium transport

Stresses distribution

Overpotential

Thank you

Giulia Blanco

giulia.blanco@gemmate-techonolgies.com

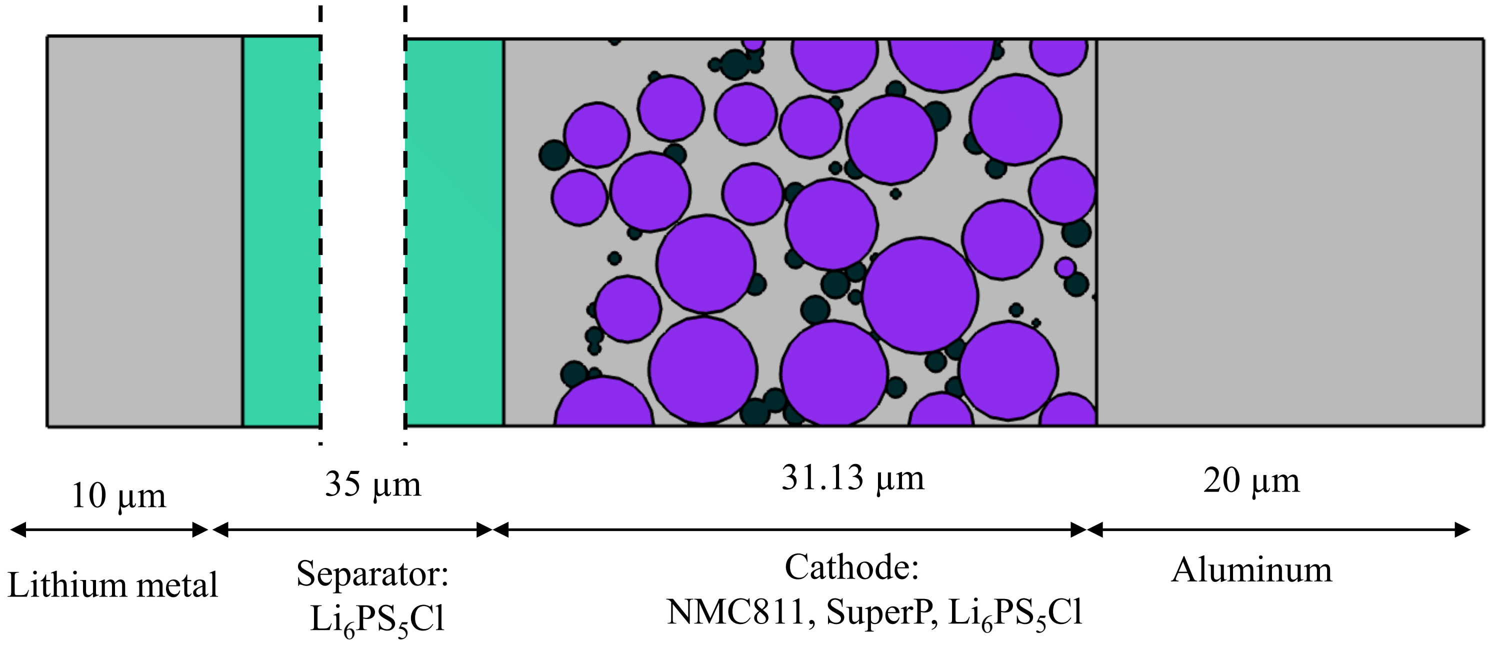
Back up simulation setup

A portion of the cell is reconstruct considering shape and size distribution of particles and volume fraction;

Spherical NMC active material
particles size: $2\ \mu m \leq R_{NMC} \leq 11\ \mu m$
vol. frac.: 49 %

Spherical Carbon black conductive material
particles size: $0.25\ \mu m \leq R_{CB} \leq 0.75\ \mu m$
vol. frac.: 5 %

Homogenous Solid Electrolyte Li_6PS_5Cl
vol. frac.: 46 %



Back up Microstructure properties

Electrode conductivity :

- Coefficient form PDE in electron-conducing domains
- Dirichlet B.C. of ΔV=1
- $\sigma_{eff} = \frac{iL_c}{\Delta V}$

iL_c → **Current density • Cathode thickness**

ΔV → **Electric differential in potential**

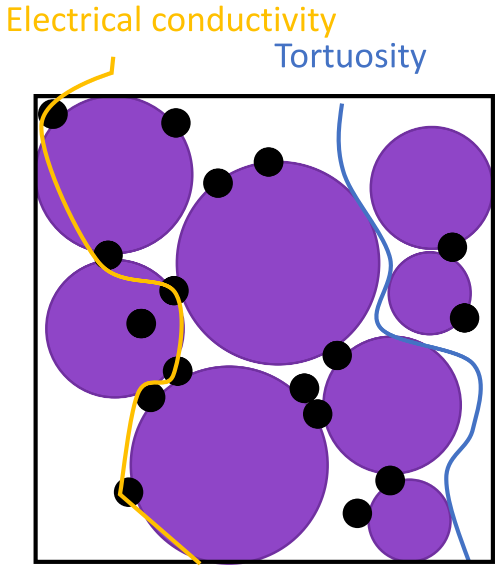
Electrolyte tortuosity :

- Laplace equation in electrolyte domain
- Dirichlet B.C. of Δc=1
- $\tau = \frac{\phi}{J}$

ϕ → **Electrolyte volume fraction**

J → **Normalized stationary species flux**

Configuration with explicit CB aggregates



Electron-conducing domains:

NMC-CB

Electrical Conductivity:

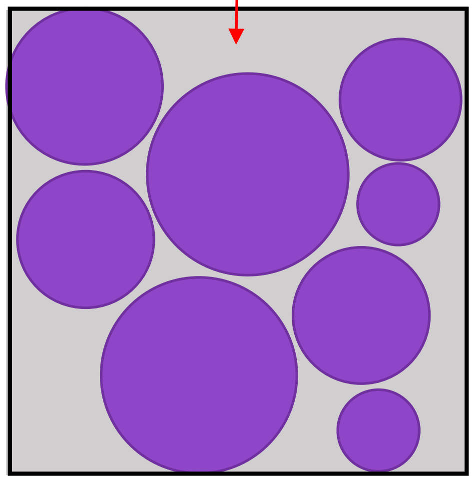
NMC: 0.17 S/m

CB: 100 S/cm

Diffusion coefficient: 1

Configuration with CB homogeneously dispersed

The transport properties corrected whit CB volume fraction ϕ_{CB} : 0.0481



Electron-conducing domains:

NMC-SE

Electrical Conductivity:

NMC: 0.17 S/m

SE: 100*$(1-\phi_{CB})^{3/2}$S/cm

Diffusion coefficient: 1- ϕ_{CB}

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Back up Assumption

$$\sigma_h = -(\sigma_x + \sigma_y + \sigma_z)/3$$

- The sign of σ_h is reversed respect the conventional definition
- The electrolyte do not exert a compressive stress to shrink the NMC surface
- But the electrolyte counteract the particle shrinkage so the this should be in traction

$$\frac{\partial c}{\partial t} + \nabla \cdot (-D\nabla c + \boldsymbol{\beta} c) = 0,$$

- Coherently with literature references D =4.2·10^{-15} m^2/s
- Two orders of magnitude lower than D of material library

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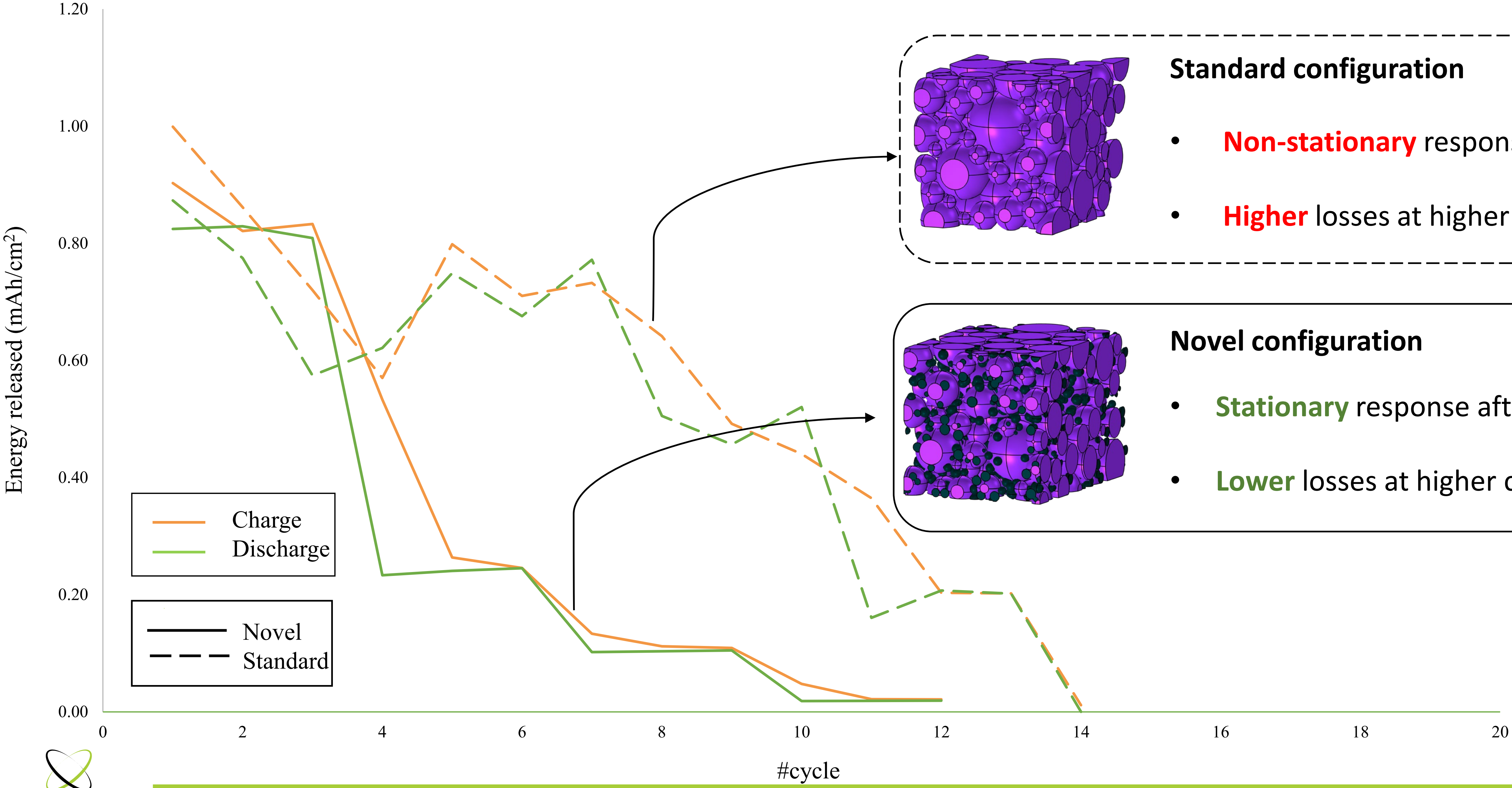
Charge transfer



Standard configuration

- **Non-stationary** response
- **Higher** losses at higher current

Novel configuration

- **Stationary** response after 3 cycle
- **Lower** losses at higher current