This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 875193.

USE OF A MULTISCALE/MULTIPHYSICS APPROACH FOR GEN 3B LI-ION BATTERIES MODELLING IN A SIMULATION TOOLCHAIN

31ST ISE TOPICAL MEETING - AACHEN

MARTIN PETIT, VIVIEN ESNAULT, JEROME BIKARD, CHEN ZHAO, FABRIZIO SILVERI, ANDREA BERTINETTI, LORENZO MASCHIO, MAURO SGROI, GAETAN DAMBLANC, FRANCK SELLIER

MODALIS 2

Next generation batteries

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Nationale Plattform Elektromobilität, Deutschland Jan. 2016

Cell generation	Cell chemistry	
Generation 5	• Li/O2 (lithium-air) • Conversion materials (LiS)	

Generation 4	• All-solid-state batteries
	  • Gr ou Si/Gr anode (Gen 4a)
	  • Li metal (Gen 4b)
		> 2025

Generation 3b	• Cathode: HE-NMC, High Voltage Spinnel • Anode: Silicon/carbon (>20% Si)	≈ 2025
Generation 3a	• Cathode: NMC 622 to 811 • Anode: Silicon/carbon (5-10% Si)	current
Generation 2b	• Cathode: NMC 532 to 622 • Anode: 100% carbon	
Generation 2a	• Cathode: NMC 111 • Anode: 100% carbon	
Generation 1	• Cathode: LFP or NCA • Anode: 100% carbon	

- New technologies relying on new materials to improve batteries performances
  - Gen 3b
    - Use of Silicon in the negative
      - Graphite 350 mAh/g ➔ + 15% vol
      - Silicon 3000 mAh/g ➔ +300% vol
    - Need to account for volumetric expansion
      - Long term effect on aging
      - Cell swelling
  - Gen 4
    - Use of solid electrolyte
      - New ionic conduction type
    - Solid/solid interfaces
      - Stability issues at the Li/electrolyte interface

Multi-scale/Multiphysics approach

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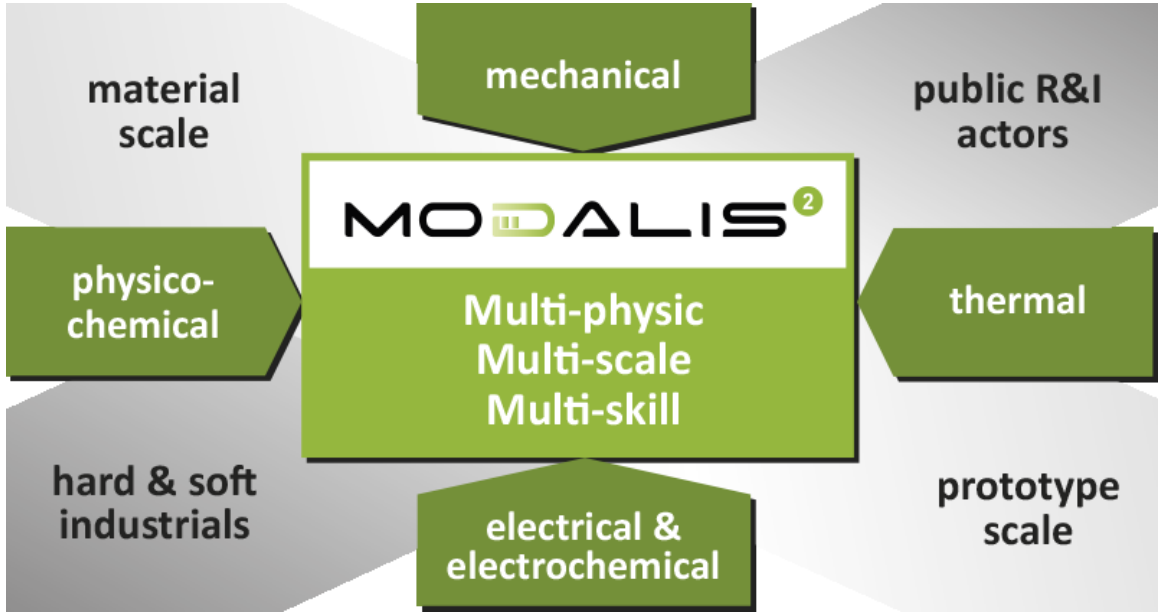

- All skill needed for battery design and manufacturing
  - Modelling from atoms to system
  - Experimentation from material to system
  - Material manufacturer
  - Battery manufacturer
- All value chain for battery
  - Academics and R&I actors
  - SME
  - Manufacturing from material to cells: European Battery alliance
    - Saft
    - Solvay
    - Umicore
    - Siemens AG
  - OEM

Expected achievement: Seamless interfaces from nano to macro scales and from ns to years

Specific needs from all stakeholders

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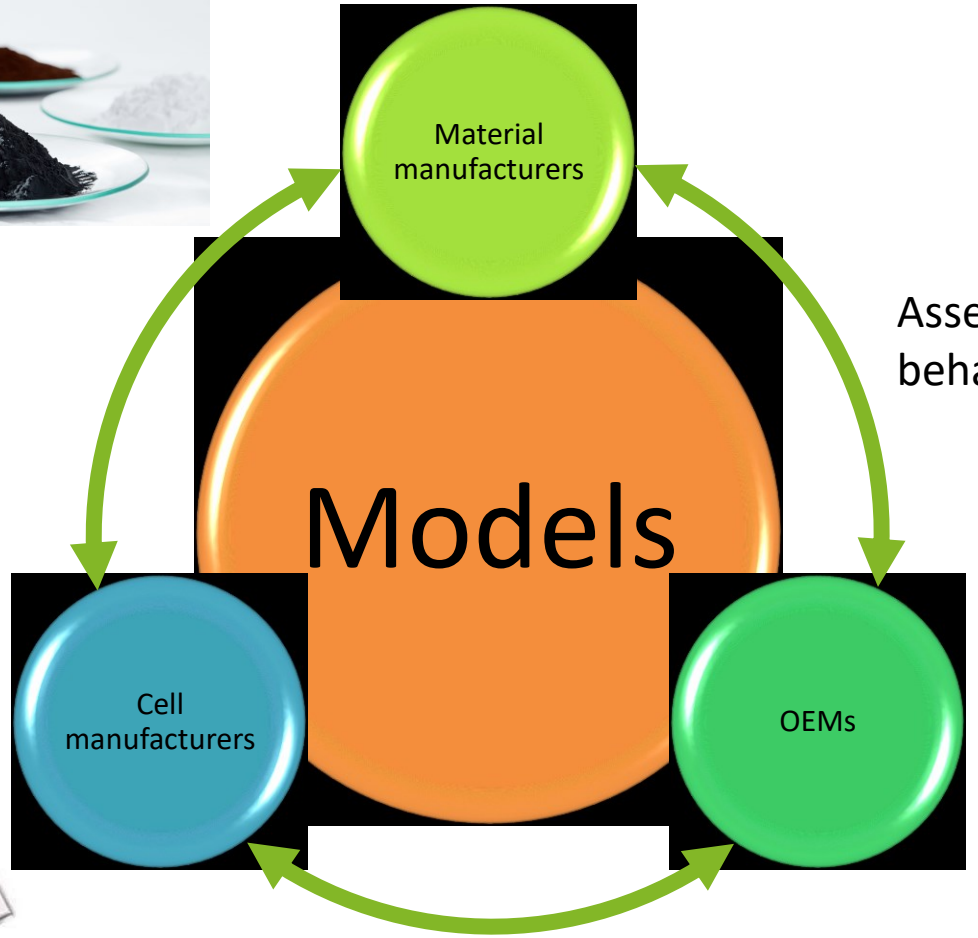
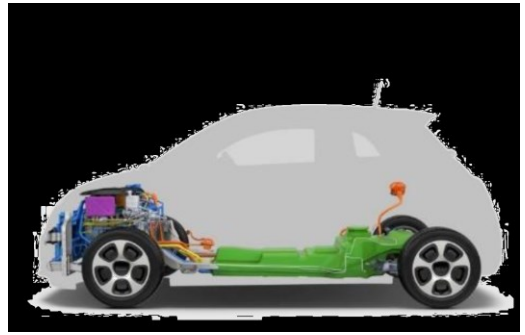
Assess new material integration in battery cells



Assess new material specific behaviour in full systems



Assess new generation cells performance in realistic systems

Gen 3b toolchain development

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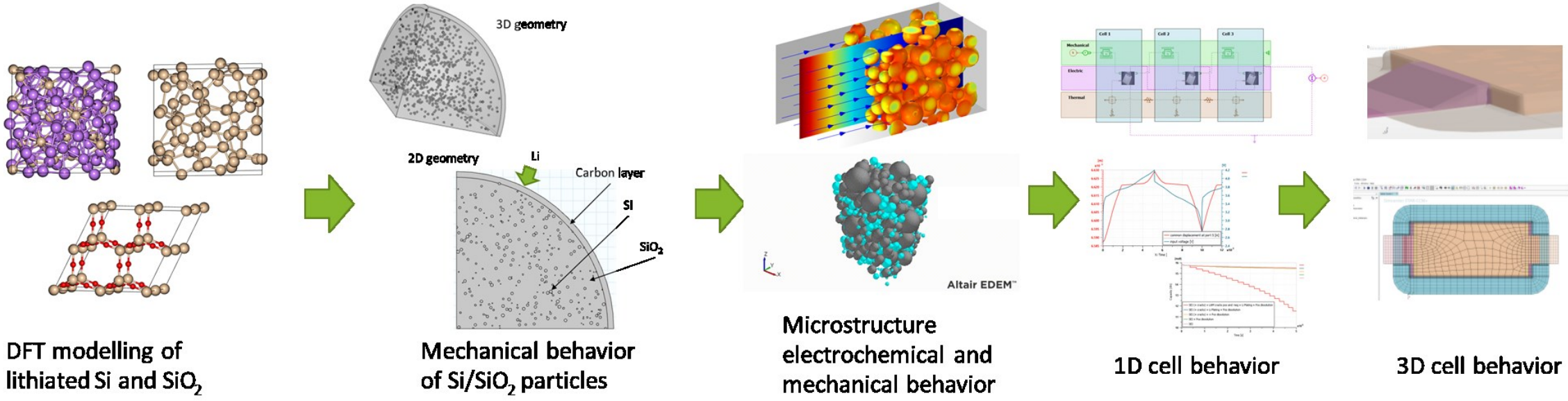

Each scale brings information necessary for understanding and forecasting the complete cell behavior

Studied system

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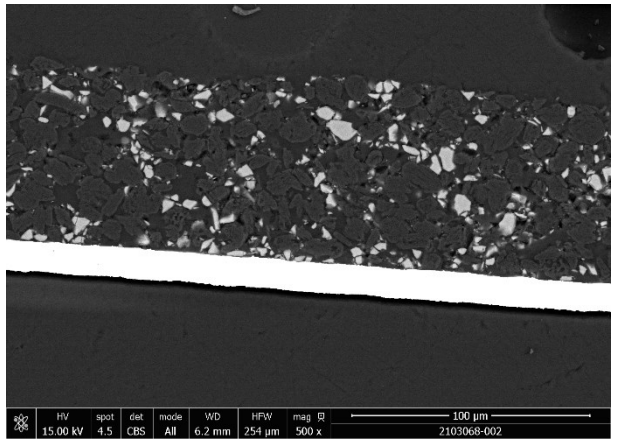
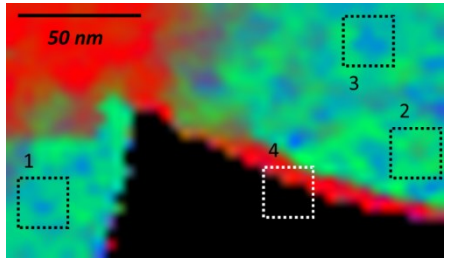
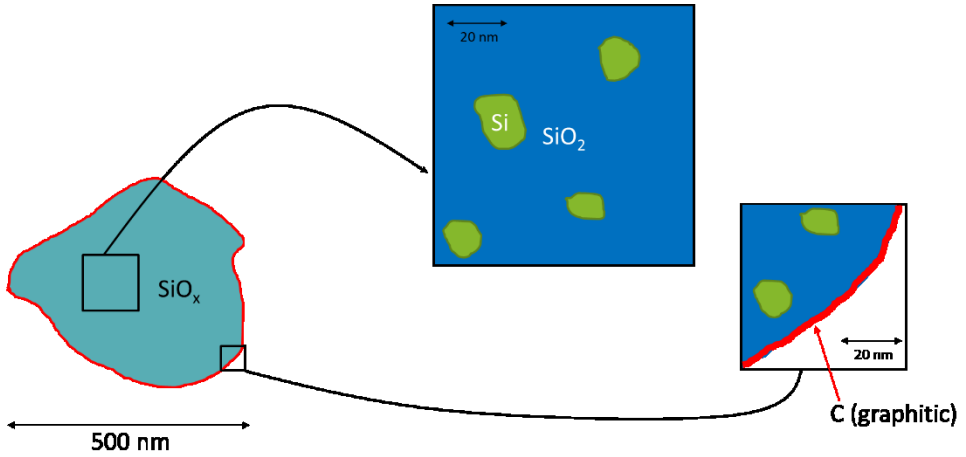
- Gen 3b cell
  - NMC811
  - SiOx/C negative electrode
  - 1M LiPF6 in EC:DMC (3:7) + 10% FEC

- Commercial negative material
  - Complex formulation needing specific characterization
    - Graphite particles: 77%
    - Si based particles
      - Si inclusion in SiO2 matrix + Graphite layer







Intrisic material properties through ab initio modelling

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 875193.

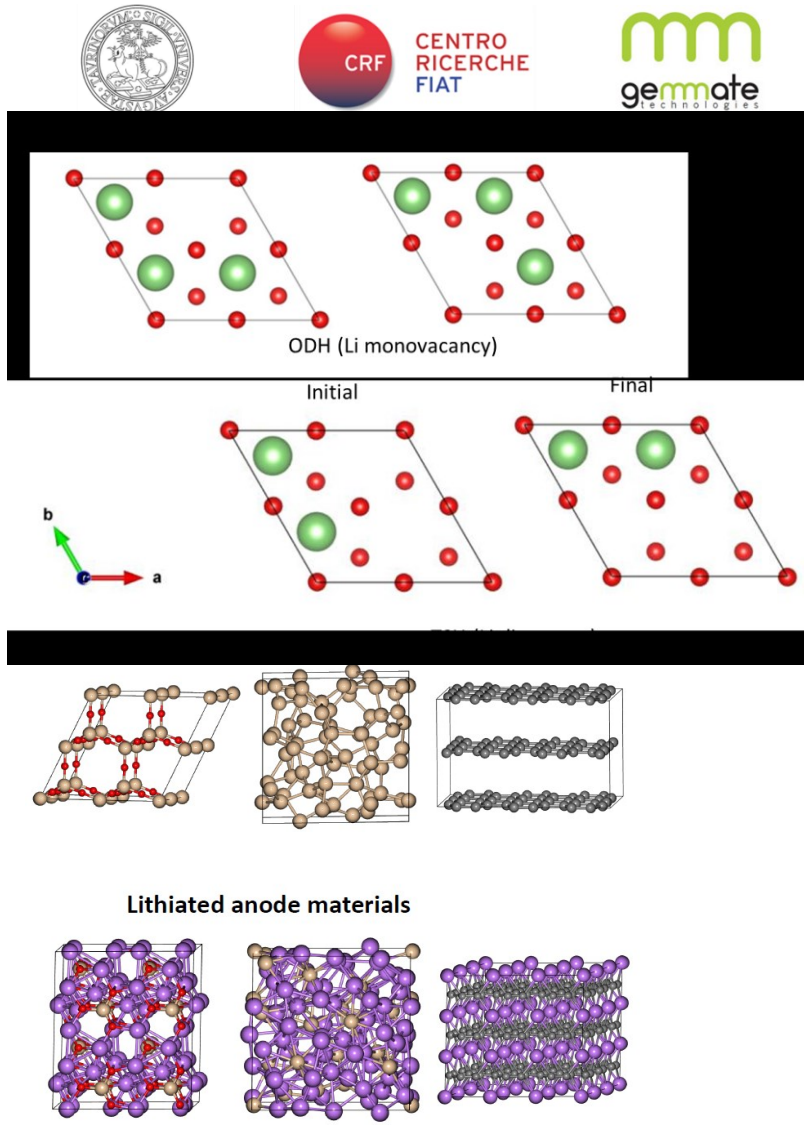
- Simulation focused on intrinsic properties for the material
  - Diffusion properties investigated through Nudged Elastic Band methodology
    - Evaluation of hoping a distance between adjacence sites

$$D(T) = a^2 \nu^* \exp\left(-\frac{\Delta G^{++}}{KT}\right)$$

      - ΔG^{++} Gibbs free energy of activation for ion hopping calculated by NEB
      - ν^* effective attempt frequency calculated by phonon calculations at the beginning and transition states

Case	ΔG^{++} (eV)	ν^* (Hz)	D(cm²/s) @T=300K
ODH	0.78	3.5E+13	2.6E-15
TSH	0.56	3.2E+12	1.6E-12

    - Same methodology applied in solid state electrolytes
  - DFT modelling of negative electrode active materials
    - Ab initio molecular dynamics
      - Creation of amorphous silicon and amorphous lithium silicide models
      - Interpolation of volumetric expansion vs. Li content curve
      - Analysis of bond-breaking patterns at low and high Li contents
    - Elastic properties:
      - Ab-initio calculation of elastic tensor and mechanical parameters
      - Consequences of lithiation and delithiation on the chemical and mechanical properties of all anode components
- Parameters can be further used in larger scale simulations



Understanding of particle behaviour

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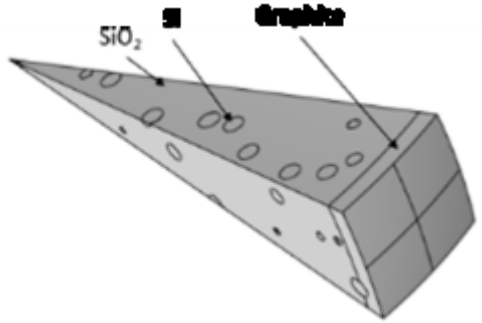
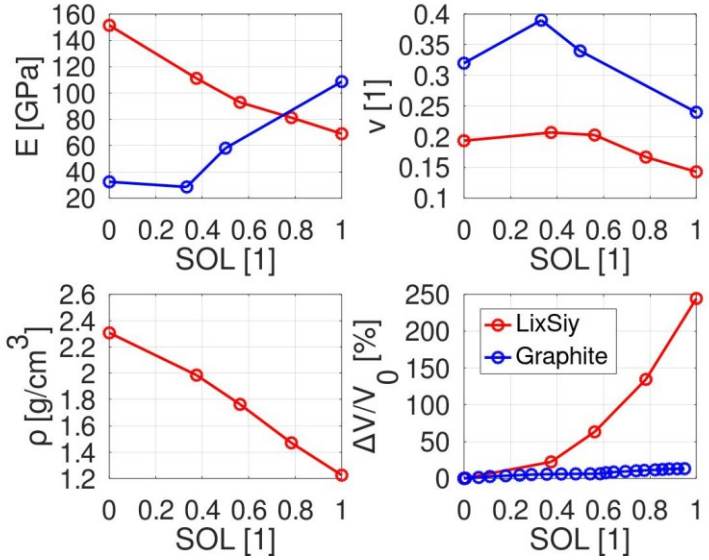
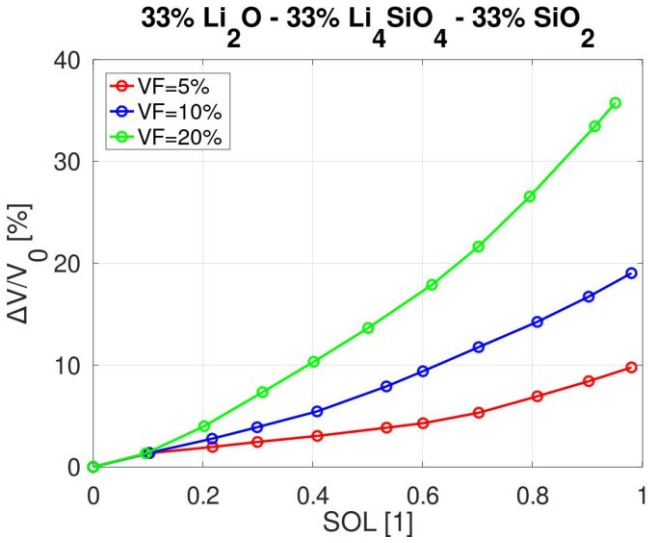
- FEM modelling of a single particle



- Study of the effect of Li insertion on particle behaviour
  - Volume variation
  - Stress generation
  - Mechanical properties variation
- Uncertainties remaining
  - Composition of the matrix
  - Amount of Si in the complete particle

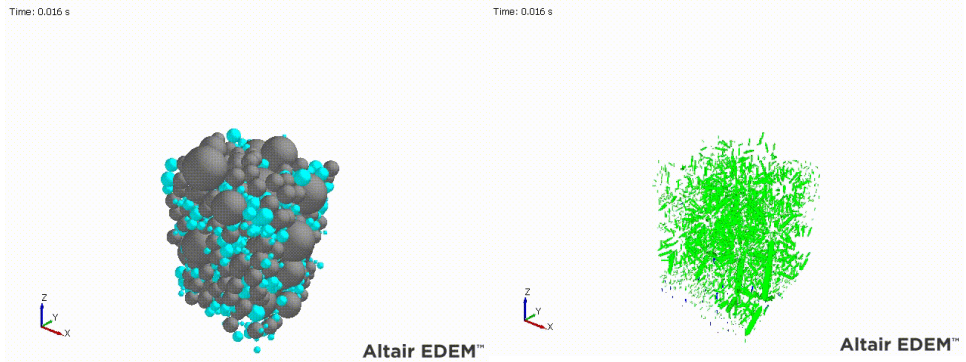


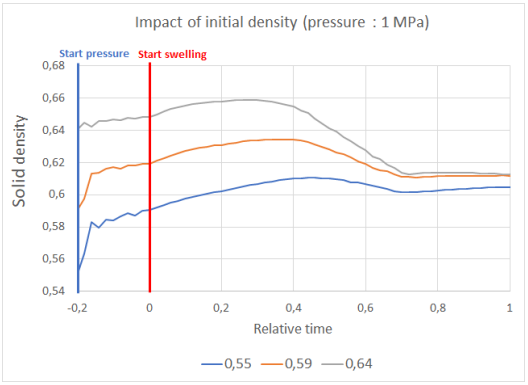


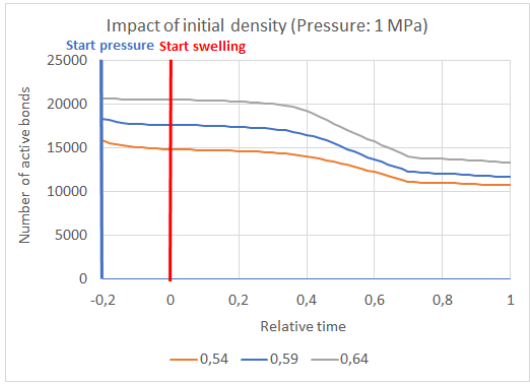
Mechanical behavior of electrode composite

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 875193.

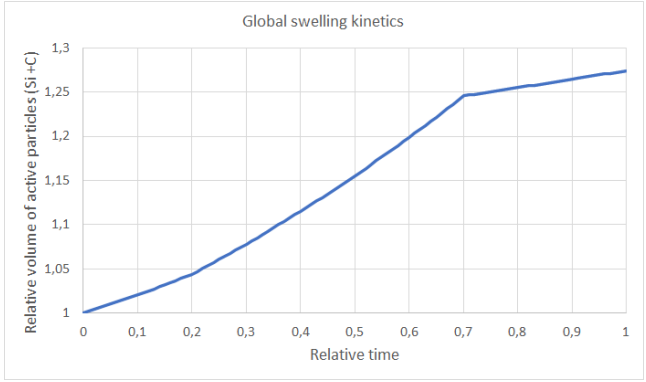
- DEM model of electrode material
  - Si/SiOx and C particles represented as an assembly sphere
  - Special bonding contact laws account for the presence of binder
- "One-way" coupling for electrochemical effect on swelling
  - Particle volume as a function of SOC is provided by other models
  - Particle swelling as a function of time is scripted
- Model variables
  - Initial density
  - Pressure on the anode
  - Binder flexibility
  - Binder dispersion
- Model output
  - Evolution of anode density/volume
  - Binder damage at first charge (no cycling)







- First interesting results
  - No observed influence of binder properties on swelling behaviour
  - Binder flexibility is the key property that pilot binder damage
  - High pressure on electrode collapse porosity and damage binder



Coupled mechanical/electrochemical 3D behaviour

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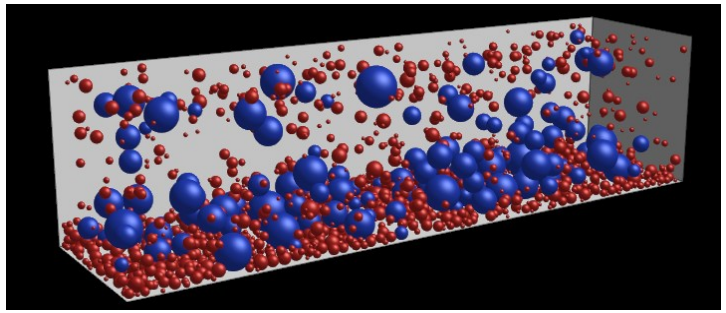
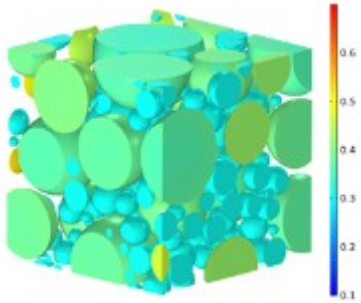
- FEM coupled modelling of the electrode interface
  - Creation of a representative electrode volume using DEM or stochastic approaches
- Coupled simulation of mechanical behavior and electrochemical behavior
  - Charge behavior of particles depends
    - Their geometry
    - Their nature (Si based or graphite)
  - Evaluation of electrode variation over cycling
    - Electrode displacement
    - Endured pressure in binder/electrolyte domain
- Remaining challenges:
  - Fully coupled model based on large deformation theory





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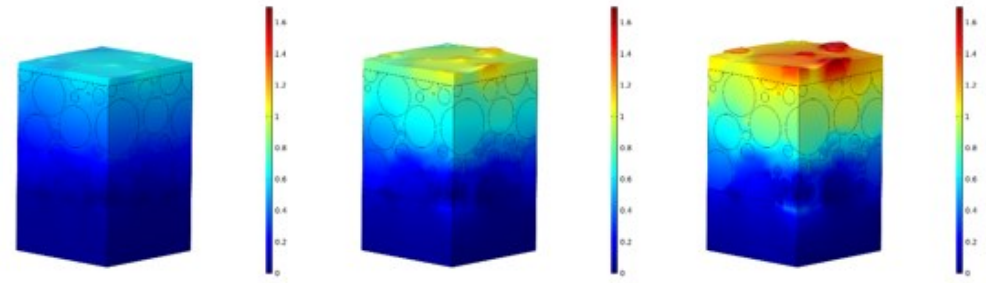
Displacement



1D model at cell level

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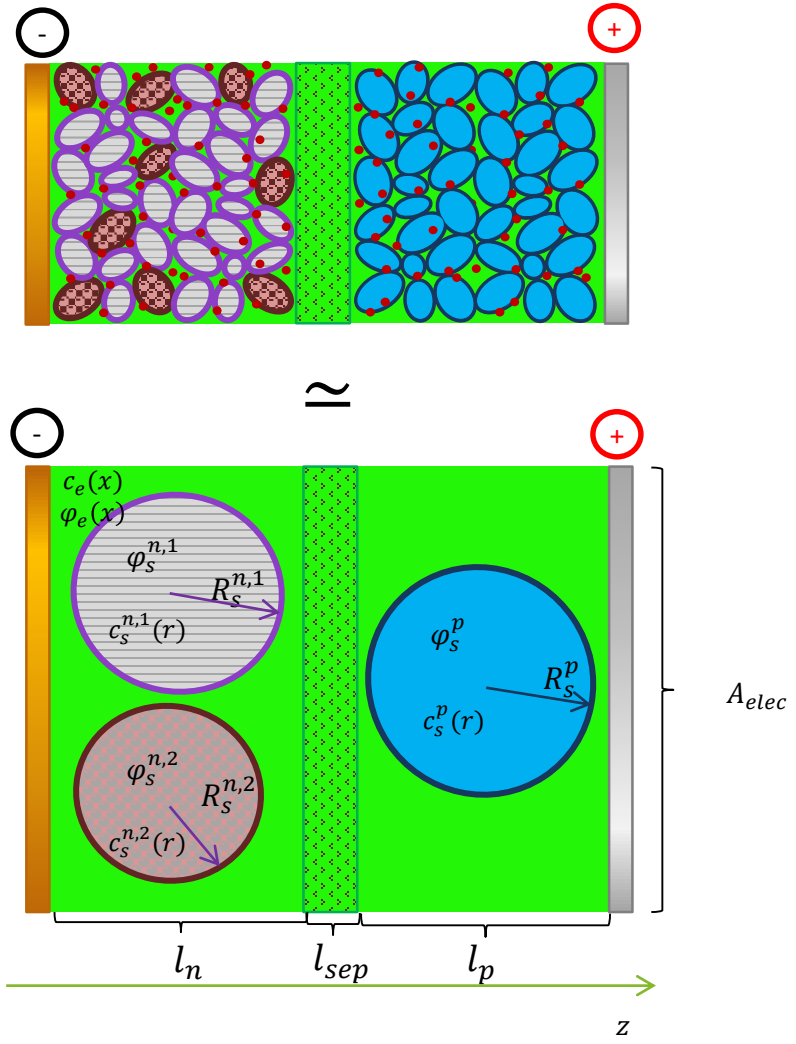
- Use of a simplified electrochemical model
- SPM-e model with blend negative electrode
  - Compatible with long term simulation for aging
  - Accounting for nominal electrochemical behaviour
  - Accounting for aging phenomena
    - SEI layer formation on both material in the negative
    - Li plating
    - Loss of active material at the positive
  - With mechanical aspects
    - Stress induced diffusion
    - Cracks induced SEI formation
    - Loss of active material due to mechanical stresses

M. Petit, E. Calas and J. Bernard, *J.Power Sources*, 2020, **479**, 228766.



Modelling of aging phenomena

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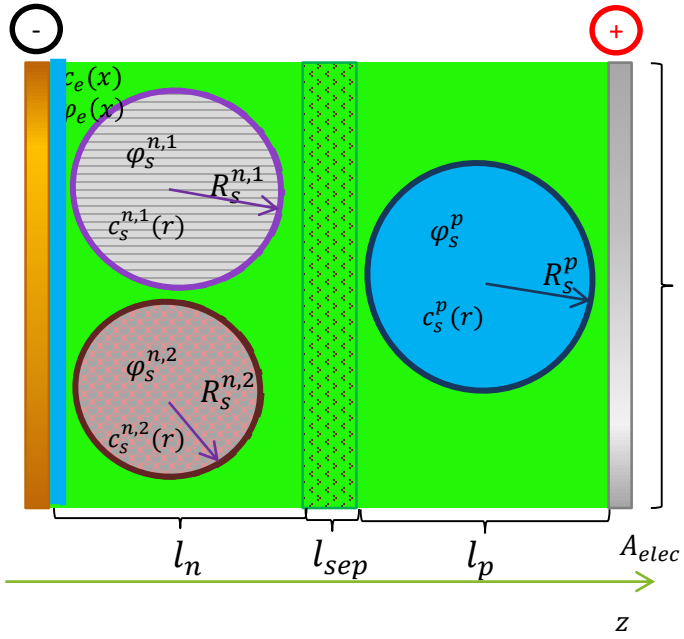
- SEI formation
  - Simplified SEI formation formulation without SEI convection
  - SEI formation current computed
    - Leading to Loss of Li inventory
    - SEI thickness increase
      - SEI formation passivation
      - Resistance increase
- Li plating
  - Reversible Li plating
  - Lithium trapping into inactive materials ➔ dead Li
- Loss of positive active material
  - Oxidation of positive active material leading to loss of active material
- Cracks induced SEI formation
  - Based on stresses computed in particles
    - $\frac{dA_{cr}}{dt} = k_{cr} \frac{d\sigma_\theta}{dt}$
  - Increased SEI formation rate
- Cracks induced LAM
  - Based on contact losses computed in DEM ➔ loss of active material
    - $\frac{d\Delta\varepsilon}{dt} = k_{LAM} \frac{dC_{loss}}{dt}\Big|_{SOC,T}$



Charge balance leading to loss of Li inventory

$$I_{neg} = I_{gr} + I_{SiOx} + I_{SEI} + I_{pl}$$

$$I_{pos} = I_{NMC} + I_{ox}$$

Impact of loss of active material

$$\varepsilon_{neg}^s = \varepsilon_{neg_0}^s (1 - \Delta\varepsilon_{LAM})$$

$$\varepsilon_{pos}^s = \varepsilon_{pos_0}^s (1 - \sum\Delta\varepsilon_{LAM})$$

Model outputs

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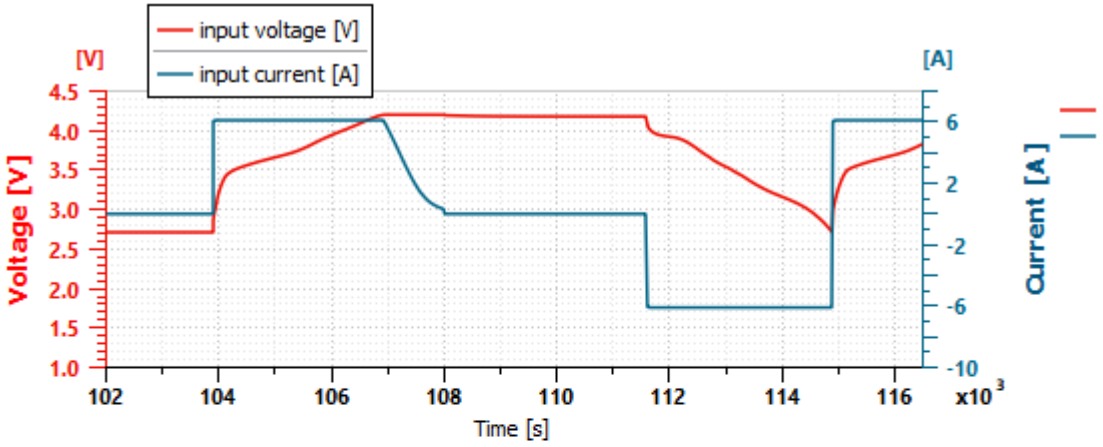
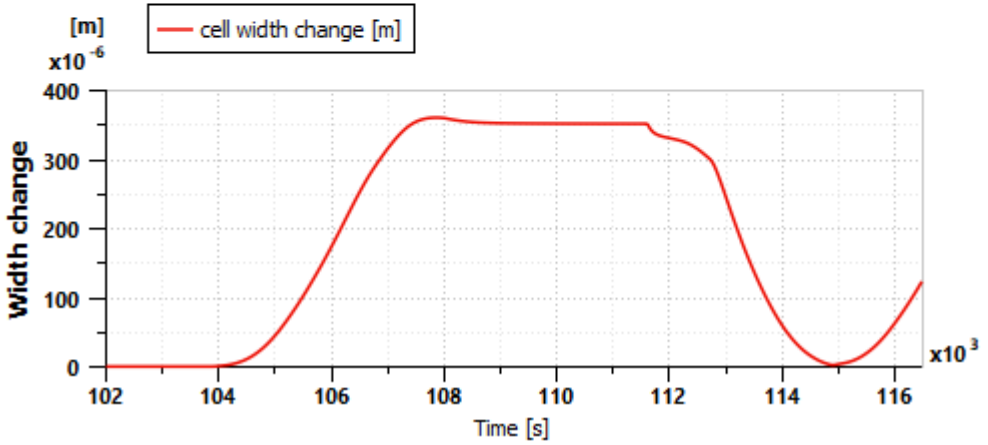
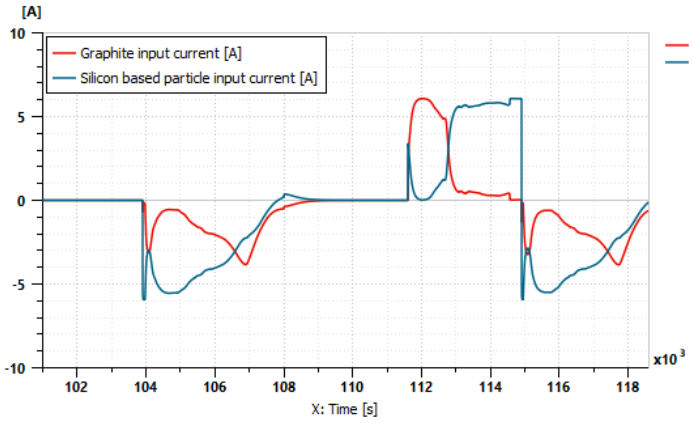
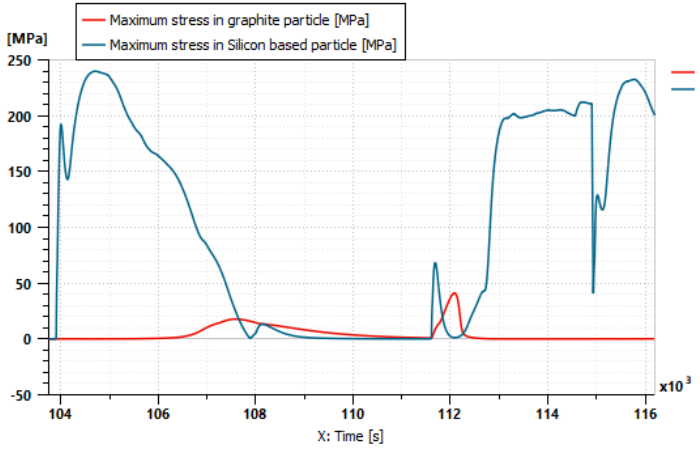
- Classical cell behaviour
  - Voltage
  - Heat release
  - Swelling
    - From DEM calculation
      - Cell length change given by material volume change
    - 2 steps during discharge
      - Gr deintercalation low volumetric change
      - Si deintercalation with high volumetric change
- Non accessible variables
  - Material concentrations
  - Current repartition between materials
  - Potentials









Evaluation of cell formation

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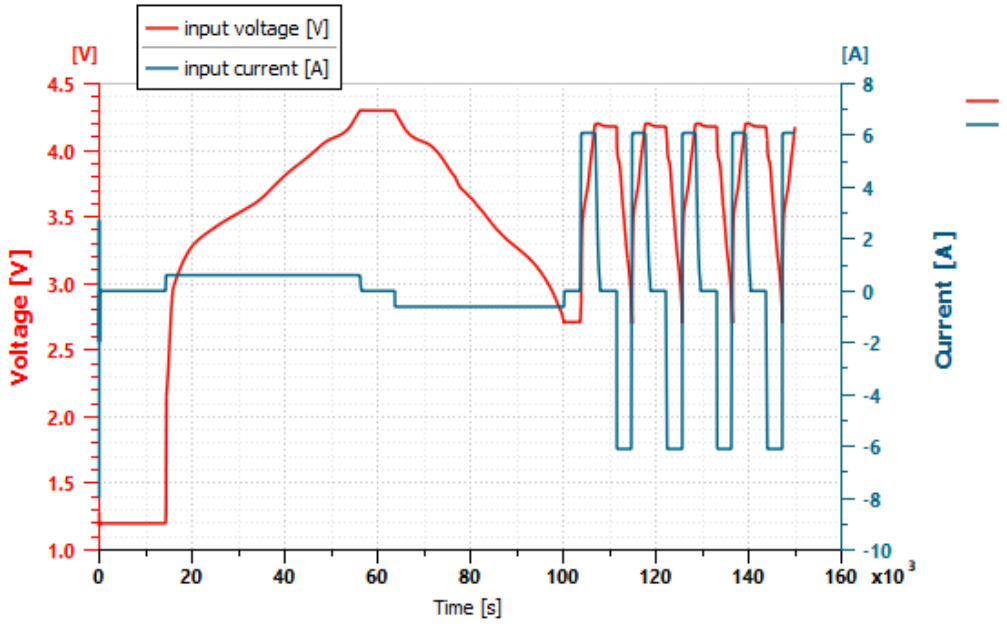
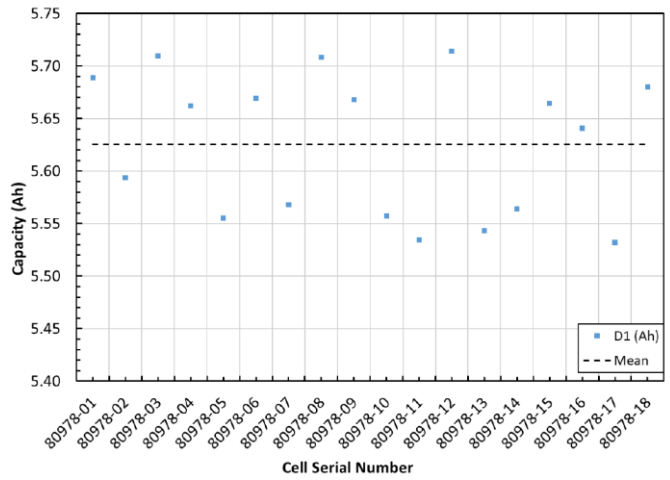
- Aim simulate a realistic formation cycle
  - Pristine electrode are set-up in the model
    - Fully lithiated NMC in the positive
    - Empty negative electrode
  - Formation cycle used for real MODALIS² cells
  - Design taken from Saft
  - Model operates as a test bench and automatically switch between rest, CC and CV
- 41 h simulated in 10 minutes
- Initial cell capacity computed
  - 5,58 Ah VS 5,63 as mean capacity for manufactured cells





Evaluation of cell aging

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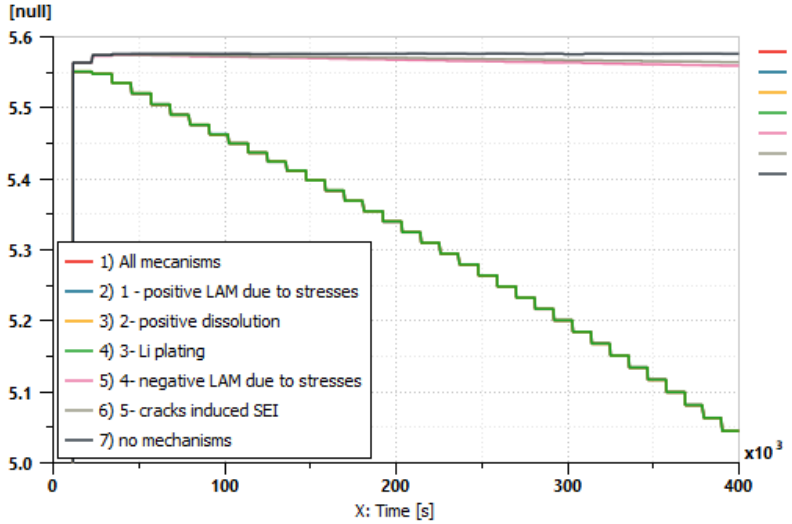
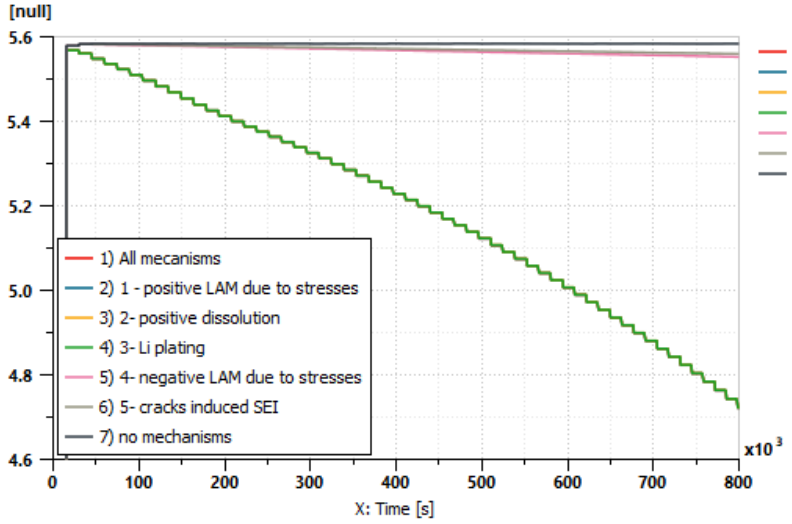
- CC/CV cycles simulated
  - From initial formation starting point
  - Fast simulation (7 parallel runs)
    - 400 000 s simulated (36 full DoD cycles)
      - 3 000 s computational time
    - 800 000 s simulated (57 full DoD cycles)
      - 4300 s computational time
  - Evaluation of the effect of each aging phenomenon
- Cycle:
  - CC at 6A or 3 A then CV at 4,2 V
  - CC at -6 A until 2,7 V
  - Cell capacity evaluated at 6A during discharge
- Main aging phenomena (qualitatively)
  - LAM due to stresses
  - Then SEI with visible impact of cracking





3D cell modelling – non-uniform aging

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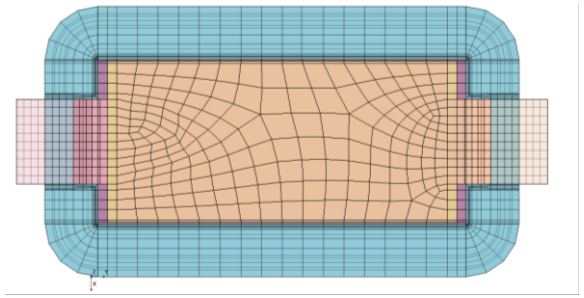
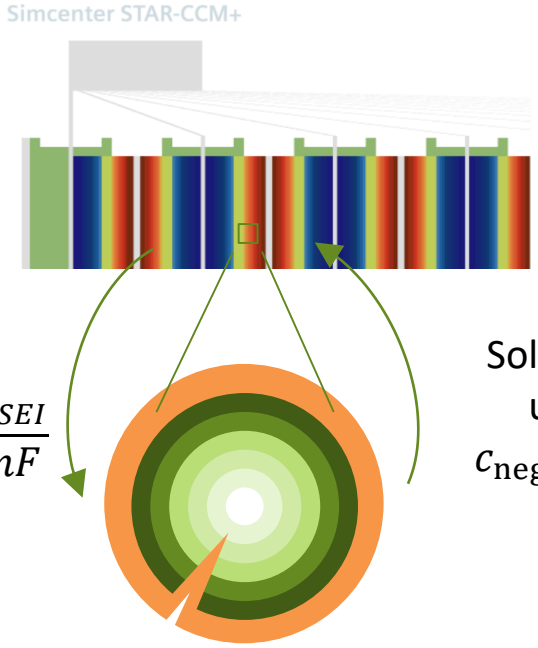
- Non-uniform aging in thermo-electro-chemically coupled macrohomogenous model (P2D) with realistic geometry



- To be presented in 32nd ISE topical meeting

(De-)Interclalation current $j_{\mathrm{neg}}(c_{\mathrm{neg}}, \varepsilon_{\mathrm{active}}, A_{\mathrm{crack}}, \delta_{\mathrm{SEI,...}})$
and side reaction current $j_{\mathrm{SEI}}(c_{\mathrm{solv}}, \varepsilon_{\mathrm{active}}, A_{\mathrm{crack}}, \delta_{\mathrm{SEI,...}})$
as sources/sinks in macrohomogeneous balance



Particle boundary conditions:

$$D_{\mathrm{neg}} \left.\frac{\partial c_{\mathrm{neg}}(r,t)}{\partial r}\right|_{r=R} = -\frac{j_{\mathrm{neg}}}{nF} - \frac{j_{SEI}}{nF}$$

Solve 1D problem and update variables:
$c_{\mathrm{neg}}, \varepsilon_{\mathrm{active}}, A_{\mathrm{crack}}, \delta_{\mathrm{SEI}}$

Conclusions and perspectives

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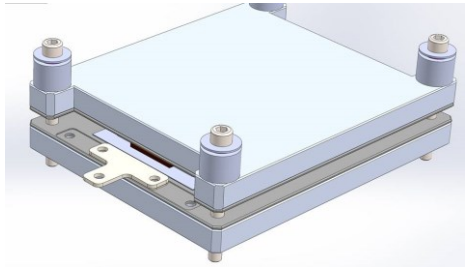
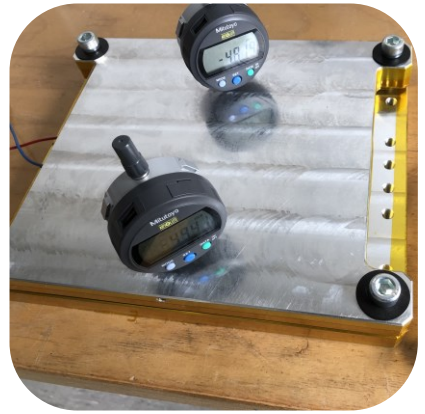
- Full toolchain implemented for Gen3b cells
  - Link between material – electrode – full cell behaviour
  - Phenomena studied
    - Mechanical behaviour
    - Diffusion
    - Aging
    - Thermal stability
- Tool chain to be validated against experimental data
  - Extensive aging campaign
  - Dedicated devices to evaluate swelling
- Future developments to focus on Gen4 cells
  - Solid electrolyes with metal Li
  - Development initiated on argyrodite behaviour
    - Li conductivity
    - Chemical stability
    - 1 D model to be adapted to account for Li electrode

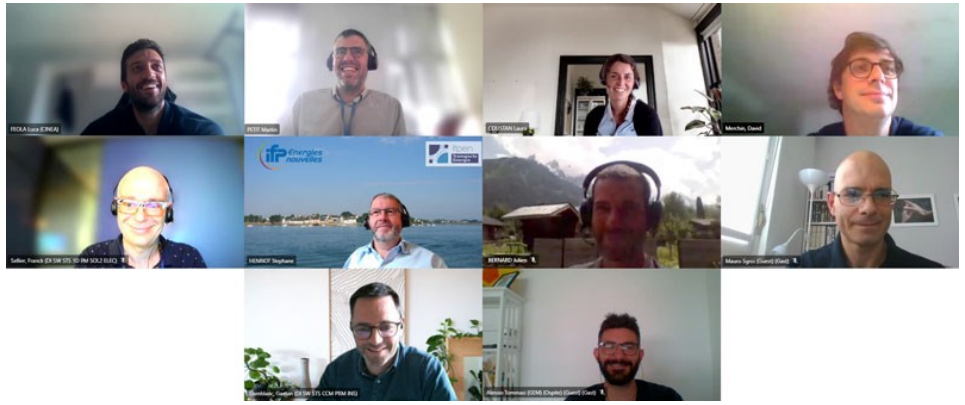




Lab cell

2 mAh
/ 0,4 cm²

High operating pressure
(>100 MPa)



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THANKS A LOT FOR YOUR ATTENTION

HTTPS://MODALIS2-PROJECT.EU/

MODALIS 2