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

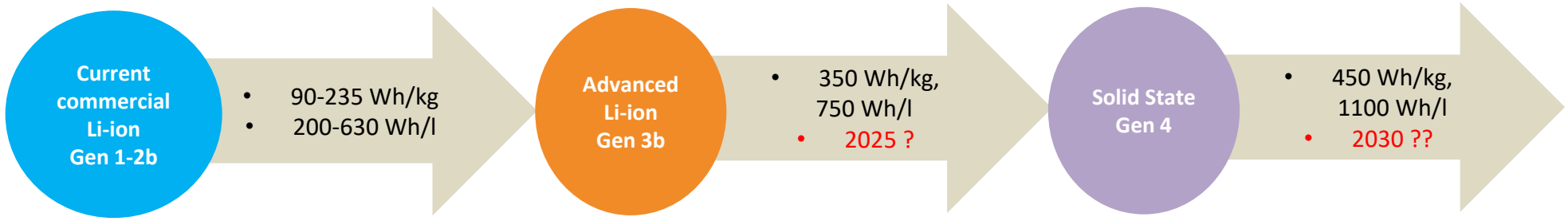
SI/C ELECTRODE MULTISCALE MODELLING FROM ATOMS TO CELLS

WORKSHOP @ POLYTECHNIQUE SCHOOL IN PALAISEAU

MARTIN PETIT – IFP ENERGIES NOUVELLES

Next generation batteries

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



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

Specific needs from all stakeholders

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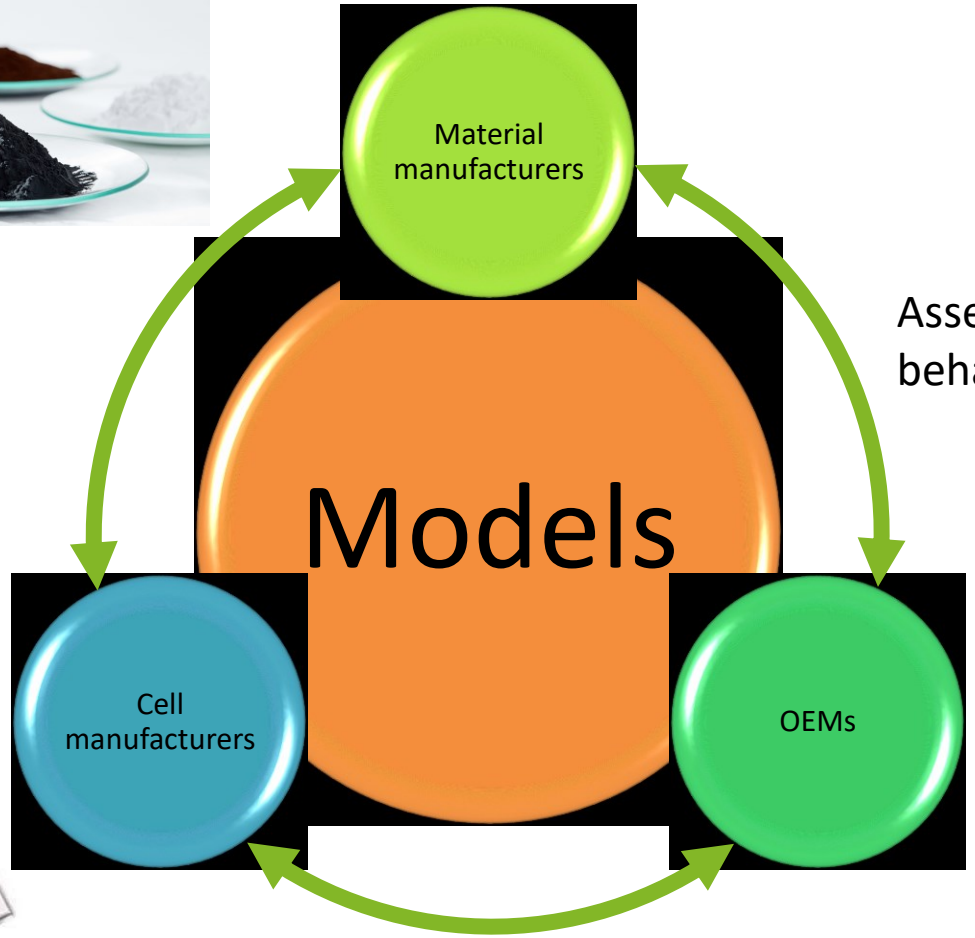
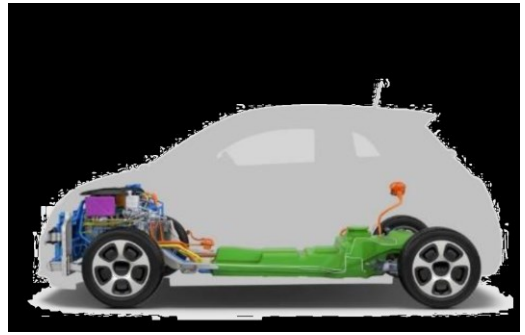
Assess new material integration in battery cells



Assess new material specific behaviour in full systems



Assess new generation cells performance in realistic systems

Si-based anode modelling toolchain

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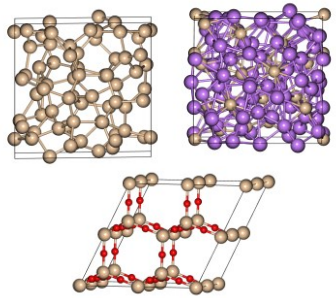
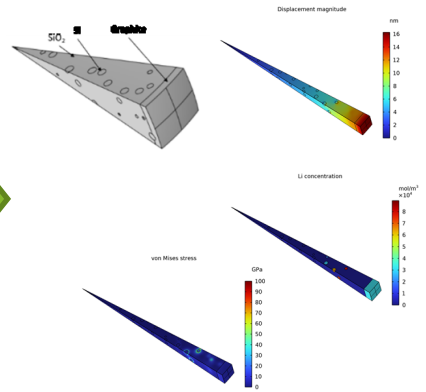
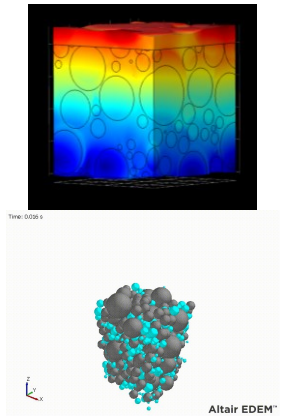


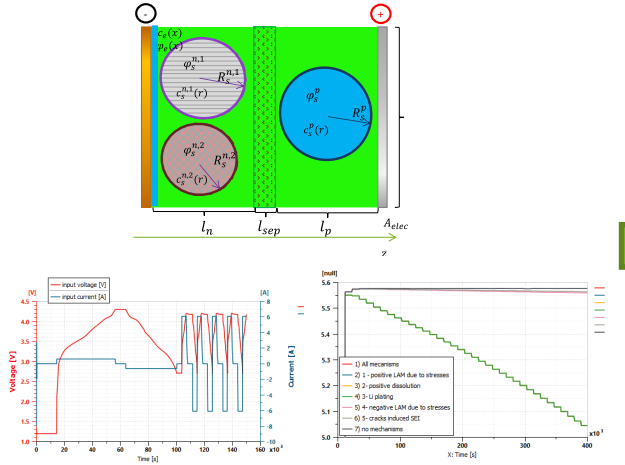
DTF modelling of Si, Graphite and SiO_2



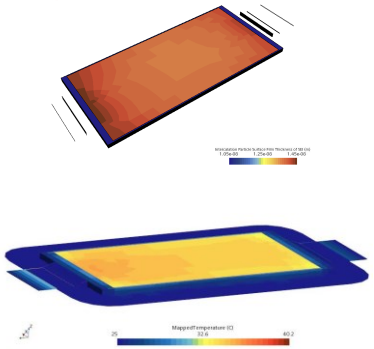
Mechanical behaviour of Si/SiO_2 particles



Microstructure electrochemical and mechanical behaviour



1D cell behaviour



3D cell behaviour

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

Studied system

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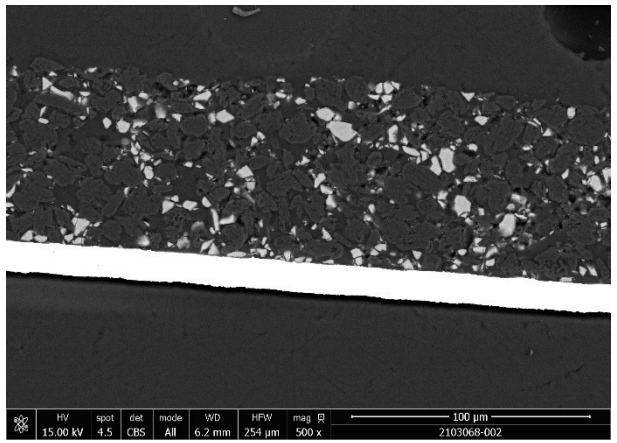
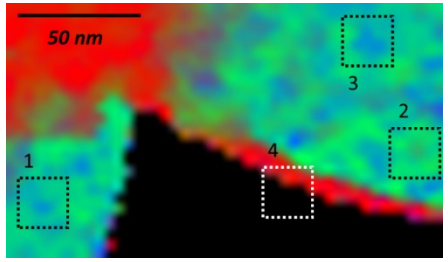
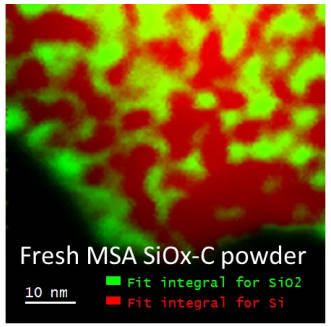
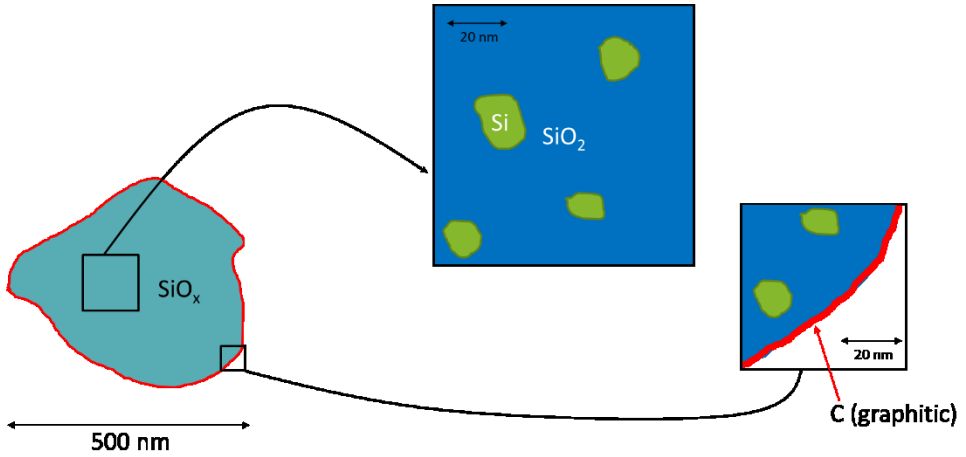
- Gen 3b cell
  - NMC811
  - SiOx/C negative electrode (aim >20% Si)
  - 1M LiPF6 in EC:DMC (3:7) + 10% FEC
- Commercial negative material
  - Complex formulation needing specific characterization
    - Graphite particles: 77%
    - Si based particles
      - Si inclusion in SiO2 matrix + 20nm Graphite layer
        - Quantification Si_0/Si_{IV} : 50/50









Initial experimental observation of material behaviour

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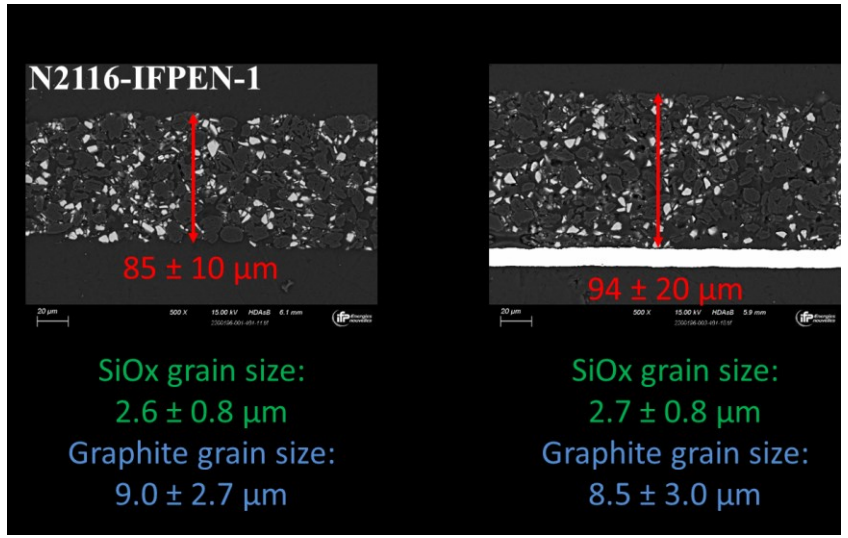
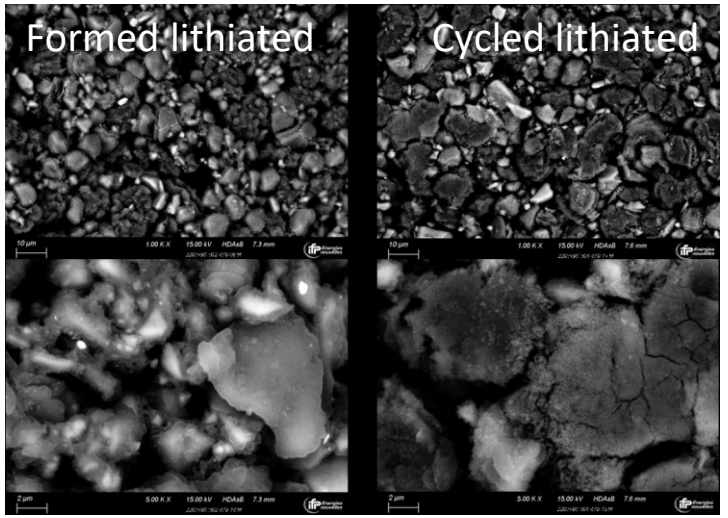
- Coin cells prepared with material
  - Formed
  - Capacity 580 mAh/g (theoretical 650 mAh/g)
  - Cycled 10 times
- SEM polished section observations (not performed on lithiated electrodes)
  - Observed swelling of cycled electrode
  - Looser packing of particles
- SEM direct powder deposition
  - Heterogeneous contrast due to
    - Heterogeneous lithiation
    - Heterogeneous SEI thickness

    ⍰Loss of electric contact with collectors
  - Cracks present on SEI in cycled samples





Intrisic material properties through ab initio modelling

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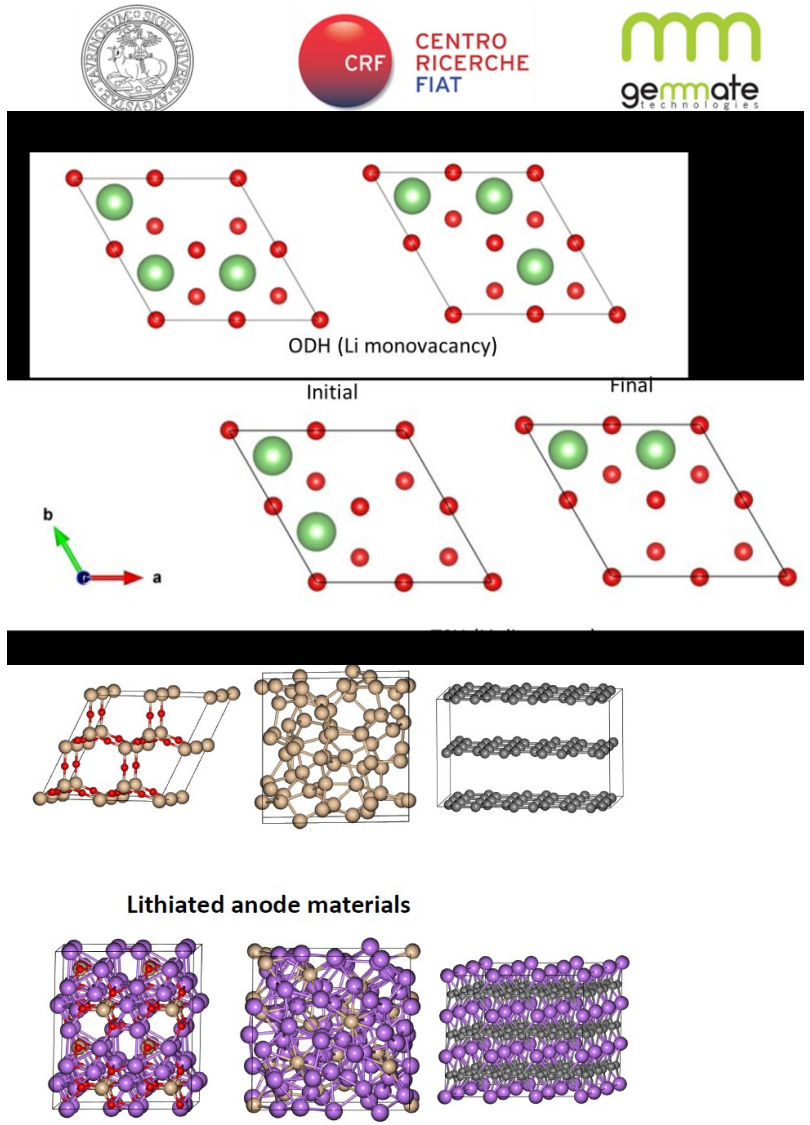
- Simulation focused on intrinsic properties for the material
  - Diffusion properties investigated through Nudged Elastic Band methodology
    - Evaluation of hoping a distance between adjacence sites

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

      - 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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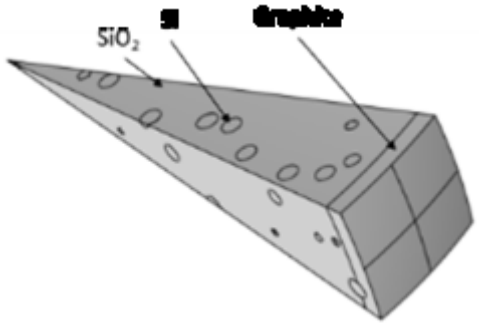
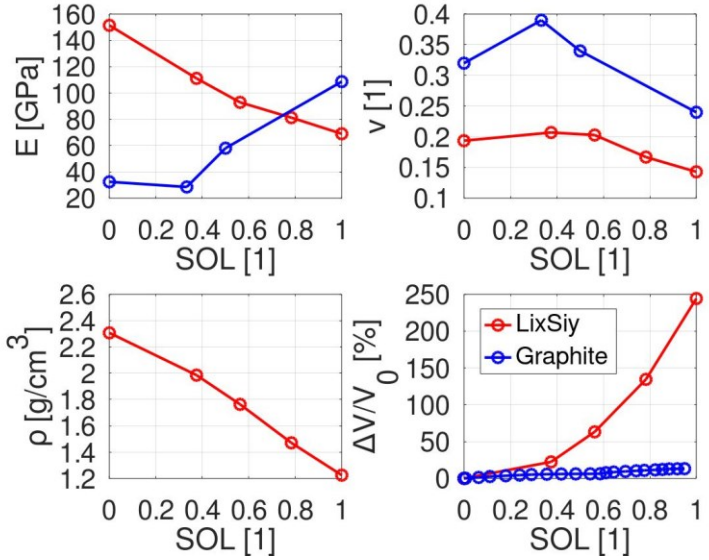
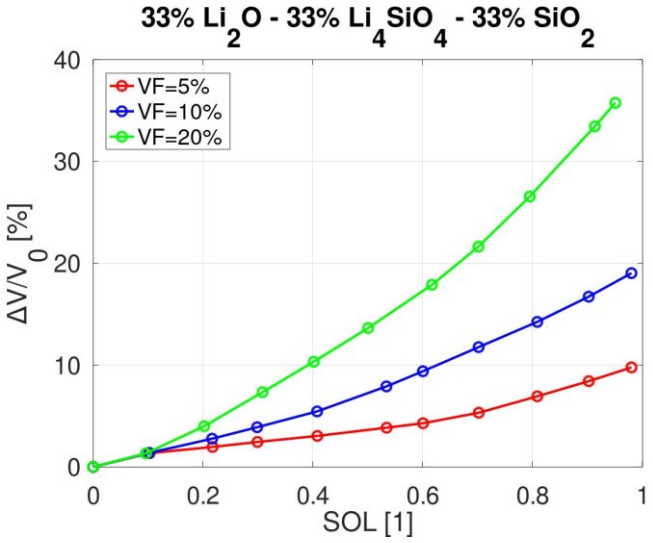
- FEM modelling of a single particle



- Study of the effect of Li insertion on particle behaviour
  - Volume variation
  - Stress generation
  - Mechanical properties variation

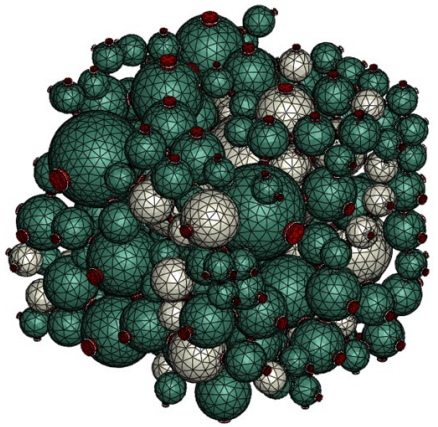


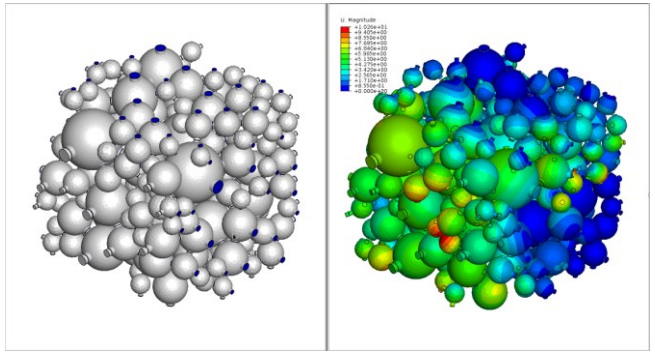


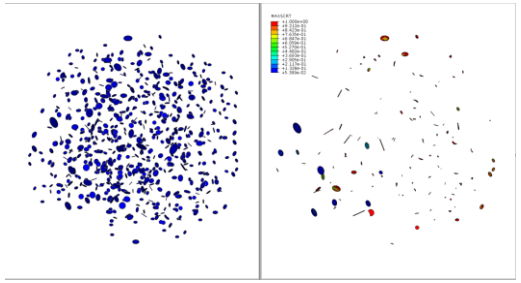
Mechanical electrode scale modelling – FEM approach

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

- Principle of the model :
  - DEM to generate an initial assembly of particles
  - Cylindrical bridges are inserted between neighbors
  - In FEM, grains are dilated linearly, depending on the material
- Key element of the model : the bridges
  - Assumption the binder is concentrating at grains contact
  - Initial model with elastoplastic bridges do not converge (too much distortion)
  - Second model use cohesive zone for breakage modeling
- Many issues encountered
  - Considerable difficulties on numerical convergence (stability, damage modeling)
  - Damage prediction on polymer is too severe
- Switch to full DEM approach







Mechanical electrode scale modelling – DEM approach

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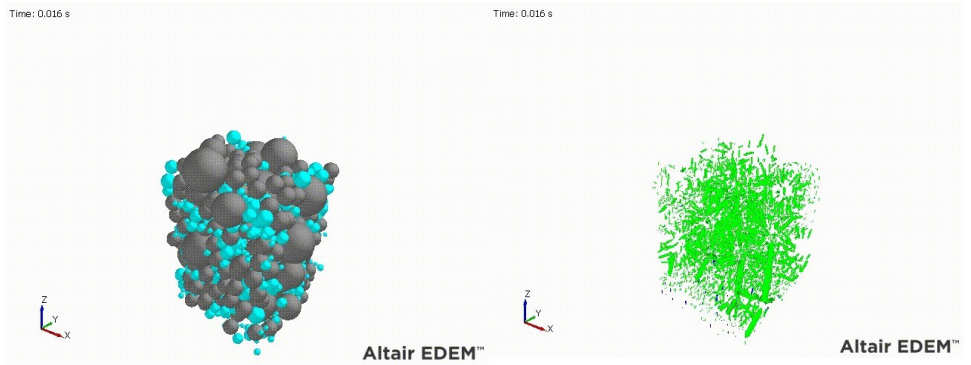
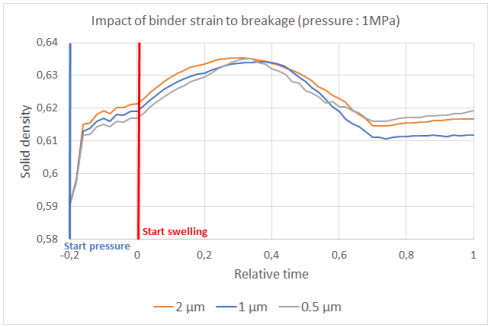
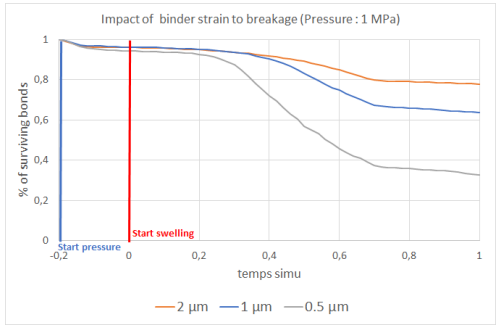
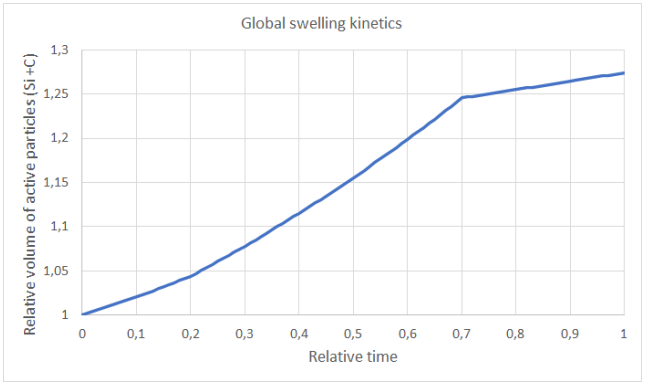
- DEM model of electrode material
  - Si/SiOx and C particles represented as an assembly sphere
  - Special bonding contact laws account for the presence of binder
- "One-way" coupling for electrochemical effect on swelling
  - Particle volume as a function of SOC is provided by other models
  - Particle 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
  - Swelling behaviour
    - No observed influence of binder properties on swelling behavior
    - Swelling seems entirely piloted by active particles topology (initial density, PSD)
  - Binder damage
    - Key property : binder strain to breakage
    - Binder bridges accommodate strains due to grain movement… or not

  ⍰ Swelling and binder damage are uncoupled !









1D model at cell level

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- Use of a simplified electrochemical model
- SPM-e model with blend negative electrode
  - Based on M. Petit, E. Calas and J. Bernard, *J.Power Sources*, 2020, **479**, 228766.
  - Compatible with long term simulation for aging
  - Accounting for nominal electrochemical behaviour
    - Electrochemical kinetics
    - Electrolyte behavior
      - Liquid mass and charge balances
    - Active material behavior
      - Solid mass and charge balance
  - 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

Physical and chemical mechanisms		Boundary conditions
Solid phase: conservation of Li^+ species	$\frac{\partial}{\partial t}c_s^k - \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\mathcal{D}_s^k\frac{\partial}{\partial r}c_s^k\right) = 0$	$\mathcal{D}_s^k\frac{\partial}{\partial r}c_s^k\Big\|_{r=0} = 0$ $-\mathcal{D}_s^k\frac{\partial}{\partial r}c_s^k\Big\|_{r=R_s^k} = \frac{I_{elec}^k}{a_s^k A_{elec}\delta_{elec}F}$
Electrolyte phase: conservation of Li^+ species	$\frac{\partial}{\partial t}\varepsilon^e c^e - \frac{\partial}{\partial z}\left(D_e^{eff}\frac{\partial}{\partial z}c_e\right) - (1-t^+)\frac{\sum_k j_f^k}{F} = 0$	$\frac{\partial}{\partial z}c^e\Big\|_{z=0} = \frac{\partial}{\partial z}c^e\Big\|_{z=L} = 0$
Solid phase: charge conservation	$\frac{\partial}{\partial z}\left(\sigma_{eff}\frac{\partial}{\partial z}\phi_s\right) - \sum_k j_f^k = 0$	$-\sigma_{eff}^n\frac{\partial}{\partial z}\phi_s\Big\|_{z=0} = -\sigma_{eff}^p\frac{\partial}{\partial z}\phi_s\Big\|_{z=L} = I/A_{elec}$ $\frac{\partial}{\partial z}\phi_s\Big\|_{z=\delta_n} = \frac{\partial}{\partial z}\phi_s\Big\|_{z=L-\delta_p} = 0$
Electrolyte phase: charge conservation	$\frac{\partial}{\partial z}\left(\kappa_{eff}\frac{\partial}{\partial z}\phi_e\right) + \frac{\partial}{\partial z}\left(\kappa_{eff}^D\frac{\partial}{\partial z}\ln c_e\right) + \sum_k j_f^k(z) = 0$	$\frac{\partial}{\partial z}\phi_e\Big\|_{z=0} = \frac{\partial}{\partial z}\phi_e\Big\|_{z=L} = 0$
Electrochemical kinetics	$j_f^i = a_s^i i_0^i\left(exp\left(\frac{\alpha\mathcal{F}}{RT}\bar{\eta}_{ct}^i\right) - exp\left(-\frac{(1-\alpha)\mathcal{F}}{RT}\bar{\eta}_{ct}^i\right)\right)$ $j_f^j = a_s^j i_0^j\left(exp\left(\frac{\alpha\mathcal{F}}{RT}\bar{\eta}_{ct}^j\right) - exp\left(-\frac{(1-\alpha)\mathcal{F}}{RT}\bar{\eta}_{ct}^j\right)\right)$	
Electrode overpotential	$i_0^i = k_0^i c_e^{\alpha_{ox,i}}\left(c_s^{i,max} - c_s^i(R_n^i)\right)^{\alpha_{ox,i}} c_s^i(R_n^i)^{\alpha_{ox,i}}$ $i_0^j = k_0^j c_e^{\alpha_{ox,j}}\left(c_s^{j,max} - c_s^j(R_p^j)\right)^{\alpha_{ox,j}} c_s^j(R_p^j)^{\alpha_{ox,j}}$ $\bar{\eta}_{ct}^k = \Delta\phi - U_{elec}^k = \overline{\phi_s} - \overline{\phi_e} - U_{elec}^k$	
Double layer capacity	$\frac{d\Delta\phi_p}{dt} = \frac{1}{a_s^p A_{elec}\delta_p C_{dl}^p}\left(I - A_{elec}\int_{L-\delta_p}^{L}\sum_j j_f^j\,dz\right)$ $\frac{d\Delta\phi_n}{dt} = \frac{1}{a_s^n A_{elec}\delta_n C_{dl}^n}\left(-I - A_{elec}\int_0^{\delta_n}\sum_i j_f^i\,dz\right)$	
Electrolyte ionic diffusional conductivity	$\kappa_{eff}^D = \frac{2RT\kappa_{eff}}{\mathcal{F}}(t_+ - 1)\left(1 + \frac{d\ln f_\pm}{d\ln c_e}\right)$	
Solid phase electronic conductivity	$\sigma_{eff} = \frac{\sum_k \varepsilon_s^k\sigma_k}{\sum_k \varepsilon_s^k}$	
Solid phase overvoltage	$\eta_s = \frac{I\delta_{elec}}{3A_{elec}\sigma_{eff}}$	

Full cell swelling assessment

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

- Main assumption:
  - Cell behave like a spring
    - Material swelling cause displacement
    - Other materials (packaging, separator…) have stiffness
  - Following results from DEM
    - Active material volumetric change = whole electrode volumetric change
- Evaluation of a displacement due to volume variation

$$\frac{dl_{cell}}{dt} = \frac{N_{stack}}{A_{elec}} \sum \frac{dV_{s_i}}{dt}$$

  - Volume variation is evaluated from material concentration

$$\frac{dV_{s_i}}{dt} = \frac{\varepsilon_s^i \mathrm{l}_{\mathrm{elec}}^0}{c_s^{max}} \left(\frac{d\bar{c_s^i}}{dt} \beta\left(\bar{c_s^i}\right) + \bar{c_s^i} \frac{d\beta}{dt}\bigg|_{\bar{c_s^i}} \right)$$

    - β is the volumetric expansion coefficient (different for Si and Graphite)

Model outputs

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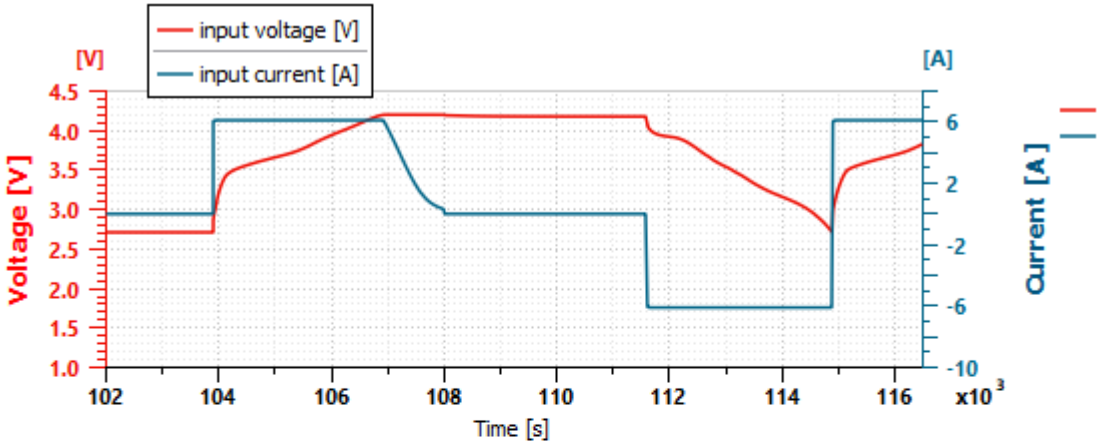
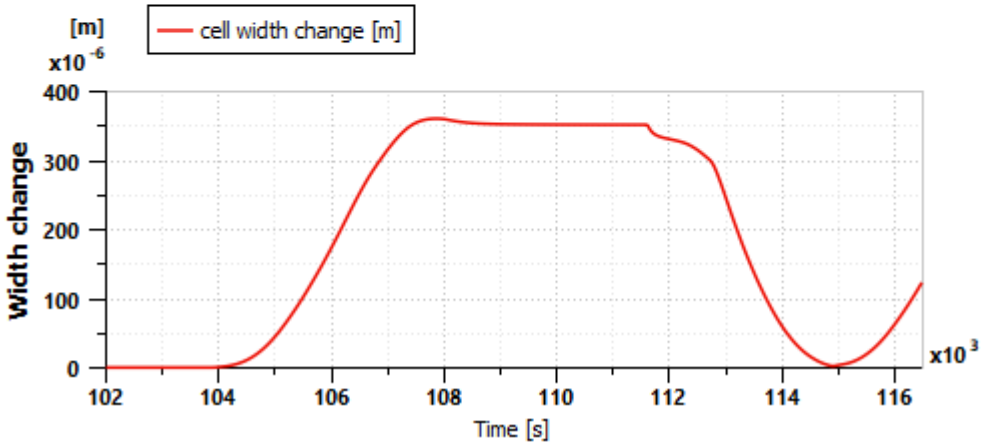
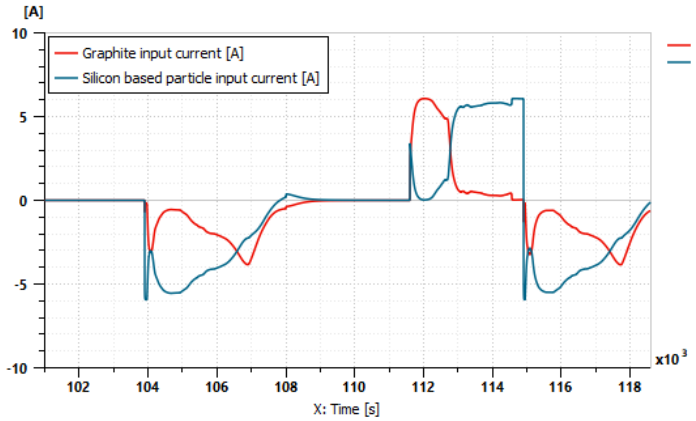
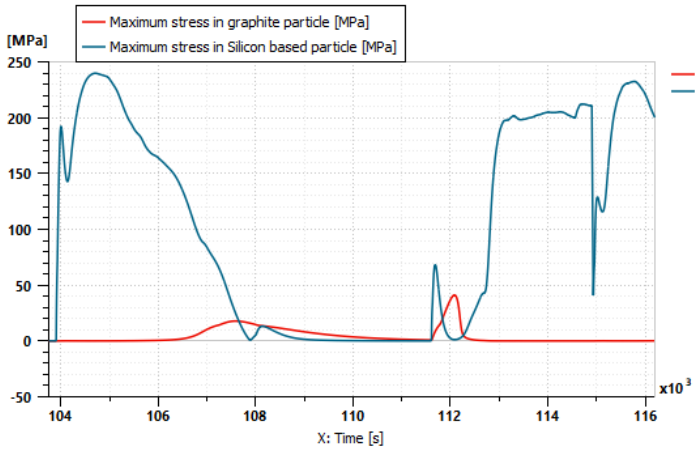
- Classical cell behaviour
  - Voltage
  - Heat release
  - Swelling
    - From DEM calculation
      - Cell length change given by material volume change
    - 2 steps during discharge
      - Gr deintercalation low volumetric change
      - Si deintercalation with high volumetric change
- Accessible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









Modelling of aging phenomena

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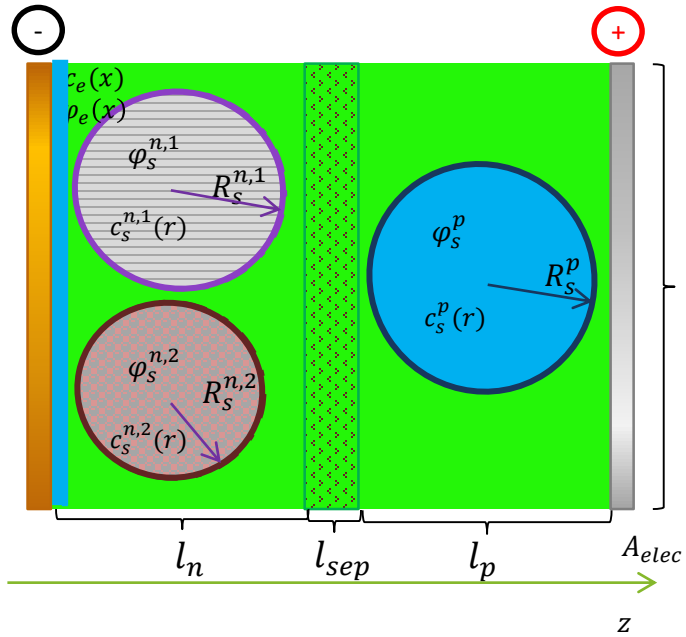
- SEI formation
  - Simplified SEI formation formulation without SEI convection
  - SEI formation current computed
    - Leading to Loss of Li inventory
    - SEI thickness increase
- Li plating
  - Reversible Li plating
  - Lithium trapping into inactive materials ⍰ dead Li
- Loss of positive active material
  - Oxidation of positive active material leading to loss of active material
- Cracks induced SEI formation
  - Based on stresses computed in particles
    - $\frac{dA_{cr}}{dt} = k_{cr} \frac{d\sigma_\theta|_{r=Rn}}{dt}$
  - Increased SEI formation rate with no SEI thickness incease
- Cracks induced LAM
  - Based on stress calculated in model $\frac{dC_{loss}}{dt} = \beta_{mec} \max_{r} \left| \frac{d\sigma_\theta(r)}{dt} \right|$
  - Or 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

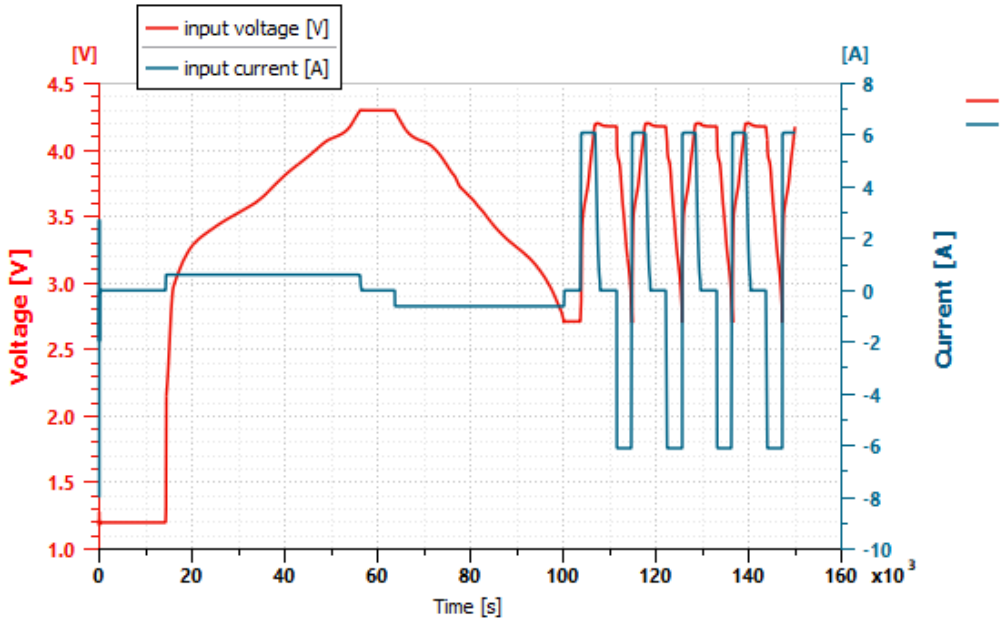
$$\varepsilon_{neg}^s = \varepsilon_{neg_0}^s (1 - \Delta\varepsilon_{LAM})$$

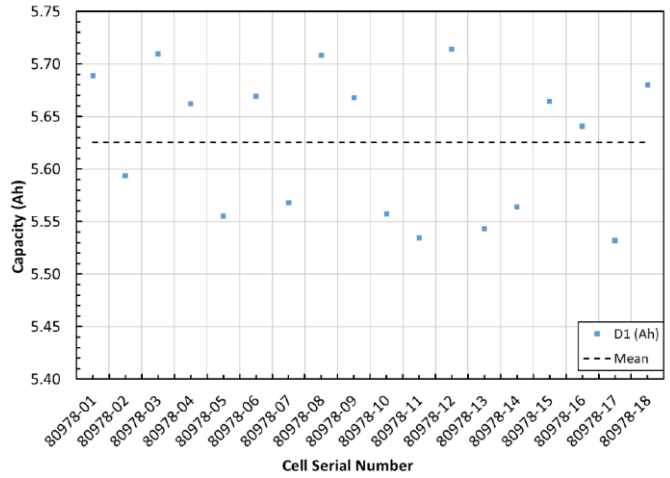
$$\varepsilon_{pos}^s = \varepsilon_{pos_0}^s (1 - \sum\Delta\varepsilon_{LAM})$$

Evaluation of cell formation

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

- 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

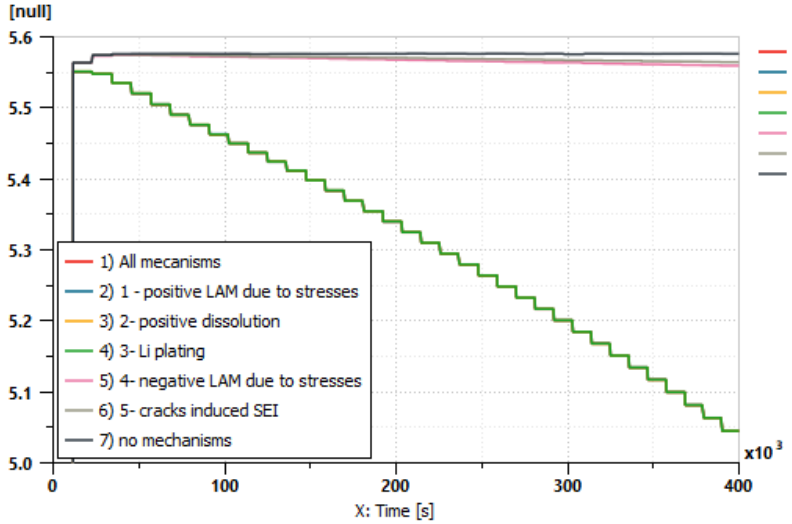


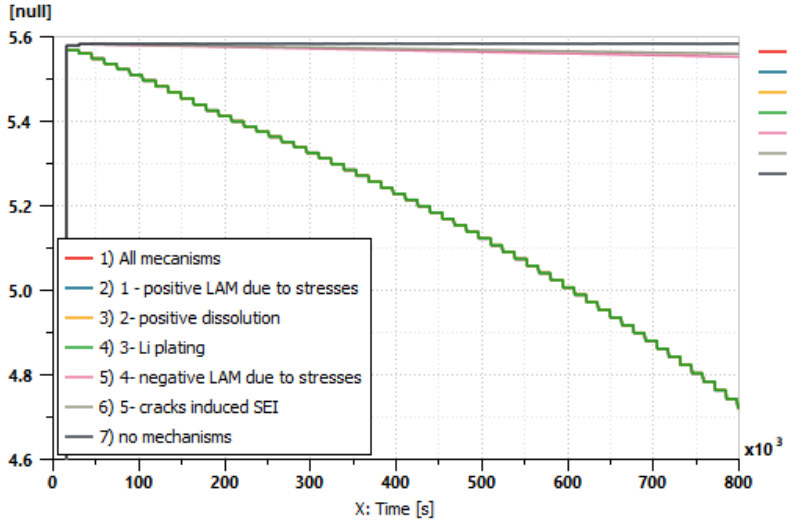


Evaluation of cell aging

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

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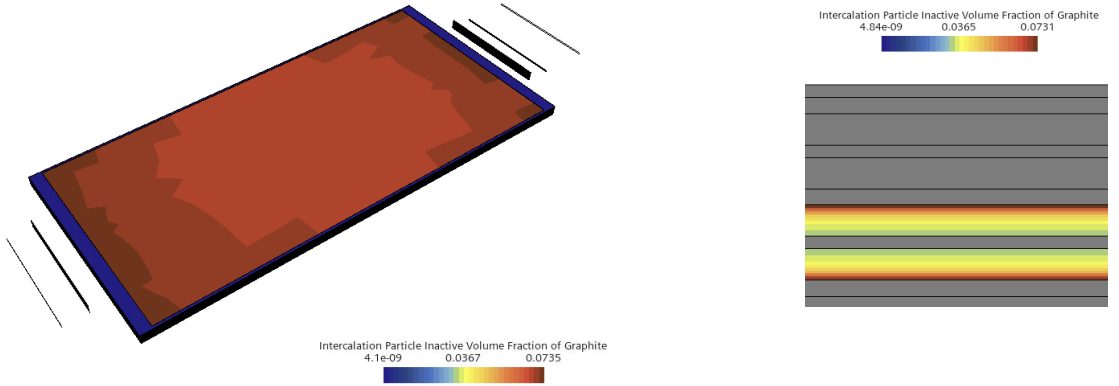
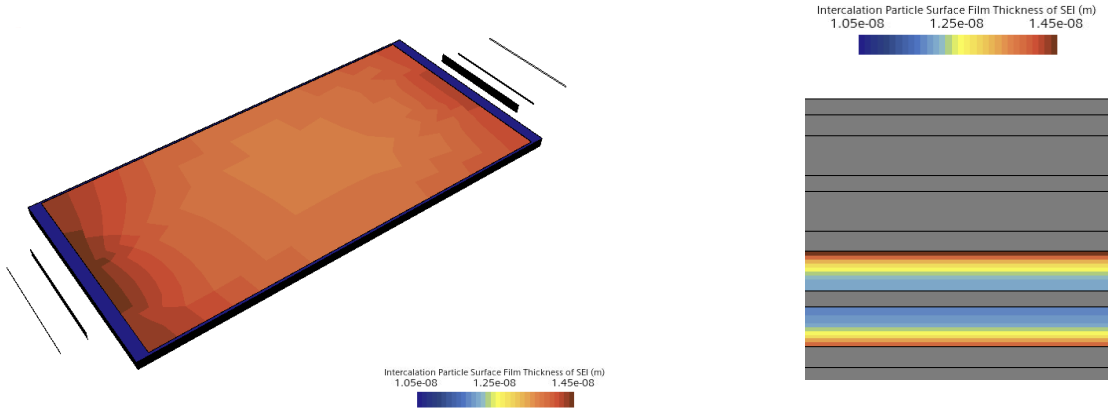
- Non-uniform aging in thermo-electro-chemically coupled macrohomogenous model (P2D) with realistic geometry

Heterogeneous loss of Active materials



Heterogeneous SEI formation



Conclusions and perspectives

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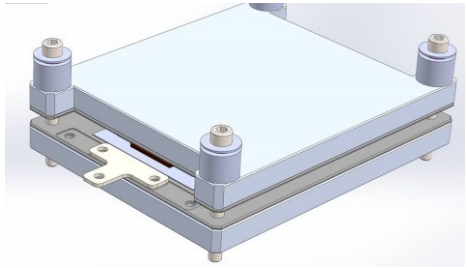
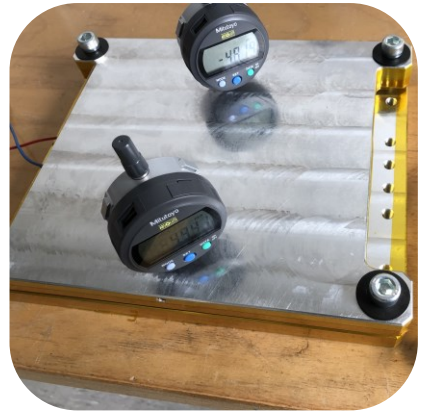
- Full toolchain implemented for Gen3b cells
  - Link between material – electrode – full cell behaviour
  - Phenomena studied
    - Mechanical behaviour
    - Diffusion
    - Aging
    - Thermal stability
- Tool chain to be validated against experimental data
  - Extensive aging campaign
  - Dedicated devices to evaluate swelling
- MODALIS² ongoing 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

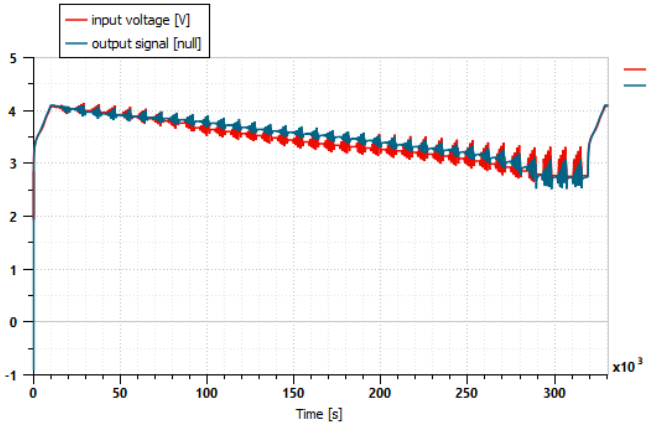




Lab cell

2 mAh
/ 0,4 cm²

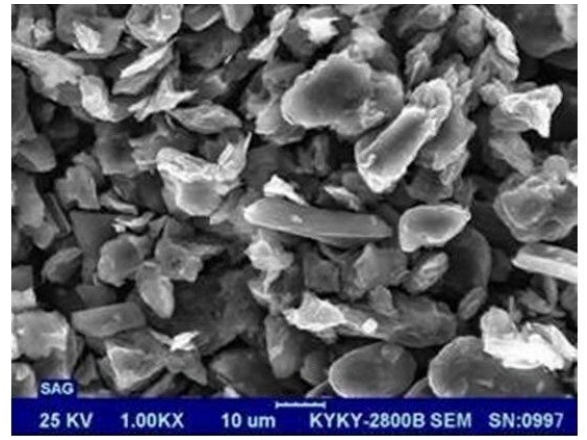
High operating pressure
(>100 MPa)

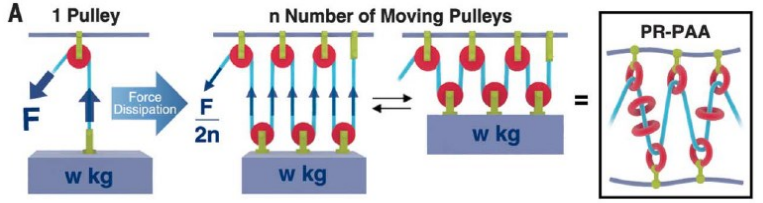


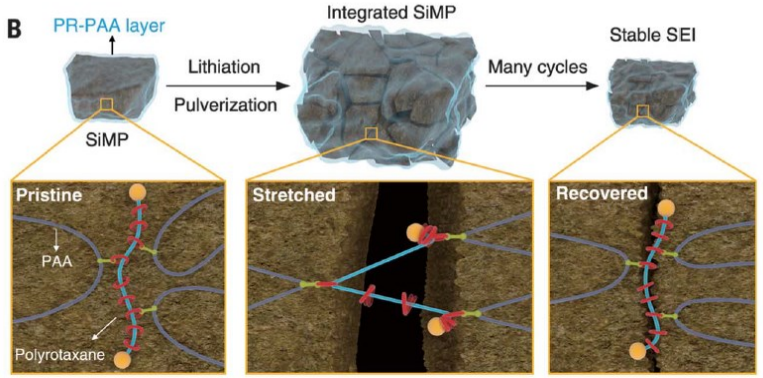
Further development in IFPEN

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

- Current PhD thesis supervised by Eric Maire (INSA Lyon Mateis)
  - Abhilash Valisammagari
  - Combined experimental/modelling assessment of Si based anode materials for Li-ion batteries
    - Use of DEM Swelling behavior
      - Implement complex particle shape (graphite platelet, angularity)
        - Key to any truly predictive work on density
      - Optimize the density you get after cycling, not after calendering
        - Density evolves heavily due to particle rearrangement
    - Binder damage
      - Link between binder topology and mechanics
      - Where do we have binder ? How much ? In which configuration ?
      - Introduce realistic binder properties to assess cycling behavior
      - Irreversible strain and fatigue, binder recovery
    - Experimental investigation of electrode behavior
      - In situ CT-XRD to evaluate electrode swelling
      - ESRF time slot in January to observe binder behavior in situ
- AURANODE project
  - Use of other type of Si based particles with lower volume variation at particle scale
  - Need of dedicated particle scale modelling







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THANKS A LOT FOR YOUR ATTENTION

HTTPS://MODALIS2-PROJECT.EU/

MODALIS 2