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MODALIS 2

MODelling of Advanced LI Storage Systems

PRODUCTION OF A GUIDELINE TO OPTIMIZE MATERIAL PRODUCTION DESIGN OF ACTIVE MATERIALS

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Executive Summary

Different parameters need to be defined when developing and producing Cathode material for SSB. In this report we will review both core and interface optimization and give insights on parameters to consider before designing the best-suited Gen 4 CAM (Cathode Active Material).

1 Introduction

1.1 Purpose and Scope of the Deliverable

The purpose of this deliverables is to show how the toolchain is developed within the MODALIS² project

1.2 Objective of the Project Deliverable

The goal of this deliverable is to explain what type of key characteristics should be carefully decided while working of Gen 4 active material. This guideline should allow cell manufacturers to optimize the catholyte (cathode + solid electrolyte mixture) depending on the solid electrolyte chosen (polymer, sulfide, ceramic).

1.3 Achievements compared to Project Objectives

The toolchain can be used to analyze the performances of Gen 3 and Gen 4 cells. From these inputs, Umicore and other material manufacturers are now able to determine characteristics of these active materials based on modelling results.

1.4 Acronyms

CAM: Cathode Active Material

CC: Constant Current

NMC: Nickel Manganese Cobalt

SSB: Solid State Battery

SEM: Scanning Electronic Microscopy

SSE: Solid State Electrolyte

SEI Solid Electrolyte

FEM: Finite Element Modelling

2 Classical design optimization

The classical approach for material optimization in Gen4 cells consists of a ‚trial and error' approach where several solutions are tested experimentally at small scale and then prototypes are build in medium to full scale in order to validate the approach.

2.1 Experimental approach

Here is a description of how tests were made at Umicore at small scale. A pellet die cell (Figure 1) is used to perform material tests and check its stability and cyclability. Materials are then tested with a dedicated electrolyte and pressure is applied in order to ensure a good contact. .

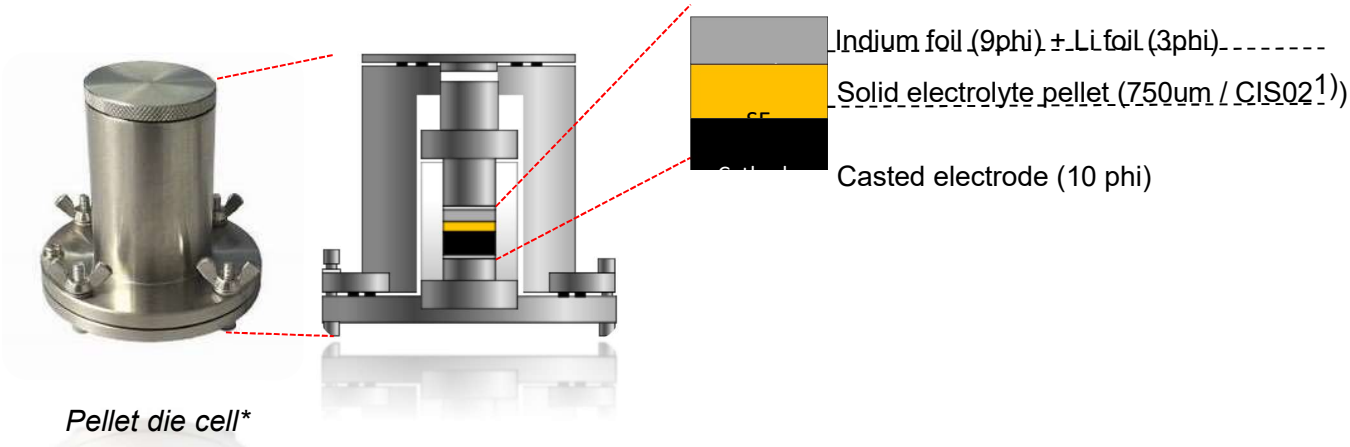


Figure 1 Pellet die cell

Among the conditions tested experimentally apart from new materials, the cathode formulation can be evaluated (Table 1). Variation of the cathode formulation can improve the stability of the cathode, power performance (by reducing the electrode resistance) and energy density (by increasing active material mass fraction and decreasing electrolyte mass fraction).

Table 1 Cathode formulation example

Cathode material	Solid Electrolyte (CIS01 2))	Conducting agent (Super-P)	Binder
64wt%	30wt%	3wt%	3wt%

1) CIS02: 8um solid electrolyte from CIS

2) CIS01: 3um solid electrolyte from CIS

Once cells are formulated and mounted, several testing protocols can be applied in order to evaluate their performance. For instance, as shown in Figure 2, the following protocol has been applied:

- Temperature: 60°C
- Loading: 5 mg/cm²-CAM
- C-rate: C/10 with CC mode
- 1C = 160mA/g

Using this protocol, specific capacity of the material can be evaluated as well as its life cycle. By using the same protocol on several cathode formulations, the benefit or drawback of each formulation can be assessed in order to choose the right one.

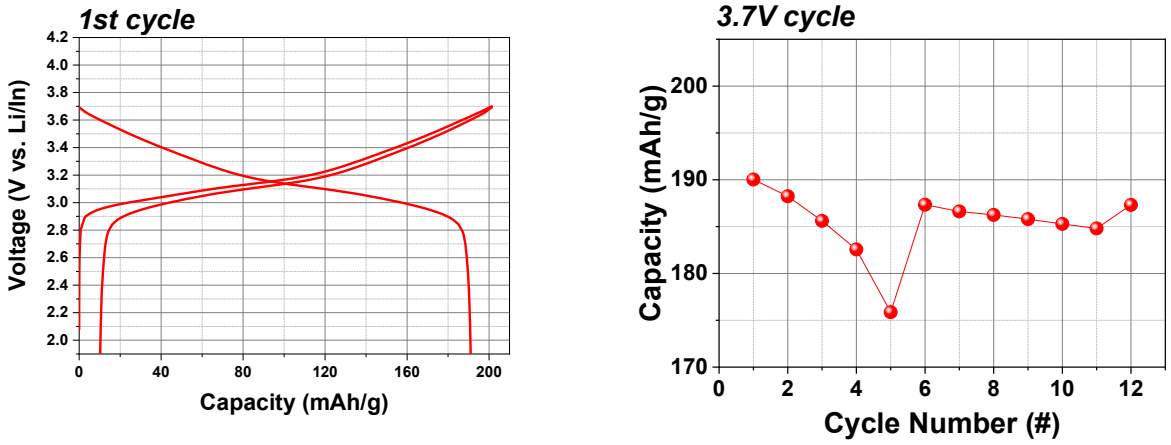


Figure 2 Cell testing example

2.2 Cathode Material development

When developing a cathode active material for SSB both core and interfaces optimization are required.

Optimization must be adapted to the operating environment: high voltage operation or not, pouch or hard casing of the cell, Power/Energy ratio.

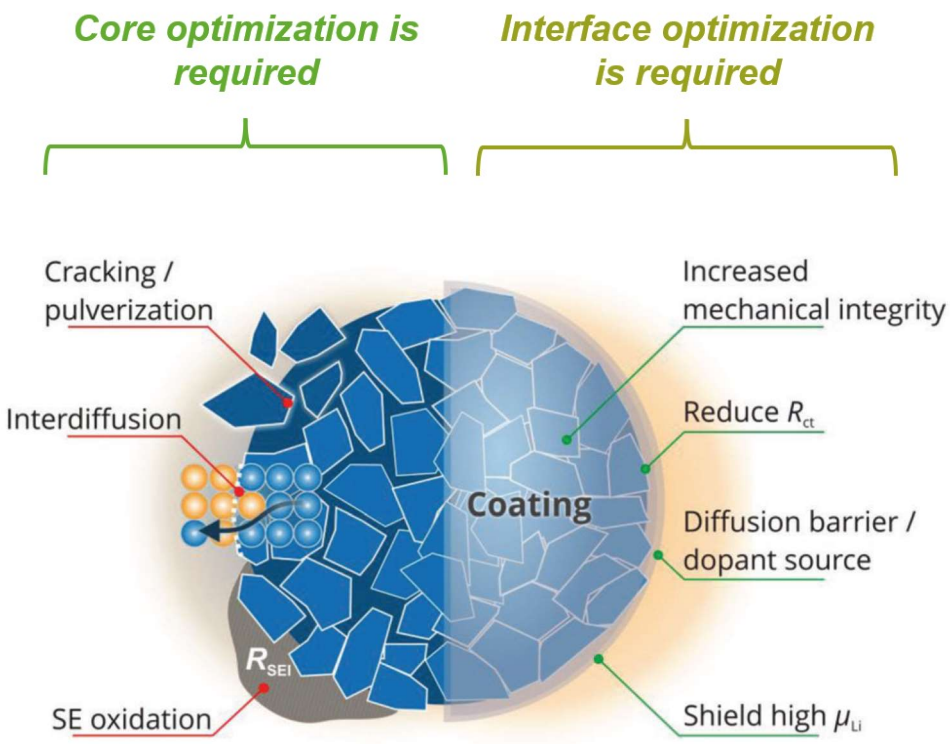


Figure 3 Core and Interface CAM optimization

(Source: Culver et al, Advanced Energy Materials (2019): https://doi.org/10.1002/aenm.201900626)

Especially CAMs for SSB call for dedicated approaches due to solid-solid interface. To achieve expected results, a building-blocks approach is applied.

2.2.1 Building blocks methodology to optimize cathode for SSB

In the building block approach, specific parameters need to be considered:

- **Composition**: Type of NMC: 6XX, 7XX, 8XX
  - High capacity can be achieved by tuning the Ni content (%)
- **Morphology** & **Crystallinity**: Polycrystalline / Monolithic
  - Particle Size can vary from 1 to 15 µm
  - Consideration for cycle life (cracking) and rate capability
- **Particle Size:** varying from 1 to 15 µm
  - Depending on solid electrolyte particle size (size matching should be optimized)
  - Consideration for press density
- **Surface:**
  - Sulfide
  - Polymer
  - Oxide
  - Needs to be optimized based on chemistry of electrolyte

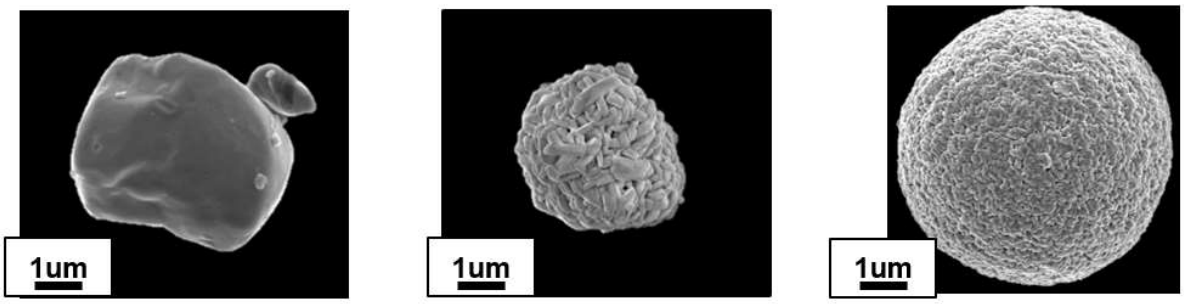


Figure 4 Umicore SEM images showing different combinations of the building blocks

2.2.1.1 Examples of building blocks with NMC 622

Here is an example, for an NMC 622, of the impact of the electrolyte type: Polymer type or Sulfide.

2.2.1.1.1 Polymer type SSB

With our NMC 622 Poly(Ethylene Oxide) (PEO) does cycle well with coated NMC even at 4.3 V vs Li/Li+.

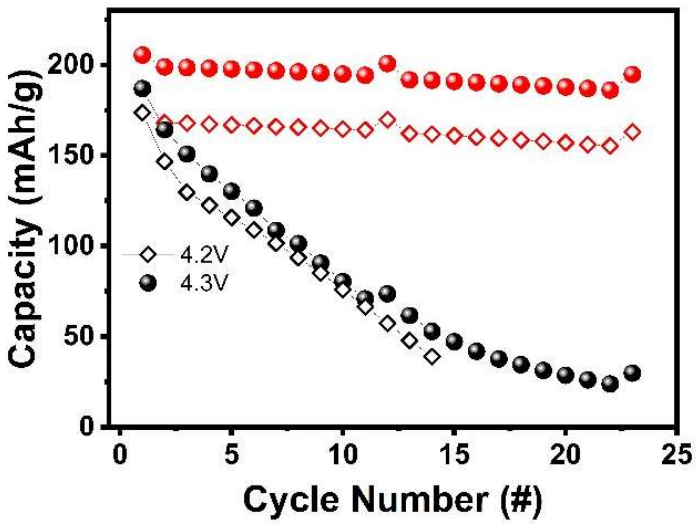


Figure 5 Cycling of Coated (Red) and non-coated (black) NMC 622 in a Polymer type SSB

- Impact of **Voltage** is visible for both bare and coated NMCs in the Figure 5, respectively in black and red markers.

- Impact of **coating** is clearly visible and allows maintaining high capacity during cycling, even at 4.3 V.

2.2.1.1.2 Sulfide type SSB:

Surface modification can impact performance as well as scalability & cost. The Figure 6 below shows that other types of coating than Niobium can increase the first cycle capacity.

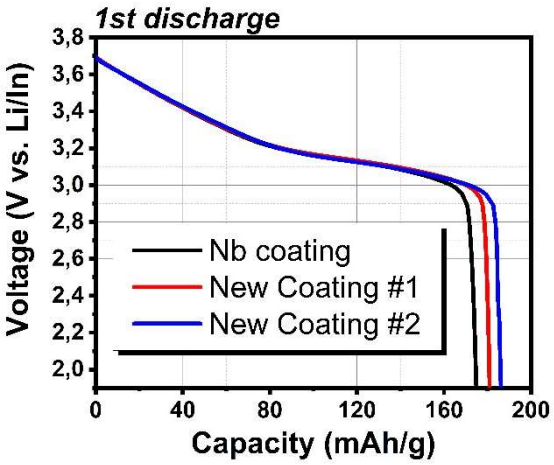


Figure 6 Impact of coating in Sulfide SSB

Figure 7 shows the improvement to performance due to a controlled morphology of CAM.

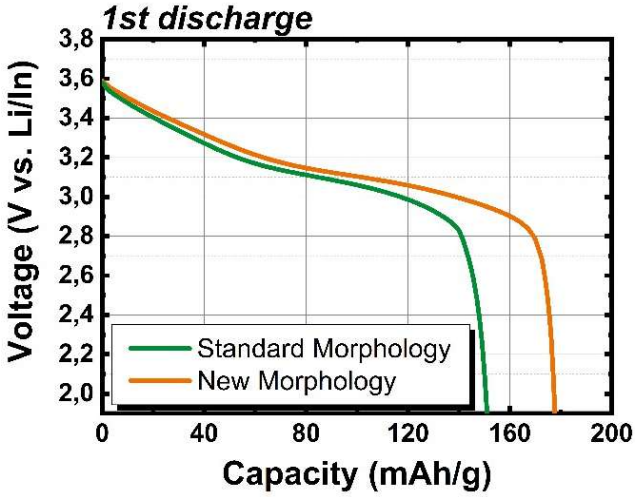
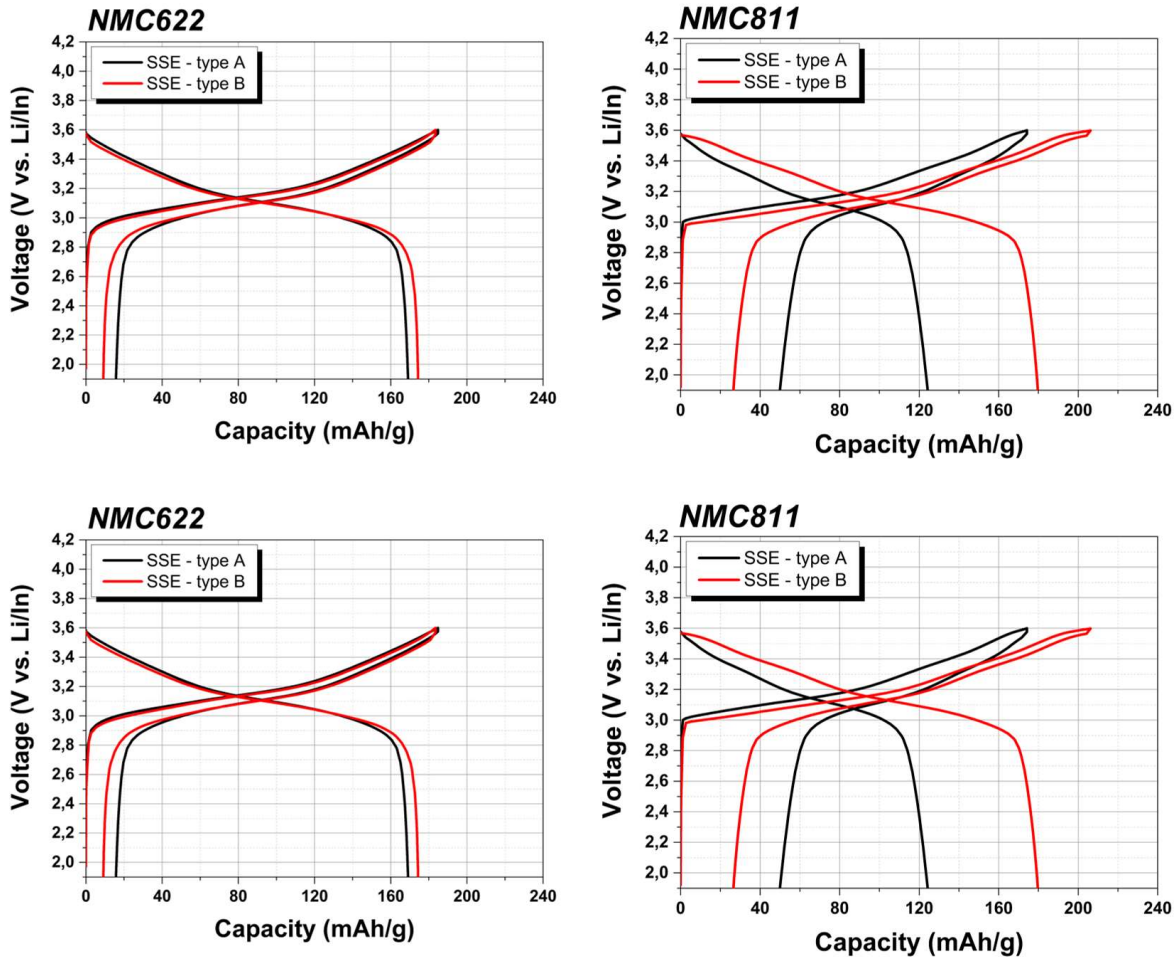


Figure 7 Impact of CAM morphology on capacity in a Sulfide type SSB

2.3 Co-optimization of components

Here are two examples of NMC 622 and NMC 811, with different types of Solid State Electrolyte (SSE).

Data shows that for a certain type of material, type of electrolyte also needs to be adapted and optimized. Multiple element within an SSB cell cannot be considered independently.



Data shows that co-optimization of components is critical for performance, As a consequence using modelling in order to understand the coupling and interferences between material is necessary for efficient material design.

3 Use of MODALIS² framework for cell optimization

MODALIS² modelling toolchain provides tools in order to help material developers to validate and choose the right material combination for Gen4 cell optimization.

3.1 Ab initio modelling for surface stabilization

Ab-initio modelling can be used to improve surface and interface stability in Solid State Batteries. Some of this work has been described in Deliverable 2.4.

3.1.1 Interface stability

After analysis of Li_6PS_5Cl argyrodite solid electrolyte surfaces, a Wulff plot has been constructed allowing to model electronic and ionic conduction.

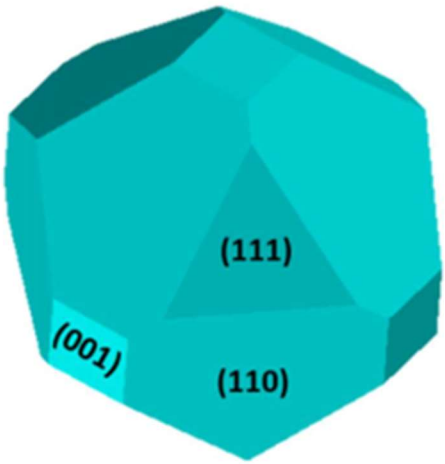


Figure 8 Wulff's polar plot for cubic symmetry of argyrodite

With this first modelling, nanocrystals surfaces could be engineered to improve surface state and dipoles.

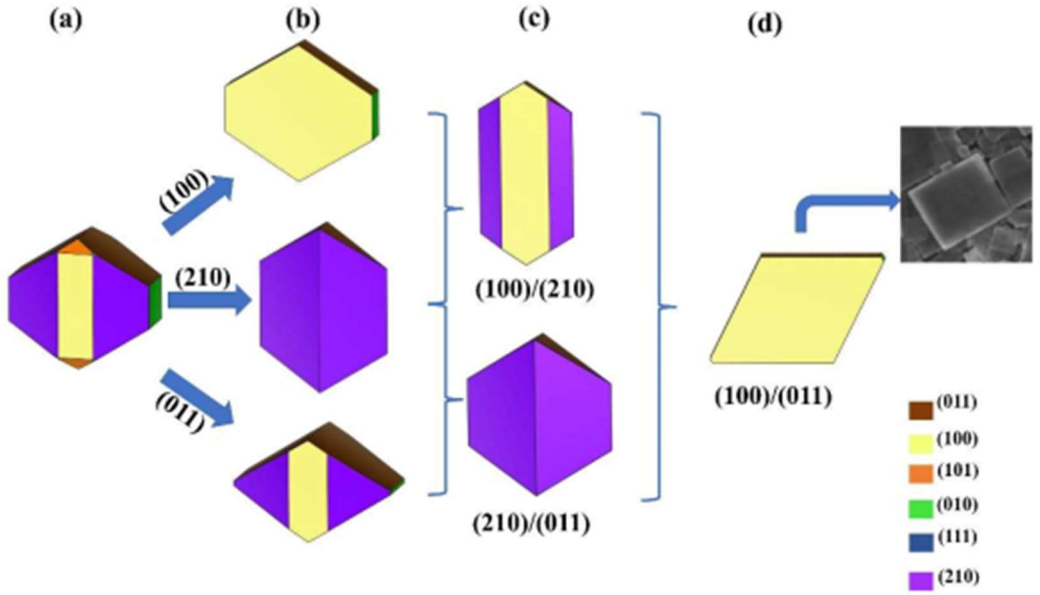


Figure 9 Different morphologies of β-Li3PS4 nanocrystals obtained by varying the relative stability of the various surfaces

Based on the analysis described above, the interface formed between the most stable surface of Li_3PS_4, (100), and the (110) surface of Li-anode was analyzed. An Li_2S surface (110) as a passivating coating material, which presented good adhesion energy with both Li and LPS surfaces, in addition to presenting the minimum modification in the electronic properties, was selected as best-suited interfaces.

In addition, models have shown that such interfaces, Li/Li_2S and Li_2S/LPS, are formed spontaneously and with low strain energy. This study has shown the need to use the surface (110) of Li2S as a **passivating material to avoid the formation of Li dendrites,** without impairing the migration of Li ions and the ionic conductivity of the LPS.

3.1.2 Mechanical properties

Mechanical properties are of utmost importance in Gen4 batteries as mechanical/electrochemical coupling plays a great role in the interfaces stability and cell performances. Thanks to ab-initio calculation as performed inthe MODALIS² project, material properties can be evaluated such as Bulk, Shear and Young moduli as well as Poisson‘s ratio.

First of all, stable structures must be computed and validated. Then, using a dedicated calculation code such as Thermo_PW, the elastic tensor can be evaluated and the elastic partameters are deduced as shown in Table 2. In this table, mechanical properties have been evaluated for Li and Li/In at various lithiation rates. Similar calculations can also be performed for solid electrolyte. The results are to be used in further scale for applicability at the scale of interest which is the cell.

Table 2 Theoretical mechanical parameters for LixIn phases.

	Li	Li3In	Li1In	Li0.45In	Li0.4In	Li0.3In	In
Bulk	142	233	319	305	327	345	315
Shear	79	184	172	110	100	110	-132
Young	200	436	438	295	272	299	-462
Poisson's	0.27	0.19	0.27	0.34	0.36	0.36	0.74

3.2 Phase field modelling for dendrite limitation

As dendrite formation is a major concern for specific modelling, a methodology was adopted in the MODALIS² project in order to assess this mechanism at the negative/electrolyte interface.

A phase-field modelling was adopted to evaluate the progression of a lithium phase inside an electrolyte phase based on initial defects. Several parameters can be changed to study their impact on dendrite formation such as the defect density (Figure 10) or solid electrolyte mechanical properties, which can be provided by *ab initio* techniques (as shown earlier).

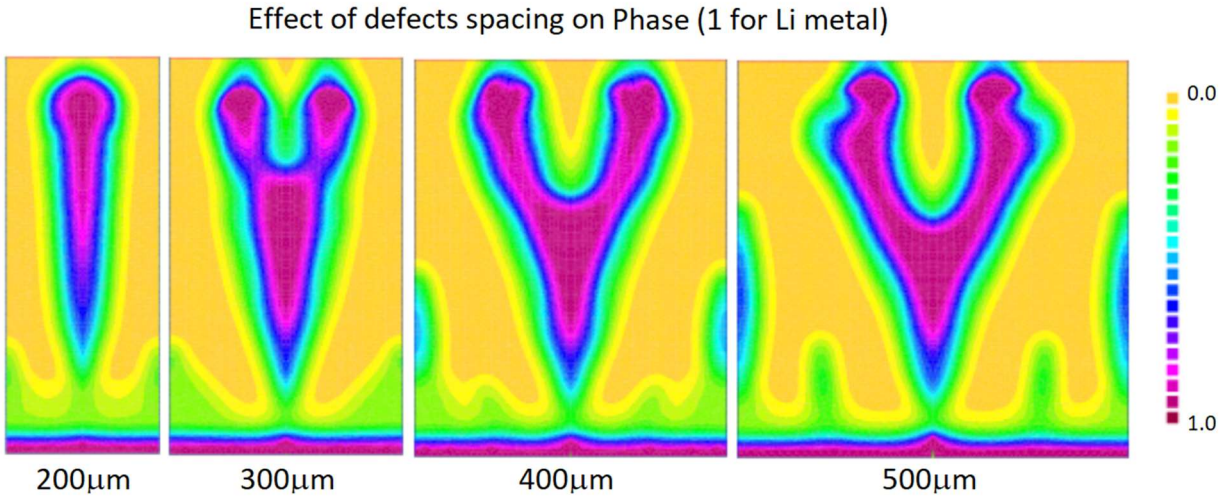


Figure 10 Snapshots of Li metal ξ for different defect spacing

Using such approach the impact of electrolyte formulation as well as the impact of its chemistry can be studied with regard to dendrite formation. In addition, several surface treatments can be tested numerically before prototyping in order to provide better negative/electrolyte interface stability. In order to perform such calculations in addition to eventual experimental values, using the results of *ab-initio* calculations presented earlier, such as interface stability/coating and mechanical properties, it is necessary to set the model parameters.

3.3 3D modelling for system stability

Similarly to the negative electrode, mechanical properties are useful to evaluate the stability of the solid/solid interface at the positive electrode. NMC materials are known to swell during lithiation/delithiation, this is not a big issue in liquid electrolyte but solid electrolyte might not cope with mechanical stresses and contact losses can happen leading to faster performance degradations. Consequently, FEM modelling can be used to investigate cycling behavior of the positive microstructure as can be seen in Figure 11. In this simulation, a microstructure was simulated with a particle size distribution of NMC. Then the electrode was cycled and the hydrostatic pressure in the electrode was evaluated. This can be used to evaluate the stability of the microstructure and linked to a fatigue modelling to assess its reliability over time.

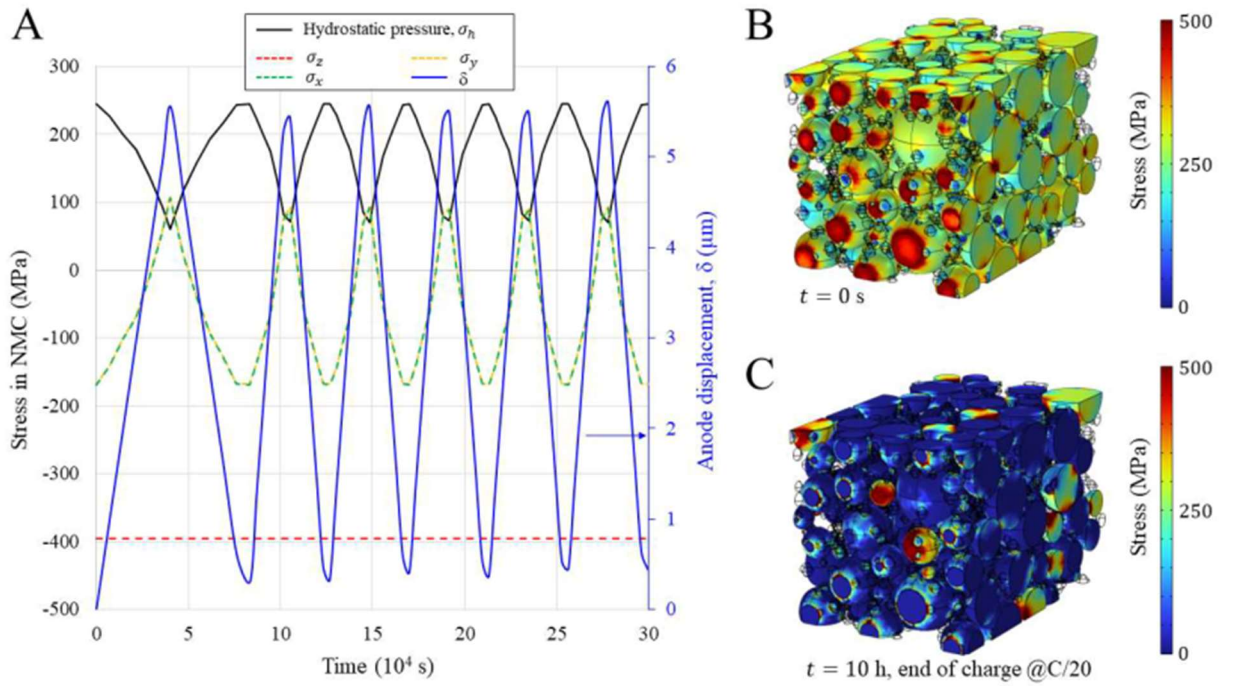


Figure 11 Mechanical stresses and deformations.

Such modelling approach can be used to optimize electrode formulation and check the impact of the modified mechanical properties on electrode stability.

3.4 Full cell modelling to optimize cell assembly

Once materials are integrated together, interactions will occur to provide the full cell performance and may exhibit counter intuitive behaviour due to adverse behaviour between positive/electrolyte and negative. To address such issues, full cell modelling is required and addresses both nominal performance as well as lifetime.

Using models developed in MODALIS², dedicated cell level modelling based on Single-Particle Modelling with electrolyte have been developed. To fit with Gen4 battery requirements, the SPM-e approach was adapted to take into account solid/solid interfaces at the positive and negative electrolyte/electrode interfaces and a dedicated model for single ion conduction inorganic electrolyte was developed. This model accounts for new electrolytic conduction as well as pressure effect on charge transfer. As can be seen in Figure 12 it is well able to account for capacity and resistance of Gen 4 cells. Furthermore, ageing phenomena, such as growth of passivation layers, can also be included in the model as is done for Gen 3b cells.

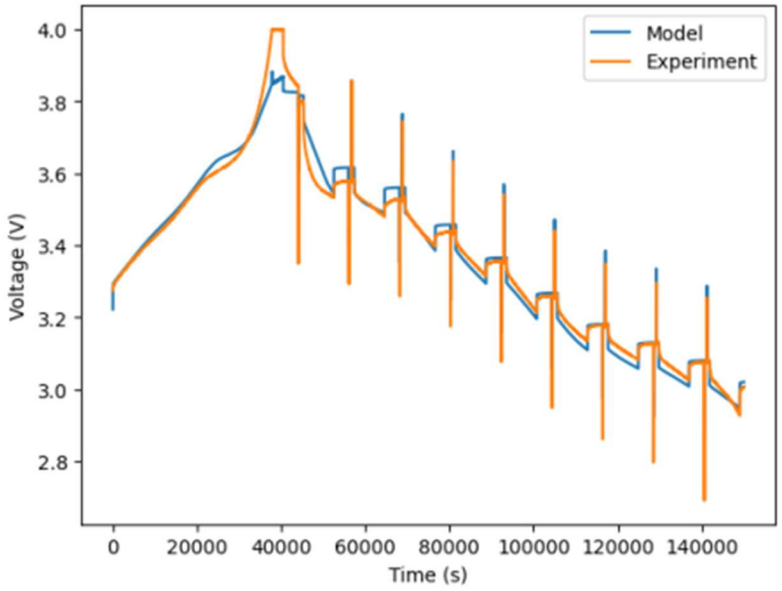


Figure 12 comparison of model and experiments on HPPC tests

Within the MODALIS² project, specific simulators using Siemens Industry Software Simcenter Amesim were developed for end-users such as material and cell manufacturers to use these models and get information on specific cell performances such as resistance and capacity. Those models replicate *in-silico* the behavior of a cell following classical experimental protocols such as HPPC tests (Figure 13). By treating this calculation data similarly to what is done on experiments, one can get the resistance of the cell as a function of its state of charge and temperature and evaluate the impact of surface treatment or electrolyte performance on overall cell performance.

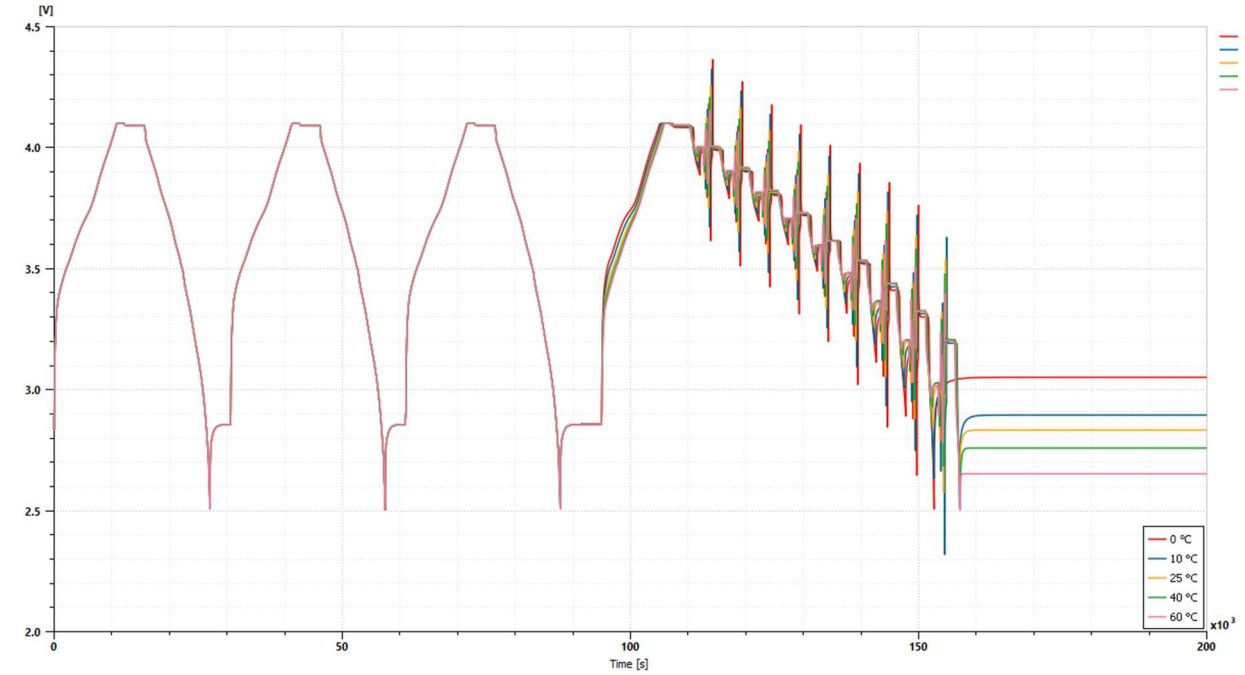


Figure 13 HPPC test at different temperatures

Full 3D simulation using Siemens Industry Software Simcenter StarCCM+ provide further information on cell behavior heterogeneities (Figure 14). Such software can link full 3D cell design with overall cell performances. Thanks to such modelling, it is possible for a given material to optimize the cell design to avoid cell behavior heterogeneities, which can be detrimental to full cell performance.

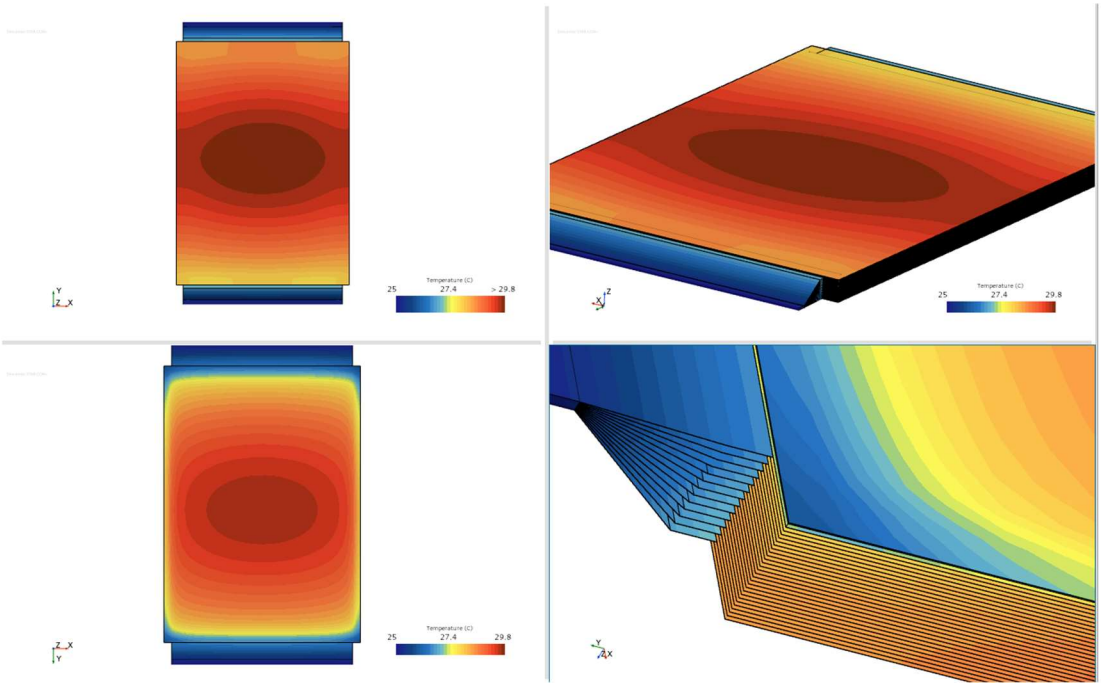


Figure 14 Skin temperature distribution over the pouch cell after a 10% charge at 1.6C

Further ageing modelling is also possible using dedicated simulator developed in Simcenter Amesim. Such simulator will cycle cell using constant current charge and discharge cycles and perform regular check-ups to evaluate the evolution of cell performance. Parallel calculations can be performed to remove the ageing mechanisms one after the other and evaluate the impact on each mechanism on overall ageing (Figure 15 & Figure 16). By doing so one can choose what is the most important ageing mechanism to address in order to increase battery lifetime.

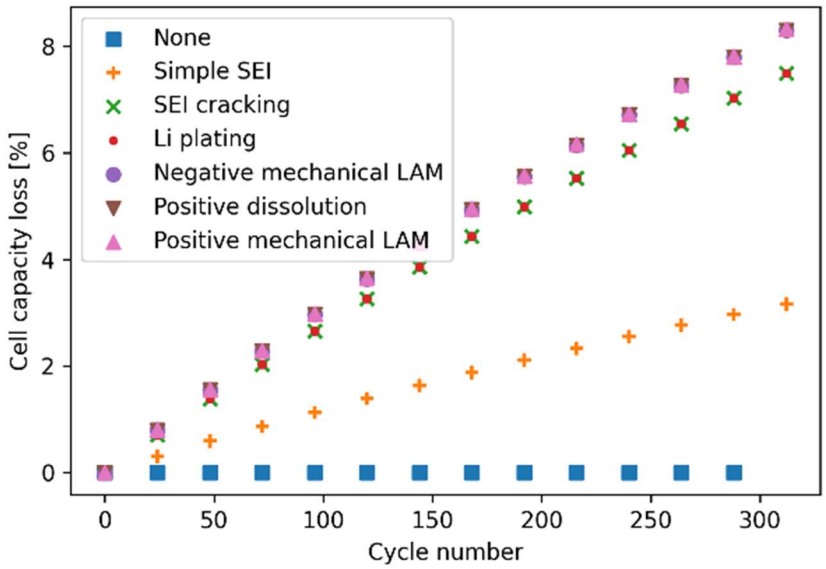


Figure 15 Impact of ageing phenomena on capacity loss

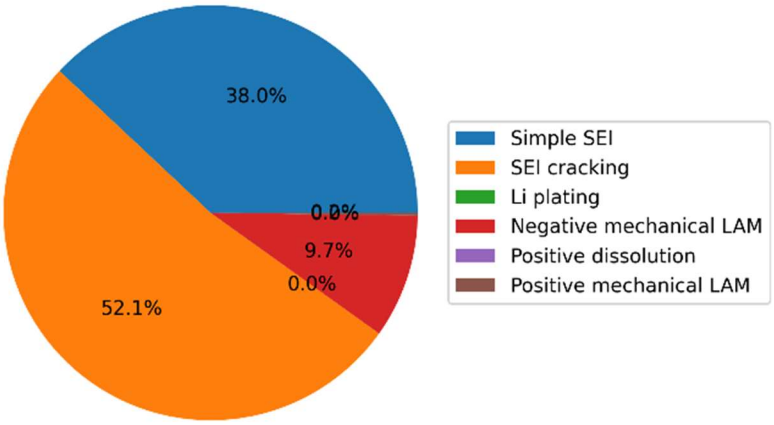


Figure 16 Impact of ageing phenomena on capacity loss

4 Conclusion

Following a block-methodology and considering multiple aspects of the SSB in CAM development is critical to increase cell characteristics.

Block methodology is usually carried out thanks to a trial and error approach which is both expensive and time consuming. By using the multiscale/multiphysics modelling approach provided by MODALIS² it is possible to accelerate material developments by:

- performing molecular scale modelling providing information on transport properties and interface stability
- performing electrode scale modelling to evaluate interface stability at the negative/solid electrolyte interface (providing information on dendritic growth) and positive electrode providing information on the mechanical stability of positive electrode materials.
- performing full scale modelling providing information on material interaction at the scale level comprising performance evaluation and also lifetime evaluation.
- 3D modelling can extrapolate the results up until the final product to evaluate potential heterogeneities issues to be accounted for and tackled.

Consequently, using the multiscale modelling within the block approach for battery material development will reduce risks and development time to bring new technologies at a higher TRL.