Halide solid state batteries for ELectric vEhicles aNd Aircraft

D7.1: Multiscale/Multiphysics modelling framework definition and requirements

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Publishable summary

Within HELENA project WP7 aims at providing material and cell manufacturers model-based guidance at three main scales (atomistic, microstructural, full cell) and tools to optimize cell and electrode design and anticipate full cell behavior and lifetime. This will rely on a Multiscale Multiphysics modelling approach able to account for optimization from material to cell design and exhibit the consequences up until the final application system.

The deliverable D7.1 is related to the task 7.1 where the first objective is the definition of the Multiscale Multiphysics modelling approaches chosen and their objectives. As higher scale modelling will rely on lower scale results, interfaces framework between scales is defined. Based on the synergy between the different HELENA WPs, interaction is required to give needed input for each modelling level on the one hand and assess the system design optimization with simulation on the other.





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SYMBOL	SHORTNAME
t	Time
WP	Work Package
ASSB	All-Solid-State Battery
LIB	Lithium-ion Battery
DFT	Density Functional Theory
CI-NEB	Climbing image nudged elastic band
РВЕ	Perdew-Burke-Ernzerhof
SE	Solid electrolyte
AM	Active material
TAPED	Topological analysis of electron density
ССР	Cage critical points
RCP	Ring critical points
DFT	Density Functional Theory
CI-NEB	Climbing image nudged elastic band
САМ	Cathode Active Material
DEM	Discrete Element Method
СВ	Carbon Black
PSD	Particle Size Distribution
REV	Representative Element Volume
SOC	State of Charge
P2D	Pseudo two-dimensional electrochemical cell model
DFN	Doyle-Fuller-Newman electrochemical cell model
SPMe	Single particle model with electrolyte dynamics
SEI	Solid-electrolyte interphase
FMU	functional mock-up unit
JRC	Joint Research Center
EEC	electrical equivalent circuit
LT	lumped thermal
WLTP	Worldwide harmonized Light vehicles Test Procedure
BEV	battery electric vehicle
HVAC	Heating, ventilation, and air-conditioning





1 Introduction 1.1 **Purpose and Scope of the Deliverable**

The deliverable D7.1 is related to the task 7.1 where the first objective is the definition of the modelling approaches chosen and their objectives. As higher scale modelling will rely on lower scale results, interfaces framework between scales will be defined. Based on the synergy between the different HELENA WPs, interaction is required in order to give needed input for each modelling level on the one hand and assess the system design optimization with simulation on the other.

1.2 **Objective of the Project Deliverable**

This deliverable will describe the Multiscale Multiphysics modelling approaches chosen for HELENA project and their objectives. The model's network and interfaces framework will be presented. Precisely, parameters given by atomistic modelling will be defined and how microstructure modelling can be integrated in fast computing full cell macroscopic model will be discussed. Finally, interactions with other WPSs will be also addressed.

1.3 **Deliverable structure**

In this deliverable the second chapter (Methods and Results) includes the description of the Multiscale Multiphysics modelling approach chosen for HELENA project. Each partner presented the approach corresponding to the modelling scale studied, where the main assumptions considered are presented, the main mathematical equations describing the phenomena are addressed and the model input/output are identified. In addition, in this chapter the main challenges facing each scale approach for the study of the HELENA's based Halide ASSB are discussed.

In the third chapter (Discussion and Conclusion), the model's interfaces framework is defined, where the parameters given by atomistic modelling which will be further used in microstructure modelling are identified. Also, how microstructure modelling can be integrated in fast computing macroscale model at cell level is presented. In addition, interactions between each scale model with the other WPs are defined. Finally, risks facing the application of the different model approach within HELENA project are addressed in this document.



2 Methods and Results

2.1 **Atomistic modelling approach (CICE)**

2.1.1 Description of the atomistic modelling approach

An atomistic modelling approach is based on the description of a chemical system as a set of interacting atoms. The interatomic interactions can be defined by an empirical force field (molecular mechanics) or calculated from the first principle (ab-initio methods). Among various atomistic modelling approaches, Density Functional Theory (DFT) (Sholl & Steckel, 2009) has high transferability and provides the best accuracy with respect to computational cost. DFT coupled with molecular dynamics (Kresse & Hafner, 1993), Monte Carlo (Metropolis & Ulam, 1949), or the Climbing Image Nudged Elastic Band (CI-NEB) (Henkelman et al., 2000) method is a powerful tool for the simulation of chemical reactions and ion diffusion processes. Within the HELENA project, DFT will be used to access the electrochemical and mechanical properties of the solid electrolyte (SE) as well as to evaluate the stability of the solid electrolyte interface with the active material (AM) of the cathode electrode.

2.1.1.1 Calculation the solid electrolyte properties

All DFT calculations will be performed by means of VASP 5.4 code (Kresse & Furthmüller, 1996a, 1996b; Kresse & Hafner, 1993) using Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, together with PBE-based projector augmented wave potentials (Kresse & Joubert, 1999). The optimal values of plane-wave kinetic energy cutoff and k-point sampling will be found based on the energy convergency test. For a set of single-point energy calculations, the energy cutoff and the number of k-points will be increase iteratively until the energy difference between the last iterations reaches the required accuracy.

The calculations of single-crystal elastic constants will be carried out based on the strain-stress relation of the deformed crystal (le Page & Saxe, 2002). The stress tensor will be obtained using DFT method. The elastic constants will be retrieved by linear least-squares fitting using singular value decomposition. The theoretical polycrystalline elastic, bulk, and shear modulus as well as Poisson's ratio will be calculated based on Voigt-Reuss-Hill average (Ravindran et al., 1998).

The minimal energy Li⁺ diffusion pathways and corresponding activation energies will be obtained by means of the CI-NEB coupled with DFT. Within the approach, the diffusion trajectory is described by a finite set of images (replicas) of the system. Starting from some guess trajectory, generally, linear interpolation between equilibrium initial and final atomic positions, the algorithm minimizes forces between images (Figure 1). The total force acting on an image is represented by the sum of the spring force along the local tangent $(F_i^S|_{||})$ and the true force perpendicular to the local tangent $(\nabla E(R_i)|_{\perp})$. To find the transition state the CI-NEB forces the intermediate image that has maximum energy to climb the hill of the potential energy surface along the minimal energy path until it reaches the top. The activation energy corresponds to the difference between the maximal and minimal energy of the images.





Figure 1 - Schematic representation of the CI-NEB method.

One of the inputs required for CI-NEB calculation is the initial and final positions of the migrating ion. Generally, ion diffusion is considered between neighboring sites of the mobile ion. This information can be obtained from the Voronoi partition of the sublattice of ions involved in the diffusion process (Figure 2) (Golov & Carrasco, 2022). The Voronoi partition of crystal structure divides space into polyhedra. Each polyhedron represents the atomic domain (crystal space belonging to the atom). Thus, atoms whose domains share common faces, edges, or vertices are neighbors.



Figure 2 - Voronoi partition of the Li sublattice of the Li3OCl structure (a), Voronoi polyhedron of Li-ion and its neighbors (b), and graph of Li neighbors (c).11 Symmetrically nonequivalent edges are depicted in blue, red, green, orange, and violet color (Golov & Carrasco, 2022).

The CI-NEB calculations will be carried out for all symmetrically nonequivalent pairs of neighboring sites derived from the Voronoi partition of the Li sublattice. To accelerate CI-NEB convergence, initial trajectories will be calculated using the Topological Analysis of Electron Density (TAPED) (Golov & Carrasco, 2022).

The main idea of the TAPED approach is to approximate ion diffusion process by the movement of a single negative point charge in the constant electron field of the structure. In this case, equilibrium and metastable ion positions can be associated with minima of electron density, cage critical points (CCP). The positions of the migrating ion at transition states are correspond to the maxima of electron density along the gradient path, ring critical points (RCP). Ion trajectory is represented as a set of gradient path of electron density. A schematic illustration of the algorithm is given in Figure 3.







Figure 3 - Schematic illustration of the TAPED approach (Golov & Carrasco, 2022). 4.8 Å Li hop in the structure of bulk lithium metal (a). Topology of the electron density (b) and its representation as a graph (c). Graph nodes are colored with respect to weight, i.e. value of electron density. Red, green, and yellow rows show steps of the algorithm for searching for the lowest barrier route between the initial and final positions (white circles) of the ion. Trajectory and electron density profile of the global minimal electron density path (d).

The resulting diffusion trajectories and activation energies will be used as input data for kinetic Monte Carlo simulation (Bulnes et al., 1998) to access the jump- and trace-diffusion coefficients. The selection of a transition to a new state and time increment will be computed using the following two formulas:

$$\frac{1}{\Gamma_{tot}} \sum_{m=1}^{k-1} \Gamma_m$$

where Γ_{tot} is the sum of individual *m*th hop frequencies, Γ_m , and *p* is a random number from 0 to 1; and

$$\Delta t = -\frac{1}{\Gamma_{tot}} \ln \xi$$

where Δt and ξ are the time increment and a random number from 0 to 1, respectively.

The hop frequencies will be calculated as:

$$\Gamma_m = v^* exp\left(\frac{-\Delta E}{k_B T}\right),$$

where ΔE is the energy barrier (derived from CI-NEB) for the hop of the ion and v* is the vibrational preexponential factor. A commonly accepted approximate value v* is equal to 10^{13} .

The diffusion coefficients will be found using the following two formulas:

$$D_J = \lim_{t \to \infty} \left[\frac{1}{2dt} \langle \frac{1}{N} (\sum_{i=1}^N \vec{r_i}(t))^2 \rangle \right],$$
$$D^* = \lim_{t \to \infty} \left[\frac{1}{2dt} \left(\frac{1}{N} \sum_{i=1}^N \langle [\vec{r_i}(t)]^2 \rangle \right) \right],$$

where *t* stands for time, *d* is the dimension of the ion migration map, *N* is the number of ions involved in the diffusion process, and \vec{r}_i is the vector that connects the position of the *i*th ion at initial (t_0) and final (t) times.

2.1.1.2 Modelling of SE/AM and SE/coating/AM interfaces

The SE/AM and SE/coating/AM interface models will be built using the lattice match algorithm (Zur & McGill, 1984) by embedding several slabs in one cell that has translation symmetry compatible with





these slabs. Interfaces will be generated along all possible symmetrically non-equivalent directions with Miller indices ranging from -3 to 3. However, to maintain a balance between the accuracy of the models and the required computational resources, the maximum maximal number of atoms within the unit cell of the models will be limited to 500. Thus, only those models that satisfy this criterion will be selected for further ab-initio of molecular dynamics (AIMD) simulation. Preliminary, the geometry of the selected models will be optimized with a residual force threshold of 0.05 eV/Å.

The AIMD simulations will be carried out applying an NVT ensemble with a time step of 1 fs. A Nose-Hoover thermostat (Evans & Holian, 1985) with a Nose-mass parameter of 0.5 will be used to maintain the temperature at 298 K. The stability of the interfaces will be evaluated based on the analysis of atomic charges and local atomic environments along AIMD trajectories (Golov & Carrasco, 2021). To assess the Li transport through the interface TAPED will be applied. The approach showed very good agreement with the DFT CI-NEB, but in contrast to the last, TAPED requires much less computational resources (Golov & Carrasco, 2022). This makes it possible to calculate thousands of symmetrical non-equivalent diffusion pathways within large interface models containing hundreds of atoms, which is unfeasible for DFT (Golov & Carrasco, 2021). The effect of the interface on ionic conductivity will be qualitatively characterized by comparing the diffusion barrier of lithium at the interface with the diffusion barriers within the corresponding bulk structures.

2.1.2 Objectives of the atomistic modelling approach

The main objectives of the atomistic modelling approach are to assess the ionic conductivity, diffusivity, and mechanical properties of the SE, as well as to evaluate interfacial stability, and Li⁺ transport through SE/AM and SE/coating/AM interfaces. This information will be further used in WP3 to optimize composition and crystalline structure improving ionic conductivity and increasing lithium transfer in bulk SE and at the interface. In additional, the resulting calculated properties will be used as inputs for microstructure models.

2.1.3 Identification of the input/output parameters of the atomistic model

The only information required for the property calculations is the SE, AM, and coating crystallographic data, i.e., lattice vectors, atomic coordinates, and chemical composition.

The output information of the atomistic simulation will include:

- 1. Mechanical properties of the SE
 - Elastic constants
 - Bulk modulus
 - Young's modulus
 - Shear modulus
- 2. Ionic diffusion characteristics of the SE
 - Li⁺ diffusion trajectories and corresponding activation energies
 - Jump and trace Li⁺ diffusion coefficient
- 3. Dependence of the SE unit cell volume on Li⁺ fraction
- Activation barriers (relative to the bulk structures) and ionic trajectories of Li⁺ diffusion at the SE/AM and SE/coating/AM interface, calculated based on the topological analysis of procrystal electron density
- 5. Stability of SE/AM and SE/coating/AM and interface
 - Reaction rate
 - Intermediate products of the reaction and degradation mechanisms

2.2 Microstructure modelling approach (FHG)

2.2.1 Description of the microstructure modelling approach

Beside an improved safety level, the ASSB technology has the capability to increase the energy density compared to conventional LIBs. One fundamental of this improvement is the higher package efficiency of ASSB. However, proper charge transfer needs to be ensured to exploit the full potential of ASSBs. Here, one major difference compared to conventional LIBs, is the particulate morphology of the SE. Therewith, the SE does not infiltrate the porous structure of cathode active material (CAM), what is the





case for liquid electrolytes. In fact, the purely solid content leads to void spaces within the electrode area. This void space can be minimized by manufacturing processes like calendaring of the electrode, down to level of 6 - 8 % (Anja Bielefeld, 2022) or lower (Sangrós Giménez et al., 2020a).

Nevertheless, the performance of the cell is strongly dependent on this complex solid structure and the distribution of different solid phases in the electrode since for the intercalation step the availability of lithium ions (Li⁺) and electrons (e⁻) at the site of reaction is indispensable. Therefore, the penetration of Li⁺-ions and e⁻ through the entire thickness of the electrode needs to be ensured under all application conditions. Here, Li⁺-ion transport is achieved through the network of solid electrolyte in the electrode as well as in the separator. CAM in combination with the conductive additive carbon black (CB) plus binder matrix ensures the transport of e⁻ towards the current collector. Finally, the charge transfer for (de-)intercalation is performed via the interface CAM/SE. The current transport (ionic and electronic) depends on the intrinsic properties of the bulk materials but also on the availability of paths through the electrode and therefore the network structure.

This shows the importance of understanding the relationship between intrinsic material properties, electrode formulations and manufacturing processes to improve the macroscopic performance of the cell. However, the role of the electrode structure is still barely understood and studied (Anja Bielefeld, 2022). At the same time, an investigation of the electrode structure is challenging and elaborated to be addressed exclusively by experiments.

Here, modelling can provide a profound understanding of the interplay between material properties, manufacturing processes, and application conditions in a non-invasive and accelerated process.

Sangrós et al. presented a modelling approach to predict the electrical conductivity of an ASSB electrode structure generated by the discrete element method (DEM). Post-processing allows deeper insights into the fundamental role of the electrode structure on porosity and tortuosity, which affect the ionic conductivity respectively. Here, the discrete element method represents a powerful modelling tool to reflect the mechanics and structure changes due to fabrication processes, like calendaring or packaging, or internal stress generation in particular because of the intercalation-introduced volume change during cycling (Sangrós Giménez, 2022, So et al., 2022). Figure 1 summarizes the application fields of DEM modelling for ASSB development. Furthermore, the fundamental steps should be described in the following sections.



Figure 4 - Application fields of the numerical simulations of composite cathodes with the DEM (adapted from (Sangrós Giménez, 2022)).

2.2.2 Description of the microstructure modelling approach

The workflow of the discrete element method simulation is schematically summarised in Figure 2 and should be generally described in the following.

2.2.2.1 Pre-processing

The first step needed for the simulation with the DEM is the generation of a compact stack of spherical particles. This procedure is not trivial, due to the fact the resulting system of particle must show a lower porosity, but at the same time a non-overlapping constrain must be ensured. The latter condition is an important initial condition for the DEM simulation, because overlap between particles would result into a non-balanced distribution of internal forced, which could compromise the convergence of the DEM algorithm. Different solutions have been proposed in order to achieve this goal. An interesting algorithm is the one proposed by Lozano et al. (Lozano et al., 2016), a constructive method of progressive filling



of the domain with sphere particle of given sizes based on the minimization of the distances between spheres. The algorithm has been shown to be efficient in terms of packing density and computational time.

An important input parameter for the generation of the particle system is the particle size distribution (PSD). In fact, the number of modelled particle sizes needs to correctly reflect the real PSD of the solid electrolyte and the active material, without resulting into an excessive computational load. A study of the influence of the number of different particle sizes considered for the DEM simulations of composite cathodes has been done by C. Sangrós (Sangrós Giménez, 2022), and a number of five different sizes has been identified as optimum between level of detail and computational cost. Due to this heterogeneity in the particle size, it is also important to define the dimensions of the simulated Representative Element Volume (REV), which is small enough to result into acceptable computational cost for the DEM simulation and, at the same time, big enough to be representative of the behaviour of the cathode. A study of the influence of the dimension of the REV has been done by C. Sangrós (Sangrós Giménez, 2022).

2.2.2.2 DEM Modelling

Once the particle system has been generated, the Discrete Element Method can be used to study the interaction between the particles under external mechanical loading or upon electrical cycling (volume change of the AM particles due to a change in the lithium concentration).

The DEM is based on the Newton's Second law:

$$F_i = m_i \frac{d^2 x_i}{dt^2}$$

This states the dynamic equilibrium of a particle i and is usually integrated in time with an explicit procedure. The key point of the DEM is the computation of the force F_i , which is the total force acting on the particle i. Except for the influence of external loading such as the gravitational force, the main contribution to F_i is given by the force generated by the particle-particle or the particle-boundary interaction. Consequently, the crucial point in the DEM is the choice of the contact model, i.e. the constitutive relationship between the particle overlap and the corresponding mutual interaction force.

One of the most common used contact models in DEM is the Hertz-Mindlin model (Hertz, Garbasso, 1895, Mindlin, 1949). A low number of necessary input parameters, reasonable calculation time, and valid results for non-linear elastic materials represent the advantages of the Hertz-Mindlin model for DEM. Here, the total force acting on a particle is calculated out of a combination of spring and dashpot components in the normal (n) and tangential (t) direction:

$$F = (k_n \delta_{n,ij} - \gamma_n n, v_{ij}) + (k_t \delta_{t,ij} - \gamma_t v_{t,ij})$$

where the indices i, j correspond to the two particles in contact, k is the spring stiffness and γ the damping coefficient, δ represents the overlap and v the relative velocity.

However, this contact model has its limitations. Sangros et al. showed in force-displacement experiments, that NMC111 particles exhibit after elastic also a plastic deformation behaviour, which is not represented in the Hertz-Mindlin approach. Based on the work of Thornton and Ning, the contact model is therefore extended. In general lines, a yield point is defined, which limits the application of the Hertz-Mindlin contact model. Under low levels of stress, the force is calculated according to the elastic contact model. Once the yield point is reached, the effect of plasticity is also considered and the theory of elasto-plastic particle contacts from Thornton and Ning is adopted (Sangrós Giménez, 2022, Thornton, Ning, 1998). Also, attractive forces between the particles for instance by van der Wal's forces or bond models to take the binder particle interaction into account can be implemented in the DEM.

In the before described pre-processing, the particles are arranged in a contactless manner. One option to achieve the desired volume content and to ensure particle contact, is the compression of the particle assembly by a top and a bottom plate moving in opposite direction. In this way, the initial porosity and particle arrangement is set. Subsequently, processing load or volume changes due to delithiation / lithiation can be investigated. Sangrós et al. investigated the calendaring process and the resulting impact on the CAM and additive+binder particle arrangement of a LIBs cathode. Therefore, the top plate was moved downwards and the resulting mechanical stress was recorded for every timestep. When the experimentally found maximal mechanical stress was reached, the compression was stopped and displacement upwards started. In this way, the DEM simulation revealed important parameters like porosity, forces on the particles, number of bonds or particle positions, which were used in the subsequent post-processing step. The found values for porosity were in good approximation to the experimental ones with an error below 5% (Sangrós Giménez, 2022).





Figure 5 - Summary of the Workflow of a DEM simulation (Sangrós Giménez, 2022)

2.2.2.3 Post-processing

Based on the data obtained in the DEM simulation (particle position, particle material, number of contacts, contact area), a pathfinding algorithm is used to determine the electric conductivity of the network. First, nodes and connecting lines corresponding to the particles and the Euclidean distance between two particles in contact respectively, are defined. Second, start and end nodes are set, where the start represents the contact to the separator and the end the contact to the current collector. The most conductive paths from the start to the end nodes are identified by the pathfinding algorithm considering the difference in the intrinsic electrical conductivity of the involved materials (Sangrós Giménez, 2022). Finally, the individual resistance of each conducting particle is calculated. Therefore, each particle is assumed as a conducting cylinder, where the dimension of the cylinder is defined based on the contact area and the Euclidean distance. According to the found electrical paths, the cylinders are connected in series leading to an equivalent circuit representing the entire REV (see Figure 3). Considering the value and the size of the REV, the specific electrical conductivity of the electrode can be finally calculated.



Figure 6 - Schematic of the equivalent electric circuit generate frome the particle contacts computed with the DEM (Sangrós Giménez, 2022).

Sangrós et al. were able to show that consideration of the contact area is crucial, as the quality of the particle contact directly affects the conductivity (Sangrós Giménez et al., 2020a). In fact, the manufacturing process and the operation of the cell strongly influence the particle-particle contact. The applied external forces result into a rearrangement of the particle network, which increases the contact area and number. However, excessive forces can also lead to the rupture of particle-particle contacts as well as the breakage of single particles. Also, delamination due to volume changes during operation lead to a degradation of the contact and thus to lower a conductivity.

Beside the electrical conductivity, the post-processing allows conclusions on the porosity and the tortuosity of the network. Sangrós et al. showed that this information can be further used to determine also the ionic conductivity of the SE, avoiding the necessity to simulate the SE structure itself (Sangrós Giménez et al., 2020a, Sangrós Giménez, 2022). However, So et al. used the DEM to simulate the sintering process of an ASSB electrode including AM and SE. Information on the contact area between



AM and SE have been generated, which might be of particular importance for the intercalation reaction during charging (So et al., 2022).

2.2.2.4 Conclusion

DEM is a powerful simulation tool to model the positive electrode of a Solid-State Battery at the microscopic scale

In particular it allows to:

- 1. Realistically represent complex particle structures based on a given particle size distribution.
- 2. Compute the evolution of internal stresses and deformation in the cathode during mechanical loading and upon electrochemical cycling.
- 3. Determine the ionic and the electrical conductivity of the cathode based on the contact area between the particles computed using the DEM.

2.2.3 Objectives of the microstructure modelling approach

One bottleneck of the cycling performance of ASSB is the charge transport from the anode to the current collector of the cathode. This includes the Li-ion transport through the solid electrolyte. Therefore, in WP 7.2.2, the ionic conductivity of the solid electrolyte network in 1) the positive electrode and 2) the separator will be estimated with the microstructural model. Starting from the particle size distribution determined in WP 3, the model will provide recommendations to optimize the particle size distribution in the sense of an increased ionic conductivity of the solid electrolyte network.

However, in some cases the improvement in ionic conductivity through the SE is accompanied by a reduction in electrical conductivity in the CAM/CB matrix. To investigate this circumstance, in WP 7.2.4 the entire cathode network including CAM and SE will be modelled to provide deeper insights into the interplay of ionic and electronic conductivity in the electrode structure. Here, the number of contacts and the contact area between two particles will serve as an indicator for the network quality, as they directly influence the conductivity of the electrode. With this, the impact of mechanical stress due to manufacturing processes or due to lithiation-related volume changes on the electrode structure can be judged. After validation of the model with experimental results (WP 7.4), the initial particle size distribution as well as the manufacturing process can be improved based on the findings of the simulation. Therewith, the microstructural model provides relevant parameters to estimate the macroscopic cell performance, also in the sense of aging phenomena due to mechanical degradation by lithiation /delithiation induced volume changes.

2.2.4 Identification of the input/output parameters of the microstructure model

2.2.4.1 Inputs parameters of the microstructure model

In Table 1 the input parameters for the microstructure model are listed. As described above, the intrinsic material properties of the involved particles are the fundament on which the network behaviour can be calculated. On the one side, mechanical properties, like Young modulus, determine the structure of the network for an external load. Beside the involved particles, also material bonds e.g. based on the binder matrix, need to be considered as an important factor for the contact quality. The manufacturing process as well as the cycling-related volume change of the cell define the applied mechanical stress. In combination with the initial component recipe and the particle size distribution, the DEM generates the structure of the particle network. On the other side, electrochemical properties of the bulk material are used in the post-processing step to calculate the conductivity of the entire network. Finally, the outcomes of the microstructural modelling are compared with experimentally found values for validation.





Table 1 - Input parameters of the microstructural model.

Parameter	Unit	Comment	Input from
Pre-processing			
Particle size distribution of SE and AM	-		WP 3/4
Mass fraction AM/SE/Binder/CB	wt%		WP 4
DEM			
Volume fractions		Includes initial porosity	WP 4
Final layer thickness	m		WP 4
Young-Modulus	Ра	Function of SOC	Atomistic model
Poisson ratio	-		WP 3 / Literature
Yield ratio	-		WP 3 / Literature
Density AM/SE/Binder/CB	kg m⁻³		WP 3 / Literature
Coefficient of restitution	-		WP 3 / Literature
Single particle strength	Ра	Nanoindenter trails	WP 3 / Literature
External stress	Ра		WP 4
2. Application (cell, cell pack)			
External stress velocity	m s ⁻¹		WP 4
Volume change due to Li-intercalation	%	in a certain SOC-range	Atomistic model
Adhesion strength 1. vdW (Hamaker Constante) 2. Etc.	J		WP 4 / Literature
Minimal distance between two particles	m	To ensure conductivity	WP 3 / Literature
Binder bond stiffness (area-related)	N m ⁻³	Difficult to be determined experimentally \rightarrow Modell can be calibrated	WP 4 / Literature
Binder ultimate bond strength	N m⁻²	Tensile and shear strength \rightarrow see above	WP 4 / Literature
Post-processing			
Intrinsic ionic conductivity of particles SE (Alternative: ionic conductivity of compressed	S m ⁻¹		Atomistic model
powder SE)			Experimental (WP3)
Intrinsic electronic conductivity of particles AM and CB	S m⁻¹		Atomistic model
(Alternative: electronic conductivity of compressed powder SE and CB (separately))			Experimental (WP3)
Validation			
lonic conductivity of separator and cathode	S m ⁻¹		WP 4
Electronic conductivity of cathode	S m ⁻¹		WP 4

2.2.4.2 Outputs parameters of the microstructure model

With the microstructural model important insights into the mechanical, electro-mechanical and charge transport behaviour of ASSB cells can be provided. In table 2 the output parameters of the DEM-based model are listed.





Based on the network structures, including contact area and number of contacts, predictions on the ionic and electronic conductivity are achieved. Beside the direct resistivity in the particle-particle connection paths, also conclusions on the porosity and tortuosity as well as on the specific surface area can be drawn, which influence the charge transfer in the ASSB electrode fundamentally. A special remark is also taken on the mechanical stresses within the layers. In this way the impact of external and internal stress sources on the network performance can be determined.

Parameter	Unit
Ionic conductivity 1. Separator 2. Electrode (cathode)	S m ⁻¹
Electronic conductivity: Electrode (cathode)	S m ⁻¹
Number of Contacts	-
Contact area	m²
Specific surface area	m ⁻¹
Porosity after processing	-
Tortuosity factor	-
Coating adhesion strength	Ра
Internal mechanical stress	Ра
Ratio of broken AM particles	%
Optimized PSD	-
Impact of 1) external stress 2) cycling (volume change of particles)	Pa %

Table 2 - Output parameters of the microstructural model.





2.3 Macroscale modelling approach modelling approach (IFPEN)

The macroscale modelling is concerned by the behaviour at the cell level, from a multi-physical point of view (electrochemical, thermal, mechanical, and ageing). IFPEN has developed an expertise into this type of modelling with the aim of finding an appropriate compromise between computing resources, accuracy, and physical meaning to be used for understanding, prognosis and optimisation of battery performances and safety.

In the battery research field, multi-physical modelling at the cell level is based on the electrochemical framework proposed by the John Newman's research group (Newman, Thomas-Alyea, 2004), with the so-called pseudo-two-dimensional model (P2D) or Doyle-Fuller-Newman (DFN) model. Many other physical models have since been proposed to simplify the model or to add new physical phenomena. IFPEN developed its own version of the electrochemical model following the works of Prada et al. (Prada et al., 2012), based on a single particle with electrolyte dynamics model (SPMe) and have made continuous improvements and additions ever since.

In the HELENA project, several challenges regarding this modelling approach arise due to the development of ASSB, requiring a holistic modelling approach (electrochemical, thermal, mechanical, and ageing). This section 0 thus describes the macroscale modelling approach (state-of-the-art at IFPEN, new approaches that are considered, and the possible challenges that are foreseen in HELENA). its main objectives, and identifies the required inputs (from lower scale models or experimental data) and the outputs (for upper scale models and contribution to the design of HELENA ASSB).

2.3.1 Description of the macroscale modelling approach

2.3.1.1 Electrochemical modelling: single particle model with electrolyte dynamics (SPMe)

The following paragraphs describe the state-of-the art of electrochemical modelling at IFPEN for the Liion chemistry, which is based on the SPMe model. Figure 7 draws a schematic representation of a realistic lithium-ion cell, the P2D model, and the SPMe model. A realistic Li-ion cell is a "sandwich", constituted from a positive and negative porous composite electrode (particles of solid active matter of different sizes and morphologies in which the lithium inserts, a conductive solid additive, and a solid binder), current collectors (copper at the negative, aluminum at the positive), and a porous separator. Finally, a liquid electrolyte permeates the porosities of the electrodes and the separator.

The standard P2D model describes three distinct cell domains: the porous negative electrode (between z = 0 and $z = \delta_n$), the separator (between $z = \delta_n$ and $z = \delta_n + \delta_{sep}$), and the porous negative electrode (between $z = \delta_n + \delta_{sep}$ and $z = \delta_n + \delta_{sep} + \delta_p = L$). Two dimensions are described: a macroscopic dimension z (the normal to the cell sandwich, or thickness), and a microscopic dimension r (radial dimension in polar coordinates of the active matter particles, that are considered spherical); hence, its name P2D. It is based on porous-electrode theory, which considers that the separator and the electrodes are a superposition of two continua: a porous solid matrix and a liquid electrolyte that fills these pores, each described by its volume fraction. Multiple spherical particles of identical radius are considered along the thickness of each electrode (along z). The main physical phenomena that are modelled are: electronic conduction in the solid matrix, electrochemical charge transfer reactions at the interface between electrolyte and electrode particles, and lithium transport in the electrode particles (by diffusion) and the electrolyte (by diffusion and migration). It thus describes several state-variables across the two spatial dimensions z, r and time dimension t: concentrations in lithium in the electrolyte c_{e} and in the electrode particles c_s^k (k means negative or positive electrode here, plus the separator for electrolyterelated variables/parameters), several current densities (electronic in the electrodes i_s^k , ionic in the electrolyte i_e , and that of electrochemical reactions j_f^k) causing overpotentials, and electrical potentials in the electrolyte ϕ_e and in the electrodes ϕ_s^k . These state-variables allow to compute the cell terminal voltage output U that results from a current input I.

The SPMe model comes directly from the P2D model but makes a simplification. Its main assumption is that the gradient of lithium concentration in the solid-phase c_s^k can be neglected along the electrode thickness; however, the gradient of lithium ions concentration in the electrolyte c_e is still considered significant (especially at high current rates) and electrolyte dynamics are kept. Thus, the lithium solidphase concentration can be represented by a single particle for each electrode; hence, the model's



name. In practice, this means that an average value of c_s^k is considered over the electrode thickness, implying as well the calculation of average (or "lumped") values of the electrochemical reactions interfacial current densities j_f^k (implying the exchange current densities i_0^k), the charge transfer overpotentials η_{ct}^k , and the solid-phase potential ϕ_s^k .



The **main equations of the SPMe model** are detailed in Table 3 and the symbols are detailed in Table 4. It is governed by a system of partial differential equations, associated with boundary conditions, and regular equations. The model accounts for the following main physical phenomena:

- Mass conservation (lithium transport):
 - In the solid-phase: lithium is assumed to be transported inside electrode particles by diffusion, under the effect of concentration gradients. Eq. (1) governs $c_s^k(r,t)$ by applying Fick's law of diffusion in polar coordinates. Boundary conditions state that there is no diffusion in the center of the particle due to the spherical symmetry, and that the flux of lithium at the outer surface of the particle is governed by the interfacial charge transfer kinetics.
 - In the liquid-phase: lithium is assumed to be transported inside the electrolyte by both diffusion, under the effect of concentration gradients, and migration, under the effect of potential gradients. Eq. (2) governs $c_e(z, t)$. Boundary conditions state that there is no concentration gradient at both extremities of the cell sandwich.
- Charge conservation (charge transport):
 - In solid phase: electrons are transported by conductivity depending on the rate of electrochemical charge transfer. Eq. (3) governs $\phi_s^k(z,t)$ by applying Ohm's law. Boundary conditions state that, at both extremities of the cells sandwich, the electrons flow is controlled by the cell current divided by the electrode plate area, and at the electrodes/separator interfaces, the electrical potential is constant.





- In liquid phase: anions and cations in the electrolyte are moved by diffusion and migration depending also on the rate of electrochemical charge transfer. Eq. (4) governs $\phi_e(z, t)$ by applying this charge balance. Boundary conditions state that there is no gradient of electrolyte potential at both extremities of the electrodes. Ionic conductivity κ_e is considered as a function of lithium concentration.
- Electrochemical kinetics: the rate of intercalation and de-intercalation processes electrodeelectrolyte interfaces are assumed to follow Butler-Volmer's model. The system of equations (5), (6), (7) governs the evolution of j^k_f(z, t) and η^k_{ct}(z, t).

Physical transport properties related to the electrolyte are modified by the porous nature of the media, which act as an obstacle compared to the bulk media. Bruggeman model computes an effective parameter considering the effect of the porosity and tortuosity on the transport parameter. Equations (8) and (9) (11) express the Bruggeman model for lithium diffusivity in electrolyte D_e^k and ionic conductivity κ_e^k .

An equivalent solid conductivity for the conductive matrix of each electrode can be obtained from Eq. (11) based on the individual solid conductivity and volume fraction of its active and inactive materials. From this, the solid phase ohmic overvoltage of each electrode can be obtained from (12).

The equilibrium potential U_{eq}^k of each active material depends on the lithium concentration in the electrode particles as expressed in Eq. (13). It intervenes in the calculation of the charge transfer overpotential η_{ct}^k in which U_{eq}^k is evaluated at the particle outer surface $r = R_k$.

Finally, the voltage of the cell can be expressed from Eq. (15).

The SPMe electrochemical model can be coupled to a thermal model as all physical phenomena are temperature sensitive. A lumped thermal model is generally sufficient to describe general cell behavior with temperature at the macro-scale. Some parameters are thus considered to be dependent on the temperature, including: D_s^k , σ_k , D_e , κ_e , k_0^k . This sensitivity is then modelled with an empirical model, often an Arrhenius' law.

Physical phenomenon	Governing equations	Boundary conditions	Eq.
Mass conservation in solid phase	$\frac{\partial c_s^k}{\partial t} - \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_s^k \frac{\partial}{\partial r} c_s^k \right) = 0, k = (n, p)$	$D_{s}^{k} \frac{\partial}{\partial r} c_{s}^{k} \bigg _{r=0} = 0$ $-D_{s}^{k} \frac{\partial}{\partial r} c_{s}^{k} \bigg _{r=R_{k}} = \frac{j_{f}^{k}}{a_{s}^{k}F}$	(1)
Mass conservation in liquid phase	$\frac{\partial(\epsilon_e^k c_e)}{\partial t} - \frac{\partial}{\partial z} \left(D_{e,k}^{eff} \frac{\partial c_e}{\partial z} \right) - (1 - t_+) \frac{j_f^k}{F}$ $= 0, k = (n, sep, p)$	$\frac{\partial c_e}{\partial z}\Big _{z=0} = 0$ $\frac{\partial c_e}{\partial z}\Big _{z=L} = 0$	(2)
Charge conservation in solid phase	$\frac{\partial}{\partial z} \left(\sigma_k^{eff} \frac{\partial \phi_s^k}{\partial z} \right) - j_f^k = 0, k = (n, p)$	$ \begin{vmatrix} -\sigma_n^{eff} \frac{\partial \phi_s^n}{\partial z} \\ z = 0 \end{vmatrix}_{z=0}^{z=0} = \frac{I}{A_n} \\ -\sigma_p^{eff} \frac{\partial \phi_s^p}{\partial z} \\ z = L = \frac{I}{A_p} \\ \frac{\partial \phi_s^n}{\partial z} \\ z = \delta_n = 0 $	(3)

Table 3 - Main equations of the SPMe electrochemical model.





		$\frac{\partial \phi_s^p}{\partial z}\bigg _{z=L-\delta_p} = 0$	
Charge conservation in liquid phase	$\frac{\partial}{\partial z} \left(\kappa_k^{eff} \frac{\partial \phi_e}{\partial z} \right) + \frac{\partial}{\partial z} \left(\kappa_{D,k}^{eff} \frac{\partial}{\partial z} \ln c_e \right) + j_f^k = 0, k = (n, sep, p)$	$\frac{\partial \phi_e}{\partial z} \bigg _{z=0} = 0$ $\frac{\partial \phi_e}{\partial z} \bigg _{z=L} = 0$	(4)
Electrochemical kinetics of the charge-transfer reactions	$j_{f}^{k} = a_{s}^{k} i_{0}^{k} \left\{ exp\left(\frac{(1-\alpha^{k})F\eta_{ct}^{k}}{RT}\right) - exp\left(-\frac{\alpha^{k}F\eta_{ct}^{k}}{RT}\right) \right\}, k$ $= (n, p)$	_	(5)
Exchange current density	$i_{0}^{k} = Fk_{0}^{k}c_{e}^{1-\alpha^{k}} \left(c_{s,max}^{k} - c_{s}^{k}(R_{k})\right)^{1-\alpha^{k}} c_{s}^{k}(R_{k})^{\alpha^{k}}, k$ = (n, p)	_	(6)
Solid phase electrode overpotential	$\eta_{ct}^k = \phi_s^k - \phi_e - U_{eq}^k \big(x_k(R_k) \big), k = (n, p)$	_	(7)
Liquid phase effective ionic diffusivity	$D_{e,k}^{eff} = D_e \epsilon_e^{k^{Brugg}k}, k = (n, sep, p)$	_	(8)
Liquid phase effective ionic conductivity	$\kappa_{e,k}^{eff} = \kappa_e \epsilon_e^{k^{Bruggk}}, k = (n, sep, p)$	_	(9)
Liquid phase ionic diffusional conductivity	$\kappa_{e,D,k}^{eff} = \frac{2RT}{F} \kappa_{e,k}^{eff} (t_+ - 1) \left(1 + \frac{d \ln f_{\pm}}{d \ln c_e} \right), k$ $= (n, sep, p)$	_	(10)
Solid phase effective electronic conductivity	$\sigma_k^{eq} = \frac{\sum_j \epsilon_j^k \sigma_k^j}{\sum_j \epsilon_j^k}, k = (n, p), j$ = (solid active and inactive materials)	_	(11)
Solid phase ohmic overvoltage	$\eta_s^k = \frac{I\delta_k}{3A_k \sigma_k^{eq}}, k = (n, p)$	_	(12)
Interfacial surface aera	$a_s^k = \frac{3\epsilon_s^k}{R_k}, k = (n, p)$	_	(13)
Equilibrium electrode potential	$U_{eq}^{k} = U_{ref}^{k}(x_{k}), \text{ where } x_{k} = \frac{c_{s}^{k}(R_{k})}{c_{s,max}^{k}}, k$ $= (n, p)$	_	(14)
Cell terminal voltage	$U = \phi_s(L) - \phi_s(0)$ = $U_{eq}^p(R_p) - U_{eq}^n(R_n)$ + $\phi_e(L) - \phi_e(0) + \eta_s^p - \eta_s^n$ + $\overline{\eta}_{ct}^p - \overline{\eta}_{ct}^n$	_	(15)





Symbol	Туре	Description	Units				
k	Sub/sup-erscript	In domain $\{n, sep, p\}$					
n	Sub/sup-erscript	In negative electrode and particle					
sep	Sub/sup-erscript	In separator					
р	Sub/sup-erscript	In positive electrode and particle					
е	Sub/sup-erscript	In electrolyte	In electrolyte				
S	Sub/sup-erscript	In solid phase (negative or positive)					
$c_s^k(r,t)$	Variable	Lithium ions concentration in electrode mol m ⁻³					
c(z,t)	Variable	Lithium ions concentration electrolyte	$mol m^{-3}$				
$c_e(z,t)$	Variable	Solid phase electric potential	V				
$\psi_s(z,t)$	Variable	Electrolyte electric potential	V				
$\psi_e(z,t)$	Variable	Electrode-electrolyte interfacial overnotential	V				
$\eta_{ct}(z, t)$	Variable	Solid phase obmic overvoltage of electrode k	V				
$\frac{\Pi_{s}(t)}{i^{k}(z,t)}$	Variable	Electrochemical reactions current density	Λm^{-3}				
$J_f(\mathbf{Z}, \mathbf{U})$	Variable		A III				
$i_0^n(z,t)$	Variable	density	Am ²				
$x_k(r,t)$	Variable	Electrode lithiation rate	_				
SoC(t)	Variable	Cell state-of-charge	—				
T(t)	Variable	Cell temperature	К				
U(t)	Variable	Cell voltage	V				
I(t)	Variable	Cell current	А				
F	Parameter	Faraday's constant A s mol ⁻¹					
R	Parameter	Universal gas constant	J K ⁻¹ mol ⁻¹				
δ_k	Parameter	Electrode/separator thickness m					
L	Parameter	Cell thickness ($L = \delta_n + \delta_{sep} + \delta_p$)	m				
A _k	Parameter	Electrode plate area	m ²				
R _k	Parameter	Electrode particle radius	m				
a_s^k	Parameter	Electrode interfacial area	m ²				
ϵ_s^k	Parameter	Active matter volume fraction	-				
ϵ_e^k	Parameter	Electrolyte volume fraction	—				
$D_s^k(T)$	Parameter	Lithium diffusivity in electrode particle	$m^2 s^{-1}$				
$\sigma_k^{j(T)}$	Parameter	Solid electronic conductivity of active or	S m ⁻¹				
	-	inactive material <i>j</i> in electrode <i>k</i>	2 1				
$D_e(T)$	Parameter	Lithium ions diffusivity in electrolyte	$m^2 s^{-1}$				
$\kappa_e(c_e, T)$	Parameter	Litnium ions conductivity in electrolyte	S m ⁻¹				
Brugg ^ĸ	Parameter	Bruggeman coefficient	_				
t_+	Parameter	Litnium ions transference number	_				
l dln f	Parameter	i nermodynamic factor	_				
$+\frac{d\ln f_{\pm}}{d\ln c_{a}}$							
α_k	Parameter	Charge transfer coefficient of the reduction	_				
		reaction ($\alpha_{ox} = 1 - \alpha_{red}$)					
$k_0^k(T)$	Parameter	Charge transfer reaction rate constant	$m^{f(\alpha)} mol^{g(\alpha)} s^{-1}$				
C_e^0	Parameter	Initial concentration of lithium ions in the $mol m^{-3}$					
		electrolyte	-				
$C_{s,max}^k$	Parameter	Maximum lithium concentration in electrode mol m ⁻³					
~k	Parameter	Electrode particle lithiation rate at 0% cell SoC					
$\frac{\lambda_{0\%}}{\mu_{k}}$	Daramotor	Electrode aquilibrium potential	V				
$U_{eq}(X_k)$	Falametel	LIECTIONE EQUILIDITUTI POLETILIAI	v				

Table 4 - Symbols used in the SPMe model.





Main challenges for SPMe model within the HELENA project:

Gen. 4b ASSB batteries differ from previous Li-ion generations in the use of a solid electrolyte instead of a liquid electrolyte, and the use of lithium metal as negative electrode instead of graphite or graphite+SiO_x. First challenge will be to adapt the electrolyte parameters to HELENA halide solid electrolyte (Li transfer, ionic conduction, ...). Second challenge will be to change the negative electrode model to consider the lithium metal electrode. As it is different to a composite electrode, a flat electrode model could be considered. Also, with the lithium metal anode comes the question of dendrite formation and growth, and the electrochemical model may be modified to account for this in the ageing model.

2.3.1.2 Mechanical model

The mechanical part aims to provide insights into the volume expansion of active materials for the macro scale modelling, where it plays an important role in ageing mechanisms.

Evaluation of stress-induced diffusion

As mechanical effects (i.e. particle swelling or volume change) are considered in the electrochemical modelling of the cell, the diffusion flux is modified to account for the hydrostatic stress σ_h^k as follows:

$$J_D^k = -D_s^k \left(\nabla c_s^k - \frac{\Omega_k c_s^k}{RT} \nabla \sigma_h^k \right)$$
(16)

The hydrostatic gradient is evaluated based on the previous expression using the fact that the integral is constant as a function of r as follows:

$$\nabla \sigma_h^k = -\frac{2\Omega_k E_k}{9(1-\nu_k)} \nabla c_s^k \tag{17}$$

Consequently, the pore wall flux is:

$$J_D^k = -D_s^k \left(1 + Z_3^k c_s^k(r) \right) \nabla c_s^k \tag{18}$$

With

$$Z_{3}^{k} = \frac{2\Omega_{k}^{2} E_{k}}{9RT(1 - \nu_{k})}$$
(19)

An equivalent diffusion coefficient is then defined as:

$$\boldsymbol{D}_{s,eq}^{k}(\boldsymbol{r}) = \boldsymbol{D}_{s}^{k} \left(1 + \boldsymbol{Z}_{3}^{k} \boldsymbol{c}_{s}^{k}(\boldsymbol{r}) \right)$$
⁽²⁰⁾

This expression of $D_{s,eq}^k$ is then integrated into the mass conservation of lithium in solid phase equation (1). This equivalent diffusion coefficient, which is a function of particle radius r, accounts for the effect of the volume change of the particle without having to effectively update its radius r in the model.

Stresses evaluation

Furthermore, as concentration gradients are developing into the particles, (Dai et al., 2014) have provided analytical expressions to evaluate hydrostatic stresses within spherical particles based on thermal expansion analogy. This study provides the expression of radial σ_r^k and tangential σ_t^k stresses as a function of the particle radius r in a particle with a R_k radius as follows:

$$\sigma_{r}^{k}(r) = \frac{2\Omega_{k}E_{k}}{3(1-\nu_{k})} \left[\frac{1}{R_{0}^{k^{3}}} \int_{0}^{R_{k}} c_{s}^{k}(r)r^{2}dr - \frac{1}{r^{3}} \int_{0}^{r} c_{s}^{k}\zeta^{2}d\zeta \right]$$
(21)

$$\sigma_t^k(r) = \frac{\Omega_k E_k}{3(1-\nu_k)} \left[\frac{2}{R_0^{k^3}} \int_0^{R_k} c_s^k(r) r^2 dr + \frac{1}{r^3} \int_0^r c_s^k \zeta^2 d\zeta - c_s^k(r) \right]$$
(22)

In these expressions, Ω_k is the partial molar volume, E_k is the Young's modulus and ν is the Poisson's ratio. The hydrostatic stress is then computed as follows:



$$\sigma_{h}^{k}(r) = \frac{\sigma_{r}^{k} + 2\sigma_{t}^{k}}{3} = \frac{2\Omega_{k}E_{k}}{9(1 - \nu_{k})} \left(\frac{3}{R_{0}^{k^{3}}} \int_{0}^{R_{k}} c_{s}^{k}(r)r^{2}dr - c_{s}^{k}(r)\right)$$
(23)

Integrals values as function of the radius are evaluated by assuming that the solid concentration is constant inside the control volumes.

Then, this can be combined with the electrochemical SPMe model to evaluate the stresses along particles.

Cell thickness variations

Material swelling leads to composite electrode swelling which in turns leads to cell swelling. The cell swelling is directly given by the individual swelling of active materials. This swelling leads to compression of other materials such as the separator or packaging which then act as springs. The springs displacement is evaluated through the volumetric swelling of the electrodes.

The volume of active material in the electrode is given by the following equation takin into account the i different materials:

$$V_{AM}^{k} = \epsilon_{s}^{k} \delta_{k} A_{k} = \sum_{i \in k} V_{0}^{i} (1 + \Omega_{i} c_{i}) = \sum_{i \in k} \epsilon_{s}^{i} \delta_{k} A_{k} (1 + \Omega_{i} c_{i})$$
⁽²⁴⁾

Consequently, the variation of the electrode thickness can be expressed as

$$\frac{\mathrm{d}\boldsymbol{\delta}_{k}}{\mathrm{d}\boldsymbol{t}} = \boldsymbol{\delta}_{k}^{0} \sum_{i \in k} \boldsymbol{\epsilon}_{s}^{i} \frac{\mathrm{d}(\boldsymbol{\Omega}_{i}\boldsymbol{c}_{s}^{i})}{\mathrm{d}\boldsymbol{t}} = \boldsymbol{\delta}_{k}^{0} \sum_{i \in k} \boldsymbol{\epsilon}_{s}^{i} \left(\boldsymbol{c}_{s}^{i} \frac{\mathrm{d}\boldsymbol{\Omega}_{i}}{\mathrm{d}\boldsymbol{c}_{s}^{i}}(\boldsymbol{c}_{s}^{i}) \frac{\mathrm{d}\boldsymbol{c}_{s}^{i}}{\mathrm{d}\boldsymbol{t}} + \boldsymbol{\Omega}_{i}(\boldsymbol{c}_{s}^{i}) \frac{\mathrm{d}\boldsymbol{c}_{s}^{i}}{\mathrm{d}\boldsymbol{t}}\right)$$
(25)

As N_{elec} are stacked in the cell, the volumetric change of the complete cell considering an infinite stiffness is given by

$$\frac{\mathrm{d}l_{cell}}{\mathrm{d}t} = N_{elec} \delta_k^0 \sum_{i \in k} \epsilon_s^i \left(c_s^i \frac{\mathrm{d}\Omega_i}{\mathrm{d}c_i} (c_s^i) \frac{\mathrm{d}c_s^i}{\mathrm{d}t} + \Omega_i (c_s^i) \frac{\mathrm{d}c_s^i}{\mathrm{d}t} \right)$$
(26)

Symbol	Туре	Description	Units
$J_D^k(r)$	Variable	Pore wall diffusion flux (stress-induced diffusion)	$mol m^{-1} s^{-1}$
$\sigma_h^k(r)$	Variable	Hydrostatic stress	$kg m^{-1} s^{-2}$
$\sigma_r^k(r)$	Variable	Radial stress	$kg m^{-1} s^{-2}$
$\sigma_t^k(r)$	Variable	Tangential stress	$kg m^{-1} s^{-2}$
$D_{s,eq}^k(r)$	Variable	Equivalent lithium diffusivity for stress-induced	$m^2 s^{-1}$
· •		diffusion	
$V_{AM}^k(t)$	Variable	Volume of active material in electrode k	m ³
$\delta_k(t)$	Variable	Thickness of electrode k	m
$l_{cell}(t)$	Variable	Total thickness of the cell	m
Ω_k	Parameter	Partial molar volume	m ³ mol ⁻¹
E _k	Parameter	Young's modulus	$kg m^{-1} s^{-2}$
ν_k	Parameter	Poisson's ratio	—
R_0^k	Parameter	Initial radius of particle in electrode k	m
V_0^i	Parameter	Initial volume of material <i>i</i> m ³	
N _{elec}	Parameter	Number of electrode stacks in the cell	_

Table 5 - Symbols of the mechanical sub-model.

Main challenges for the mechanical sub-model within the HELENA project

The mechanical sub-model was initially coupled to the SPMe model to account for the important swelling of silicon particles in Gen3b batteries negative electrode, which gives information at the macro-scale on cell width evolution. Blended silicon-graphite negative electrode is not expected to be used for





ASSB within HELENA, but mechanical issues are expected in ASSB. Some of chemo-mechanical issues of ASSB include dendrite growth within the solid electrolyte, interphase formation at the anode/SE interface and its mechanical stability, and mechanical stability of the various components of the solid-state composite electrodes (Bistri et al., 2021). This challenges the mechanical sub-model to account for the significant mechanisms with an adapted framework to be coupled with the SPMe and ageing model.

2.3.1.3 Ageing model

To account for cell ageing, main state-of-the-art mechanisms in lithium-ion batteries models are described here (Reniers et al., 2019), (O'Kane et al., 2022). Generic approaches are considered to easily fit few model parameters while keeping relevant physical behaviours. Main mechanisms considered here are:

- Solid electrolyte interphase (SEI) growth,
- Cracks-induced SEI formation,
- Lithium plating on the negative electrode,
- Cracks on both positive and negative electrode,
- Oxidation of the electrolyte on the positive electrode.

SEI formation

SEI formation is one of the major mechanisms leading to performance degradation in Li-ion batteries. In this mechanism, an interphase layer is created by the reduction of solvent molecules at the negative electrode interface creating the SEI layer. Solvent diffuses from the SEI/electrolyte interface until the SEI/active material interface. Thus, this phenomenon is limited by diffusion in the formed SEI layer as well as electrochemical kinetics. To reduce this model complexity, the convection of solvent due to SEI layer movement is neglected. The impacts of SEI layer formation are:

- A parasitic current leading to Li de-intercalation from the negative electrode or loss of lithium inventory
- Creation of a resistive layer leading to power fade
- Clogging of electrode porosity

It is mathematically described by equations in Table 6 (Prada 2013, Edouard 2016). Mathematical symbols are listed in Table 7.

The hypotheses for developing this model are as follows: there is only a single uniform organic porous layer surrounding the particles while the inner inorganic layer is neglected. The solvent molecules travel through the SEI by diffusion to reach the particle surface followed by an irreversible reaction to form the SEI compound.

Following this, the mass balance for the solvent within the SEI layer is given by Eq. (27), governing the solvent concentration c_{solv} with a diffusion law. The boundary condition states that the flux of solvent molecules at the outer surface of the particle is governed by the kinetics of the parasitic reaction, and also states the continuity between solvent concentration at the SEI/electrolyte interface, which is equal to the solvent concentration in bulk electrolyte c_{solv}^{bulk} . If the rate of change of the solvent concentration gradient is negligible within the SEI layer, the steady-state solution in Eq. (28) can be used. As the SEI is a porous media, an effective diffusivity coefficient can be used following Bruggeman's model as in Eq. (29).

After the diffusion of the solvent molecules across the SEI, the solvent molecules reach the particle surface where its reduction occurs. This is an irreversible reaction, and its rate kinetics are described using Tafel's model as in Eq. (30). When coupling to the SPMe model, the interfacial current density in the negative electrode j_f^n must be replaced by j_{tot}^n , which is the sum of j_f^n and the current density of the parasitic solvent reduction reaction i_{sei} , as is stated by Eq. (31). The growth rate of the SEI layer thickness δ_{sei} can then be estimated by Eq. (33). The capacity loss due to the SEI parasitic reaction and associated loss of lithium inventory can be computed from Eq. (34). The SEI opposes an electrical resistance to current due to its conductivity, which is given by Eq. (35). The growth of the SEI leads to pore-clogging in the negative electrode (i.e., it reduces its porosity, which is accounted for by Eq. (36).





To complete the coupling to the SPMe model, the terminal voltage equation is modified to account for this added overvoltage η_{sei} as written by Eq. (38).

To couple the SEI growth sub-model to the electrochemical-thermal model, the solvent diffusivity D_{solv} and reaction rate constant k_{sei} can be considered as temperature-sensitive by an empirical Arrhenius' relationship such as Eq. (37).

Table 6 –	Governing equations	Boundary conditions	Eq.
Equations of			
the SEI growth			
sub-			
model.Physical			
phenomenon			
solvent		$\partial c_{solv} = i_{sei}$	
	$\partial c_{solv} = \partial^2 c_{solv}$	$\left \begin{array}{c} -D_{solv} \overline{\partial r} \right _{r} = P = \overline{2F}$	(27)
	$\frac{\partial t}{\partial t} = D_{solv} \frac{\partial r^2}{\partial r^2}$	$(P + \delta) = c^{bulk}c$	(27)
		$c_{solv}(R_n + 0_{sei}) = c_{solv} + c_{sei}$ $c_{solv}(t = 0) = c_{solv}^0$	
Solvent diffusion if	$\epsilon_{sei} c_{solv}^{bulk} - c_{solv}^{surf} i_{sei}$		(20)
steady state	$D_{solv} - \frac{\delta_{sei}}{\delta_{sei}} = -\frac{1}{2F}$	_	(20)
Effective solvent diffusion	$D_{solv}^{eff} = D_{solv} \epsilon_{sei}^{Brugg^{sei}}$	_	(29)
Solvent reduction	$i = 2Ek e^{surf} arm \left[-\beta_{sei}F\right] (\beta_{sei}F)$		(30)
kinetics	$l_{sei} = -2I^{r}\kappa_{sei}c_{solv} \exp\left[-RT\right]\left(\psi_{s} - U_{sei}\right)$	_	
	$-\frac{\delta_{sei}}{i_{tot}}$		
Oursenthalanaa far	$\kappa_{sei}a_s^{nftot}$		
the negative	$i_{r}^{n} = i_{c}^{n} + a_{r}^{n} i_{r}$	_	(31)
electrode	Jtot Jf + ws vsei		
Negative reactive	$S = a^n W = \frac{3\epsilon_s^n \delta_n A_{sep}}{2}$	_	(32)
surrace	$S_n - u_s v_n - R_n$		
SEI layer growth	$\frac{\mathrm{d}\delta_{sei}}{\mathrm{d} \mathrm{d} \mathrm{d} \mathrm{d} \mathrm{d} \mathrm{d} \mathrm{d} $	$\delta (t=0) = \delta^0$	(33)
	$dt = 2F\rho_{sei}$	$\sigma_{sel}(t=0) = \sigma_{sel}$	(00)
Canacity loss due			(34)
to SEI	$\frac{\mathrm{d}Q_{loss}^{set}}{\mathrm{d}Q_{loss}} = S_{i}i_{i}i_{i}$	$Q_{loss}^{set}(t=0)=0$	
Desistance	$dt = S_n t_{set}$		
increase due to SEI	$R_{sei} = \frac{\sigma_{sei}}{2}$	_	(35)
Clogging of	$\kappa_{sei}S_n$. ,
electrode porosity	$\epsilon_e^n = \epsilon_e^{n,0} - \frac{\epsilon_n o_{sei}}{p}$	_	(36)
Arrhenius	R_n		
expression for	E_{a}^{ψ}		
temperature	$\Psi(1) = \Psi^{(3)} exp\left(\frac{1}{R}\right)$		
dependency of			(27)
and reaction rate	1)	_	(37)
kinetics	$\left(-\frac{1}{T_{ref}}\right)$, with ψ		
	= (D + h)		
Modification of cell	$= (D_{solv}; \kappa_{sei})$		(00)
terminal voltage	$U = U_{eq}^{\nu}(R_p) - U_{eq}^{n}(R_n) + \phi_e(L) - \phi_e(0)$	_	(38)
	$+ \eta_s^p - \eta_s^n + \overline{\eta}_{ct}^p - \overline{\eta}_{ct}^n - \eta_{sei}$		





Symbol	Туре	Description	Units
solv	Sub/super-	Solvent	
	script		
sei	Sub/super-	Solid electrolyte interphase	
	script		
bulk	Sub/super-	In the bulk electrolyte	
	script		
surf	Sub/super-	At the particle surface	
	script		
$c_{solv}(r,t)$	Variable	Solvent concentration	mol m ⁻³
i _{sei} (t)	Variable	Current density of the parasitic solvent reduction reaction	A m ⁻²
$j_{tot}^n(\mathbf{z}, \mathbf{t})$	Variable	Total solid current density in the negative electrode	A m ⁻³
$\delta_{sei}(t)$	Variable	Thickness of the SEI layer	m
$Q_{loss}^{sei}(t)$	Variable	Capacity loss due to SEI layer growth	Ah
$R_{sei}(t)$	Variable	Electrical resistance of the SEI layer	Ω
$\eta_{sei}(t)$	Variable	Overpotential of the SEI layer	V
$\epsilon_e^n(t)$	Variable	Electrolyte volume fraction of the negative	_
		electrode at time t	
U _{sei}	Parameter	Potential at which the solvent is reduced	V
$\epsilon_e^{n,0}$	Parameter	Initial electrolyte volume fraction of the negative	_
		electrode	
<i>S</i>	Parameter	Negative reactive surface	m ²
€ <i>sei</i>	Parameter	SEI layer porosity	-
$D_{solv}(T)$	Parameter	Solvent diffusivity in SEI layer	$m^2 s^{-1}$
Brugg ^{sei}	Parameter	SEI layer Bruggeman coefficient	-
$k_{sei}(T)$	Parameter	SEI formation reaction rate constant	s ⁻¹
β _{sei}	Parameter	SEI layer formation reaction charge transfer coefficient	—
κ _{sei}	Parameter	SEI layer conductivity	S m ⁻¹
M _{sei}	Parameter	SEI molar mass	kg mol⁻¹
ρ _{sei}	Parameter	SEI layer mass density	kg m ⁻³
A _{sep}	Parameter	Separator/electrode surface area	m ²
D ^{ref} _{solv}	Parameter	Solvent diffusivity in SEI layer reference at $T = T_{ref}$	$m^2 s^{-1}$
$E_a^{D_{solv}}$	Parameter	SEI formation reaction rate constant activation energy	J mol ⁻¹
k ^{ref}	Parameter	SEI formation reaction rate constant at $T = T_{ref}$	s ⁻¹
$E_a^{k_{sei}}$	Parameter	SEI formation reaction rate constant activation energy	J mol ⁻¹

Table 7 - Symbols of the SEI growth sub-model.

Lithium plating

As the electrical potential of the negative electrode goes below 0 V vs. Li⁺/Li, metal lithium can be directly deposited on the negative electrode in an inhomogeneous manner. This leads to I dendrite formation and sometimes short-circuits. During subsequent discharge, this same metallic lithium can be oxidized back to Li⁺ leading to its recovery. However, part of this lithium is trapped due to SEI formation on the newly formed interface or from contact losses.

One of the simplest ways to take this into account is to introduce a new parasitic current density for the lithium metallic deposition electrochemical reaction. This is done by Eq. (39), with Tafel electrochemical kinetics, and with a coefficient to account for only a partial recovery of lithium ions in the charge balance. Eq. (40) update the current balance in the negative electrode to account for the introduction of a new parasitic reaction. Eq. (41) computes the capacity loss caused by irreversible lithium plating.



Physical phenomenon	Governing equations	Boundary conditions	Eq.
Parasitic lithium plating current	$i_{LiP} = \beta_{irrev} i_0^{LiP} \exp\left(-\frac{0.5F}{RT} \phi_s^n\right)$	_	(39)
Current balance for the negative electrode	$j_{tot}^n = j_f^n + a_s^n i_{sei} + a_s^n i_{LiP}$	_	(40)
Capacity loss due to lithium plating	$\frac{1}{S_n} \frac{\mathrm{d}Q_{loss}^{LiP}}{\mathrm{d}t} = i_{LiP}$	_	(41)

Table 8 - Equations of the lithium plating sub-model.

Table 9 - Symbols of the lithium plating sub-model.

Symbol	Туре	Description	Units
LiP	Sub/super- script	Lithium plating	
$i_{LiP}(t)$	Variable	Lithium plating parasitic reaction current density	$A m^{-2}$
$Q_{loss}^{sei}(t)$	Variable	Capacity loss due to irreversible lithium plating	Ah
β _{irrev}	Parameter	Fraction of plated lithium irreversibly trapped leading to loss of lithium inventory	_
i ₀ ^{LiP}	Parameter	Lithium plating reaction exchange current density	A m ⁻²

Dendrite formation and growth

The stability of the Li/SE interface and defects at the interface can result in dendrite initiation and propagation through the electrolyte and limit the life of the battery. The phenomena involved undoubtedly occur over a wide range of length scales, from the atomic to the continuum scale. As stated repeatedly in the literature for solid-state battery, phase-field method, as a mesoscale method, appears the appropriate approach compared with those of finite-element methods for example. This method is indeed more and more used for qualitative studies in SSBs, such as microstructure evolution process and deposition morphologies which seem the focus of current work. The contribution of this method seems crucial for quantitative studies to predict or guide the designs of advanced battery systems.

In electrochemical simulation models, interfacial reactions with the motion of phase boundaries are complex for conventional approaches. The phase-field method seems an effective tool for bypassing the evolving complex geometry in conventional sharp inter-phase methods to simulate for example the dendrite growth in Li metal batteries. In the phase field method, the evolution of the phase field ξ is described in the form of Equation below owning here a source term for demonstrating the structure evolution (Sun, 2022).

$$\frac{\partial\xi}{\partial t} = -L\frac{\partial F}{\partial\xi} - \Gamma \tag{42}$$

 Γ the electrochemical reaction at the solid/liquid or solid/solid interface is described by a Butler-Volmer type equation, whose equilibrium can be disturbed, for example, by the Li ion diffusion kinetics through the electrolyte. Numerous modified expressions of this electrochemical equation are already proposed in literature.

L stands for the mobility at the interface for ξ and looks a coefficient rate coefficient (Ren, 2020). We can introduce more than one phase-field variables to describe a multiphase system. For example, with a granular electrolyte (Tantratian, 2021), two phase-field parameters (ξ and ϕ) are generally introduced to distinct the three-phase system: the Li metal phase ($\xi = 1, \phi = 0$), the Grain Boundary phase ($\xi = 0, \phi = 1$), and the grain phase ($\xi = 0, \phi = 0$).





F stands for the total free energy density of the system. F drives the spatio-temporal evolution of the phase-field evolution. Free energies drive phase-field evolution, which can be further separated into several contributions shown below.

$$F = \int_{V} fchemical + fgradient + fmechanical + fexternal + \cdots)dV$$
(43)

In which first term is the chemical free energy functions, second one is the interface/gradient free energy functions, third one is the displacement gradients in local free energy functions, and last one is the external force (e.g., electrical field for electrochemical phase-field models) free energy functions.

According to a recent paper (Sun,2022), for a pure phase-field problem, free energy functional with *fchemical* and *fgradient* is enough for the simplest phase separation and phase transition process. However, the electrochemical process in SSBs is a multiphysics problem. More free energy density function terms and differential equations for other physical fields are needed to investigate the Multiphysics coupling problem thoroughly.

Strong coupling between different physical fields (electrochemical-mechanical-thermal ...) can make it difficult to apply phase field modelling strategies (i) to predict the growth of dendrites possibly combined with cracks in solid state systems, and (ii) to be predictive under well-defined service conditions. A great deal of effort should be needed to develop the model, but also to disentangle the outputs from the models developed at other scales in order to feed the phase field model with appropriate inputs. (Tantratian, 2021) and (Sun, 2022) seem to be a good starting point for the implementation of the approach for the SSBs studied in Helena project.

Loss of active material due to electrolyte oxidation

On the positive electrode, high potential leads to instability of the electrolyte with the positive active material. A parasitic reaction occurs leading to electrolyte oxidation and active material losses. In this case, the reaction will impact the active material mass fraction which is reduced due to this reaction as described by (Reniers et al., 2019)

The equations of the sub-model for the active material loss at the positive electrode are detailed in Table 10. It is considered that the oxidation of the electrolyte happens over a voltage U_{paml} , and is driven by an anodic irreversible reaction kinetic, modelled by Tafel's expression such as in Eq. (44) which governs the capacity fade with an ordinary differential equation. The overpotential driving this reaction is given by Eq. (45). This reaction leads to a reduction of the positive active material volume fraction, which Eq. (47) accounts for.

Physical	Governing equations	Boundary conditions	Eq.
phenomenon			
Rate of capacity fade due to dissolution	$\frac{1}{A_p} \frac{\mathrm{d}Q_{loss}^{paml}}{\mathrm{d}t} = i_{paml} = i_{0,paml} \exp\left(\frac{F}{RT}\gamma\eta_{paml}\right)$	$Q_{loss}^{paml}(t=0)=0$	(44)
Current balance for the positive electrode	$j_{tot}^p = j_f^p + a_s^p i_{paml}$	_	(45)
Dissolution overpotential	$\eta_{paml} = \phi_s^p - \phi_e - U_{paml}$	-	(46)
Active material volume fraction	$\epsilon_s^p = \epsilon_s^{p,0} - \frac{Q_{paml}}{\delta_p A_p F c_s^{p,max}}$	_	(47)

Table 10 - Equations of the active material loss at the positive electrode sub-model.





0	T	Description	11
Symbol	Туре	Description	Units
paml	Sub/super-script	Positive active matter loss	
$Q_{loss}^{paml}(t)$	Variable	Capacity loss due to positive active matter loss	Ah
i _{paml} (t)	Variable	Current density of positive active matter loss	$A m^{-2}$
$\eta_{paml}(t)$	Variable	Overpotential due to positive active matter loss	V
$\epsilon_s^p(t)$	Variable	Volume fraction of active material in positive	—
_		electrode	
i _{o,paml}	Parameter	Positive active matter loss exchange current density	A m ⁻²
γ	Parameter	Charge transfer coefficient of the positive active matter loss side reaction	-
U _{paml}	Parameter	Electrical potential at which the electrolyte oxidation is triggered	V
$\epsilon_s^{p,0}$	Parameter	Volume fraction of active material in positive electrode at beginning of life	_

Table 11 - Symbols of the active material loss at the positive electrode sub-model.

Stress-induced ageing

Mechanical stresses can have an important impact on the long-term performances of electrodes. For example, it can create cracks into the SEI leading to SEI re-formation, cracks into active matter particles or loss of electrical contact, leading to active matter isolation. Here, two stress-induced ageing mechanisms are considered: the SEI cracking and re-formation, and the loss of active material.

Cracks into the SEI layer can lead to the exposition of new surfaces to the electrolyte, and ultimately to SEI re-formation. To assess the impact of such cracks, the derivative of concentration induced stresses at the particle edge is evaluated in Eq. (48). SEI cracks increase the SEI formation rate compared to the previous SEI sub-model, leading to higher loss of lithium inventory, while not increasing the SEI layer thickness which reduces the kinetics of SEI layer formation, as expressed by Eq. (49).

As mechanical stress builds up in the composite electrode due to material swelling, loss of electrical contact between some active material particles and other components of the conductive matrix can happen. It has for consequence the loss of active material. As for the SEI cracking, the loss rate is proportional to the stress variation rate inside the electrode. In an initial implementation of the model, the maximum hydrostatic stress in particles has been used. The variation of the active material volume fraction is governed by an ordinary differential equation expressed by Eq. (50) and Eq. (51) updates the volume fraction after active material loss.

Table 12 - Equations of the stress-induced ageing sub-model

Physical phenomenon	Governing equations	Boundary conditions	Eq.
SEI cracks area evolution	$\frac{\mathrm{d}A_{cr}}{\mathrm{d}t} = \frac{\beta_{cr}}{\sigma_{yield}} \left \frac{\mathrm{d}\sigma_h(R_n)}{\mathrm{d}t} \right $	$A_{cr}(t=0)=0$	(48)
Current balance for the SEI layer growth	$i_{sei}^{tot} = i_{sei} \left(1 + \frac{A_{cr}}{S_n} \right)$	_	(49)
Active material loss rate in electrode k	$\frac{\mathrm{d}\delta\epsilon_s^k}{\mathrm{d}t} = \beta_{lam} \left \max_r \frac{\mathrm{d}\sigma_h(r)}{\mathrm{d}t} \right $	$\delta\epsilon_s^k(t=0)=0$	(50)
Active material volume fraction variation	$\epsilon_s^k(t) = \epsilon_s^{k,0} - \delta \epsilon_s^k(t)$	_	(51)





Symbol	Туре	Description	Units
cr	Sub/super-script	Cracks	
lam	Sub/super-script	Loss of active material	
$A_{cr}(t)$	Variable	Surface exposed by SEI cracks	m ²
$i_{sei}(t)$	Variable	Current density of SEI layer growth reaction	$A m^{-2}$
		without accounting for cracks (previous SEI sub-	
		model)	
$i_{sei}^{tot}(t)$	Variable	Current density of SEI layer growth reaction	$A m^{-2}$
		accounting for cracks	
$\epsilon_s^k(t)$	Variable	Volume fraction of active material in electrode k	—
σ_{yield}	Parameter	Yield stress (rupture) before SEI cracking	$kg m^{-1} s^{-2}$
β _{cr}	Parameter	Kinetic coefficient of SEI cracks formation	—
S _n	Parameter	Negative reactive surface	m ²
β_{lam}	Parameter	Kinetic coefficient of loss of active matter caused	_
		by mechanical stress	

Table 13 - Symbols of the stress-induced ageing sub-models

Main challenges for degradation mechanisms sub-models within the HELENA project

ASSB have a different design as lithium-ion batteries and are thus expected to show some differences in their significant degradation mechanisms and failure modes. Main difficulties in ASSB arise from the various solid-solid interfaces, between the solid electrolyte and both electrodes (and eventually their passivation layers). The chemical, electrochemical and mechanical properties of each component as well as the cell microscopic design will be key for the effective ageing.

The negative electrode is expected to be a lithium metal electrode, for ASSB to improve the energy density compared to lithium-ion intercalation electrode such as graphite. Main problem is expected to come from lithium plating, not in a homogenous way (desirable) across the electrode surface, but rather in an in-homogenous way (undesirable) as localized dendrites on some surface dendrites. These dendrites could grow in the pores of the solid electrolyte and reach the positive electrode leading to a short circuit. This is also linked with the mechanical properties of the solid electrolyte. Also, electrochemical compatibility and the formation of an interphase region might play a role in the degradation.

The positive electrode is expected to be a porous electrode composite such as for lithium-ion batteries, with active material, solid electrolyte, conductive additive, and binder. Due to their lower capacity density compared to the lithium metal negative electrode, it is expected that rather thick electrode will be used to match the high capacity of the lithium metal electrode, allowing ASSB to improve energy density. Main problems are expected to come from mechanical issues, notably the stability of the composite and of the solid contact with the electrolyte, but also particle cracking. Such as for the negative electrode, the formation of an interphase region might play a role in the degradation.

2.3.1.4 Thermal runaway model

Thermal runaway is an event occurring when heat exchange is not sufficient to evacuate the heat flow generated from the cell during abuse operating conditions, such as, overheat, overcharge, external short circuit. The main reactions taken into account in the existing IFPEN model are based on (Petit et al., 2018) as following:

- 1. Metastable SEI (Solid Electrolyte Interphase) reaction
- 2. Solvent reduction on the negative electrode (SEI formation)
- 3. Positive electrode decomposition
- 4. Electrolyte decomposition
- 5. Self-discharge / short-circuit (caused by the separator fusion)
- 6. Venting

The main assumptions used to describe the cell behavior during TR are:

The parameters inside the cell, such as composition, temperature, concentration, and reaction
rate are equal everywhere. The cell is considered to be a homogenous element with no
dimension.



- During TR reactions, the internal temperature of the cell is the same as its surface temperature, i.e. no gradient is considered (0D).
- Loss of the cell capacity during TR is assumed to be related to the positive electrode decomposition.
- The reaction of the positive electrode is considered as an autocatalytic reaction.
- Venting is considered adiabatic, i.e. without any mass variation of the cell due to venting but the amount of material ejected from the cell is linked to the Mach number.
- The composition of the gas released from TR reactions is not specified.

An empirical approach is chosen to describe thermal runaway phenomenon, where thermochemical reactions are represented by dimensionless figures based on (Kim et al., 2007) and (Abada et al., 2016, Abada et al., 2018) works.

The aim of the thermal runaway model is to evaluate the global heat released by the degradation reactions as follows:

$$\boldsymbol{\Phi}_{TR} = \boldsymbol{\Phi}_{sei} + \boldsymbol{\Phi}_{neg} + \boldsymbol{\Phi}_{pos} + \boldsymbol{\Phi}_{e} + \boldsymbol{\Phi}_{ec} + \boldsymbol{\Phi}_{vent}$$
(52)

Where:

- Φ_{sei} : is the heat released from the metastable SEI reaction [W]
- Φ_{neg} : is the heat released from the reaction between the negative and the electrolyte [W]
- Φ_{nos} : is the heat released from the reaction between the positive and the electrolyte [W]
- Φ_e : is the heat released from the electrolyte decomposition [W]
- Φ_{ec} : the heat released by the self-discharge [W]
- Φ_{vent} : the heat released by the venting [W]

Each heat source term is calculated based on the following relation:

 $\Phi_i = h_i \cdot w_i \cdot R_i$

The reactions 1 to 5 are exothermal, they are described by the Arrhenius's law. The related reactions rates are presented in the Table below.

Exothermic	Governing equations	Eq.
degradation		
reactions		
Metastable SEI	$\frac{dx_{SEI}}{dx_{SEI}} = -R_{em} = -A_{em} \exp\left[-\frac{E_{a,SEI}}{2}\right] r^{m_{SEI}}$	(53)
reaction	$dt = \frac{m_{SEI} - m_{SEI} - m_{SEI}}{k_B T}$	(00)
Solvent reduction on the negative electrode	$\frac{dz_{SEI}}{dt} = -\frac{dx_{neg}}{dt} = -R_{neg} = -A_{neg} \exp\left[-\frac{z_{SEI}}{z_{SEI,ref}}\right] \exp\left[-\frac{E_{a,ne}}{k_BT}\right] (x_{neg})^{m_{pos}}$	(54)
Positive electrode decomposition	$\frac{dx_{pos}}{dt} = -R_{pos} = -A_{pos} \exp\left[-\frac{E_{a,pe}}{k_B T}\right] (x_{pos})^{m_{pos}} (1 - x_{pos})^{m_{pos}}$	(55)
Electrolyte decomposition	$\frac{d\theta_e}{dt} = -R_e = -A_e \exp\left[-\frac{E_{a,e}}{k_B T}\right] \theta_e^{m_e}$	(56)
Self-discharge	$I_{TR} = \left[-3600 \cdot A_{ec} \cdot exp(\frac{-E_{a,ec}}{k_B \cdot T}) \cdot U_{cell} \cdot Q_{cell}\right] / (1V)$	(57)

Table 14 - Exothermic degradation reactions governing equations.





The reactions 1 to 4 may release gases which increase the pressure inside the cell. When the pressure is higher than a venting burst pressure, venting occurs.

During the thermal runaway exothermal reactions, gas is being released leading to pressure increase inside the cell. If a burst pressure is passed, venting will occur.

Gas formation:

During each degradation reaction, gas can be emitted. The amount of gas formed is given by parameters, $V_{g_{sei}}$, V_{g_n} , V_{g_p} and V_{g_e} which are the amount of gas released by decomposition reactions per kg of reactant. The total amount of gas produced by the reaction *i*, n_i (mol) is then given by:

$$\frac{dn_i}{dt} = R_i \cdot W_i \cdot V_{g_i} \tag{58}$$

Adiabatic venting:

M = 0

Due to the increase of gas in the cell as well as the temperature, the pressure builds up and increases as follows:

$$P = P_0 + \frac{R \cdot T}{1e5 \cdot V_h} \cdot \left(n_{sei} + n_{neg} + n_{pos} + n_e - y \right)$$
⁽⁵⁹⁾

The vent opens when the difference between the internal and ambient pressure reaches the burst pressure of the venting device: $(P - P_{amb}) \ge P_{burst}$

Once the vent is open, an adiabatic venting occurs. It is mathematically described using a lumped approach following the work from (Coman et al., 2016). It is assumed that there is no mass variation of the cell due to venting. The amount of material ejected from the cell is linked to the Mach number M. The Mach number is a dimensionless number, representing the ratio of the local flow velocity of a fluid to the local speed of sound. Since the speed of sound in a gas varies with its nature and its temperature, the Mach number depends on the local conditions, its value varies between 0 and 1. This dimensionless number is defined as:

if venting has not occurred yet

if venting has occurred

$$M = \max\left(\sqrt{\frac{2}{\gamma-1} \cdot \left(\frac{P}{P_{amb}}\right)^{\frac{\gamma-1}{\gamma}}}, 1\right)$$

Based on the Mach number, the pressure P_{vent} , the temperature $T_{vent}(K)$ and the velocity V_{vent} (m/s) of the gas escaping the cell are assessed as follows:

$$P_{vent} = \frac{P}{\left(1 + \frac{\gamma - 1}{2} \cdot M^2\right)^{\frac{\gamma}{\gamma - 1}}}$$
(60)

$$T_{vent} = \frac{T}{1 + \frac{\gamma - 1}{2} \cdot M^2} \tag{61}$$

$$V_{vent} = \sqrt{\frac{\gamma \cdot R \cdot T}{M_{gas}} \cdot M}$$
(62)

These variables allow to evaluate the amount of gas escaping the cell, y as follows:





$\frac{dy}{dy}$	$P_{vent} \cdot V_{vent} \cdot A_{vent}$	dn _{gas}	(63)
dt [–]	$\boldsymbol{R}\cdot \boldsymbol{T}$	dt	
$\frac{dn_{gas}}{dt}$ =0			if vent is closed

$$\frac{dn_{gas}}{dt} = \frac{dn_{sel}}{dt} + \frac{dn_{neg}}{dt} + \frac{dn_{pos}}{dt} + \frac{dn_e}{dt}$$
 if vent is opened

The energy loss in the cell due to the pressure drop during venting is expressed as follows:

$$\boldsymbol{\Phi}_{vent} = \boldsymbol{V}_h \cdot \frac{d\boldsymbol{P}}{dt} = \boldsymbol{R} \cdot \boldsymbol{T} \cdot \frac{d\boldsymbol{y}}{dt} \tag{64}$$

Table 15 - Symbols of the thermal runaway model.

Symbol	Туре	Description	Units
R_i	Variable	reaction rate of reaction <i>i</i>	1/s
W _i	Parameter	mass of reactant relative to reaction <i>i</i>	kg
V_{g_i}	Parameter	amount of gas produced by reaction <i>i</i> relative to its mass of reactant	mol/kg
h _i	Parameter	specific enthalpy of the reaction <i>i</i>	J/kg
x _{SEI}	Variable	fraction of lithium inside metastable SEI	-
Z _{SEI}	Variable	dimensionless number representing the SEI layer thickness	-
Z _{SEI,ref}	Parameter	dimensionless number representing the SEI layer thickness reference	-
x _{neg}	Variable	insertion rate of the negative electrode	-
α	Variable	decomposition advancement reaction of the positive degradation	-
θ_e	Variable	disappearance reaction rate of the electrolyte	-
A _{SEI}	Parameter	frequency factor of the metastable SEI stabilization reaction	1/s
A _{neg}	Parameter	frequency factor of the solvent decomposition reaction on the negative electrode	1/s
A _{pos}	Parameter	frequency factor of the decomposition reaction on the positive electrode	1/s
A _e	Parameter	frequency factor of the electrolyte decomposition reaction	1/s
A _{ec}	Parameter	frequency factor of the self-discharge reaction	1/s
E _{a,SEI}	Parameter	Energy activation of the metastable SEI stabilization reaction	J
E _{a,neg}	Parameter	Energy activation of the solvent decomposition reaction on the negative electrode	J
E _{a,pos}	Parameter	Energy activation of the positive decomposition reaction	J
E _{a,e}	Parameter	Energy activation of the electrolyte decomposition reaction	J
E _{a,ec}	Parameter	Energy activation of the self-discharge reaction	J
n _{sei}	Variable	amount of gas formed by the SEI reaction	mol
n _{neg}	Variable	amount of gas formed by the solvent reduction on the negative electrode	mol
n _{pos}	Variable	amount of gas formed by the electrolyte reaction at the positive electrode	mol
n _{gas}	Variable	amount of gas released while the vent is open	mol
n _e	Variable	amount of gas formed by the electrolyte decomposition	mol





y	Variable	amount of gas ejected due to the venting	mol
Р	Variable	pressure inside the cell	barA
P ₀	Parameter	internal pressure before gas release	barA
P _{amb}	Parameter	Ambient pressure	barA
P _{burst}	Parameter	Burst pressure of the venting device	bar
V _h	Parameter	the headspace volume of the cell	m^3
γ	Parameter	heat capacity ratio of the formed gas	-
M _{gas}	Parameter	molar mass of the formed gas	kg/mol
A _{vent}	Parameter	area of the vent	m^2

Main challenges for the thermal runaway sub-model within the HELENA project

Contrary to liquid-electrolyte LiB, ASSBs safety is less studied. However, it is generally accepted that ASSBs are safer than liquid-electrolyte LiB for different reasons: 1) ASSBs do not contain a combustible organic electrolyte. 2) No interface between the negative and solid electrolyte is expected, i.e., they do not have an SEI. It is than assumed that, without liquid electrolyte and without an SEI, it can be considered that ASSBs are less likely to have a thermal runaway.

But thermal runaway mechanisms can be different between liquid-electrolyte LiB and ASSB. For example, the accelerated TR linked to short-circuit and separator damage in liquid-electrolyte LiB technology, could be related for ASSB technology, to the positive destabilization or Li metal damage.

As ASSB technology is considered not mature today, it is difficult to found pertinent description of the thermal runaway mechanism. Thanks to HELENA project, we will have access to the different component's stability parameters, we will perform abuse tests on the full cell prototype to understand the ASSB based halide electrolyte cell safety behaviour and update the thermal runaway sub-model with a novel mechanism.

2.3.2 Objectives of the macroscale modelling approach

The main objectives of WP7 are to provide material and cell manufacturers model-based guidance at three main scales and tools to optimize cell and electrode design and anticipate full cell behaviour and lifetime.

At the macroscale, some parameters will already be fixed on the material side (at the microscale), and the optimization will concern the macroscale cell design. For example, electrodes, electrolyte, and coating materials nature will be fixed, as well as their mass and charge transport properties. This information will come from project partners, that is from lower scale modelling as well as experimental data from material and cell manufacturers of HELENA project. The macroscale model will then be employed to optimize cell design by tuning parameters such as electrodes thickness, electrode particles radius, electrodes porosity, or coatings thickness. The optimization goal can either be seen as maximizing the cell energy density or finding a compromise between maximizing the cell energy density and maximizing the cell lifetime (and power density as well).

To achieve this goal, the objective of IFPEN for the macroscale modelling within HELENA is to build a meaningful multi-physical model framework capable of providing cell manufacturers with valuable design optimization recommendations. This will require an adapted electro-chemo-mechanical model framework for ASSB specificities, and more importantly its coupling with dominant degradation mechanisms.

2.3.3 Identification of the input/output parameters of the macroscale model

From the description of the modelling approach that is considered and its objectives, the following inputs parameters (needed from partners and literature) and outputs (delivered to partners) of the macroscale are listed here.

2.3.3.1 Inputs parameters of the macroscale model

Input parameters needed for the macroscale model mainly concern the nature of materials (electrodes, coatings, electrolyte) that will be chosen and their physical properties:

- Electrolyte material:
 - Lithium diffusivity in electrolyte (function of temperature)





- Lithium conductivity in electrolyte (function of temperature and of lithium concentration)
- Mean lithium concentration
- o Thermal stability
- Electrodes material (positive and/or negative):
 - Active matter:
 - Particle size distribution (positive)
 - Volume fraction (positive)
 - Surface contact area (positive) and electrode plate area (Li metal negative)
 - Lithium diffusivity in particles (function of temperature)
 - Equilibrium potentials (function of lithium concentration) (positive)
 - Maximum lithium concentration
 - Electrochemical reactions kinetic constants (function of temperature)
 - Mechanical parameters: volumetric expansion, elastic modulus, Poisson Ratio (also for grain boundary if exist) in function of temperature
 - Thermal stability: CTE (coefficient of thermal expansion), kinetic and heat released
 - Coating:
 - Lithium diffusivity in coating
 - Binder and conductive additive:
 - Electronic conductivity

2.3.3.2 Outputs parameters of the macroscale model

The macroscale model will give outputs for the optimization of the cell design as well as general simulation of cell behaviour, usable in upper scale model (system level).

For the optimization of cell design, allowing to propose guidelines to manufacturer:

- Positive electrode thickness
- Negative electrode thickness
- Positive electrode particle radius
- Positive electrode porosity
- Positive electrode active matter volume fraction
- Positive electrode electrolyte volume fraction
- Positive electrode coating thickness
- Negative electrode coating thickness
- Solid electrolyte thickness between the two electrodes

For general simulation, allowing to evaluate cell energy/power/safety/lifetime performances for automotive and aeronautic applications, as well as in cell-to-system simulation:

- Cell terminal voltage/current
- Average cell temperature
- Cell width
- Thermal runaway onset and heat released
- Capacity loss
- Resistance increase



2.4 System modelling approach (AIT)

2.4.1 Description of the system modelling approach

2.4.1.1 AIT system simulation – modelling language and tools

AIT system simulation is builds up AIT's inhouse Modelica libraries and uses Dymola as simulation tool. Inhouse libraries are:

- EES (Electrical energy storages), implementing electrical equivalent circuit (EEC) and lumped thermal (LT) models for Generation 2, 3 and 4 Li-ion battery cells
- SPT (Smart power trains)
- SC (Smart cooling)
- AC (air conditioning)

The EEC battery model is parameterised with measurement data. After break-in test, the cell characterization with pulses is performed at different C rates and at three temperatures. The EEC parameters are estimated with Particle Swarm Optimisation to find the global optimum and further fine-tuned using Gauss-Newton algorithms, see (Dvorak, Bäuml, Holzinger, & Popp, 2018).

2.4.1.2 AIT system simulation - automotive

The EV simulation for BEV was developed and validated in previous projects, e.g. H2020 Quiet (H2020 Quiet - QUalifying and Implementing a user-centric designed and EfficienT electric vehicle, 2017-2021). It implements system simulation of light duty BEVs, see Figure 8. It combines models for battery, electric machine (motor/generator), power train, thermal management (drive train and passenger compartment), vehicle dynamics, drive cycle, operating strategy and ambient conditions. The model can be used to identify (a) the energy flows regarding powertrain and auxiliaries and (b) the energy needed for heating and cooling of the passenger compartment.



Figure 8 - AIT Modelica system simulation model for BEV (Cvok, et al., 2020).



The BEV model is specified by the main vehicle parameters:

- Vehicle mass
- Transmission ratio
- Differential ratio
- Tire radius
- Chassis frontal area
- Driving resistance coefficients (cw, cf) (road load parameters)
- Machine and inverter operating maps (efficiency)
- Battery parameters (resistances and capacity)

Model parameters representative for B to D class vehicles are provided in Figure 9. WLTP Class 1-3 driving cycles are implemented, see Figure 10.

		vehicle				
parameter	unit	Fit EV (B)	B-SUV	С	D	D-SUV
mass	kg	1644	1700	1520	1757	2585
\mathbf{f}_0	Ν	84.78	110.58	115.16	160.18	159
\mathbf{f}_1	N/kph	1.12	-0.55	0.95	-0.36	1.07
\mathbf{f}_2	N/kph ²	0.03	0.04	0.03	0.03	0.03
Cw	-	0.33	0.33	0.29	0.23	0.28
A _{Front}	m ²	2.16	2.37	2.3	2.22	2.65
V _{Cabin}	m ³	2.53	2.66	2.61	2.75	2.92

Figure 9 - Model parameters for B to D class vehicles (Paffumi, Wang, Nunnendorf, Jahn, & Dominik, 2021).



Figure 10: WLTP Class 3 driving cycle (Paffumi, Wang, Nunnendorf, Jahn, & Dominik, 2021)

The thermal cabin model considers various thermal loads: short-wave solar and long-wave body radiation, convection and conduction. Obstructed view factors between surfaces are taken into account for correct consideration of radiation. The outer vehicle surfaces are separated in order to evaluate individual contributions of conduction, convection and radiation of surfaces, see Figure 11. Material characteristics are included.





Figure 11: Exterior surfaces considered in the thermal cabin model (Paffumi, Wang, Nunnendorf, Jahn, & Dominik, 2021).



Figure 12: Cabin model schematic overview. (Dvorak, Basciotti, & Gellai, 2020)





Figure 13: Heating, ventilation, and air conditioning (HVAC) system model schematic overview: cooling mode (left) and heat pump mode (right). (Dvorak, Basciotti, & Gellai, 2020)



Figure 14: HVAC system models available for BEV system simulation: simple (left) and complex (right). (Paffumi, Wang, Nunnendorf, Jahn, & Dominik, 2021).

The simplified or complex HVAC system models are available, see Figure 14.

The validation of the EV model was performed with measurement data obtained from a Honda B segment vehicle in the JRC Vehicle Emission Laboratories (VELA) in Ispra (Italy). Further details on the EV model and its validation are provided in (Cvok, et al., 2020) and (Paffumi, Wang, Nunnendorf, Jahn, & Dominik, 2021).



2.4.1.3 AIT system simulation – aeronautics

The system modelling for aeronautic battery systems is developed in various projects, e.g. H2020 ORCHESTRA (H2020 ORCHESTRA - Optimised Electric Network Architectures and Systems for More-Electric Aircraft, kein Datum), see Figure 15.

The blocks of the model implemented so far are:

- Coupled EEC and LT model of the battery: currently implemented as single cell instance (as Ns×Np pack) and optionally to be subdivided into multiple instances, e.g. representing subpacks or modules. Alternatively, simulation of a module with individual cell instances is feasible. The electrical and thermal models are independent and can be combined as needed.
- Minimalistic thermal management
- Electrical loads and charger with several charging strategies
- Mission cycle (e.g. load profiles for design and typical missions of the aircraft)
- Environmental conditions, based on ISA (international standard atmosphere)



Figure 15: Minimal system simulation model for aeronautic battery.

2.4.2 Objectives of the system modelling approach

The main objective of the system modelling approach is to evaluate the cell mean behaviour in realistic use cases from automotive and aeronautic applications. AIT will adapt and/or extend their battery system simulation to the requirements for the automotive and aeronautic use cases specified in T2.1, T2.2 and T2.3 and deliver concept designs for aeronautic batteries. The system simulation will be upgraded with models developed in T7.3, i.e. integrating the electrochemical model developed by IFPEN either directly via FMU (functional mock-up unit) and/or as fast electrical and thermal equivalent circuit cell model, derived from testing the electrochemical model in a virtual environment. Alternatively, the EEC/LT cell model could be parameterized from measurement data obtained for pouch cells in WP6. The full scale equivalent circuit modelling will be validated based on WP6 results. Furthermore, AIT will conduct a sensitivity analysis to propagate the uncertainties at lower scale on the cell performance in realistic application.

2.4.3 Identification of the input/output parameters of the system model

2.4.3.1 Inputs parameters of the system model

- Use case definition, cell and system requirements (from T2.1, T2.2 and T2.3)
- Cell electrical performance as function of C-rate, SOC and operating temperature
- Heat release as function of the electrical performance
- Target operating conditions, e.g. temperature range
- Physical dimensions of the cell



- Thermal parameters of the cell: thermal conductivity (in plane and out-of-plane), specific heat capacity, either averaged for the cell or its components
- Thermal runaway onset and heat released
- Capacity loss (cycling and calendar ageing)
- Parameter variance (ranges) concerning uncertainties and cell dispersion
- Pouch cells testing results from WP6

2.4.3.2 Outputs parameters of the system model

- Battery system sizing to meet the systems' electrical performance for the various use cases
- System thermal management demand
- System behavior in failure cases
- Cell/system performance considering uncertainties at lower scale / cell dispersion



3 Discussion and Conclusions

3.1 **Definition of the model's interfaces framework**

The approach of modelling within HELENA project is based on a Multiphysics and Multiscale models. This approach allows to study the ASSB from the atomistic level to the batterie pack system level. Each model is inherently different from others by the: phenomena considered, degree of detail, dimension of the system, parameter time constant and the calculation time.

Today none of the existing modelling software can address coupling all these different models. Thus, within HEZLENA project a modelling network will be developed and a model's interfaces framework will be defined to assess the ASSB performance and optimization from the atomistic level to the full system application simulation (see Figure 16).

Thanks to the HELENA model's interfaces framework a deeper understanding of the relationship between intrinsic and network properties will be addressed. Also, relevant parameters related to the transport phenomena in the bulk will be optimized. In addition, aging phenomena due to mechanical degradation by lithiation /delithiation induced volume changes will be investigated. Finally, a fit from the cell to the system through equivalent circuit simplification for integration in full system simulation will be validated.



Figure 16: model's network and interfaces framework

3.1.1 Interface between atomistic and microstructure models

In order to draw conclusions about the electronic and ionic conductivity from the particle structure generated by DEM, the intrinsic electrical properties of the individual particles are required. Also, the response of the structure to mechanical load depends, among other things, on the mechanical properties of the individual particles. Some of these intrinsic parameters can be found in the literature. However, the novel halide solid electrolytes in particular are still poorly described in literature. Therefore, parameters will be determined experimentally in the course of WP 3 and 4. However, for the ionic conductivity of the single particle, for example, it may be necessary to do this in an indirect way by powder measurements. With the measured conductivity of the pellet together with the information about particle size distribution and porosity, the DEM structure is then calibrated to determine the bulk material conductivity. However, a direct determination of the intrinsic properties would be more straightforward. Here, the atomistic model can provide important input. As shown in Table 1, the atomistic model allows predictions on the Young's modulus, the volume expansion due to intercalation and the Li self-diffusion coefficient of the investigated materials. The latter can be converted into the ionic conductivity using the Nernst-Planck-Equation (Park et al., 2010). Thus, the atomistic model makes an important contribution to the microstructural modelling avoiding outstanding experimental effort and providing a deeper understanding of the relationship between intrinsic and network properties.

Conversely, the results of the atomistic model can also be critically reviewed. In the atomistic model, a perfect material is assumed starting from the unit cell. However, errors and imperfections in the material

structure and thus deviations in the properties cannot be avoided. The project will show what influence these deviations may have.

3.1.2 Interface between microstructure and full cell models

In order to calibrate the SPMe model, some parameters are required as input (see section 2.3.3). These parameters will be provided either by experimental tests (from WP3 and WP4) or simulation from both atomistic and microstructure modelling framework. With the microstructural model important knowledge into the mechanical, electro-mechanical and transport behaviour of ASSB can be provided to the macroscale (SPMe) model. The ionic and electronic conductivity, the porosity as well as the specific surface area will be calculated from the microsctural model and taken as inputs for the SMPe model. In addition, the impact of mechanical behavior on the conductivity and the volume change of the particle will be addressed by the microstructural model since the ratio of broken particles due to the stress upon cycling and the impact on number of contacts/ bonds can be represented in the DEM. The microstructural model provides relevant parameters to estimate the macroscopic cell performance,

also in the sense of aging phenomena due to mechanical degradation by lithiation /delithiation induced volume changes.

3.2 Interaction with the other WPs/Tasks

3.2.1 Atomistic modelling approach interaction

As mentioned in section 2.1.3 the only information required for the atomistic calculations is crystallographic data of bulk structures of solid electrolyte, active material, and coating. This information will be provided by the partners involved in WP3 Subtask 3.1 and 3.2 (Fig. 4). The calculated electrochemical and mechanical characteristics of electrolyte as well as stability and Li⁺ transport through AM/SE and AM/coating/SE interface will further be used in WP3 Subtask 3.1 and 3.2 for optimization electrolyte and interstitial properties.

Figure 17 - Scheme of atomistic modelling approach interaction with other WPs/Tasks.

3.2.2 Microstructure modelling approach interaction

As shown in Table 1, the microstructural network is mainly based on input parameters from WP3 and WP4. The initialization of the electrode and separator structure is generated based on the given particle size distributions, the recipe and the porosity. Beside the initialization, the validation of the model-based results regarding structure conductivity has an outstanding role. Therefore, the impact of the manufacturing process and the recipe will be compared and validated based on the results from WP4. Also, the intrinsic properties of the involved materials are needed as input parameters for the microstructural modelling. As already described in section 2.2.3.1, an experimental determination is required here, especially if data from the literature or the atomistic model are not available.

Conversely, the microstructural model provides important information to WP and 4 for the optimization of the formulation and the manufacturing process, in order to increase the performance of the cell with less experimental effort.

As mentioned in section 3.1.2, the results can also be incorporated into the macroscopic modelling of the cell considered in WP7.4. The relationship between ionic conductivities and porosity/ tortuosity is often described using approximations such as the Bruggeman equation. However, for conventional LIBs these assumptions often fit quite well, but for ASSB they might not (Sangrós Giménez et al., 2020b). The microstructural model can provide deeper insights into the interplay between charge transport along the cell cross-section and the underlying electrode structure.

Overall, it should be noted that models are always based on a mathematical description of the problem and associated simplifications. This is what makes modelling such a fast and comparatively inexpensive tool in battery development. Due to the different degree of detail and the dimension considered, the findings of different modelling approaches can interact and complement each other. However, the assumptions made must always be reflected with the experimental findings. Hence, a continuous exchange between the WP3/4/7 and within the WP7 is essential.

3.2.3 Macroscale modelling approach interaction

As mentioned above, in order to calibrate/validate the macroscale model some parameters are required as input (see section 2.3.3). These parameters will be provided either by experimental tests or downscale model through simulation from both atomistic and microstructure modelling framework:

From WP3 and WP5: material properties will be provided as particle size distribution, mean/maximum lithium concentration and volume fraction.

From WP7, downscale model simulation: from both atomistic and microstructural models, simulation allows the evolution of the ion/electronic transport parameters according to intercalation/deintercalation state and mechanical induced damage. In addition, from the atomistic model mechanical properties as elastic constants, bulk modulus, Young's modulus and shear modulus will be provided

From WP6, experimental tests results, as 1) electrochemical analysis that allow to identify the electrochemical reaction kinetic parameters, equilibrium potentials. 2) accelerated aging tests that allow to identify different aging mechanism and estimate the related performance change. 3) abuse tests at both material and full cell level used to identify the different thermal runaway mechanisms and the identification of the related kinetic and thermal parameters.

From WP4, post-mortem analysis: it provides information on the structural/chemical characterization at the cell pristine state and after different aging level (different SOH).

From WP2, based on the EV/aereo application requirements, a specific profile will be used as input for the model simulation.

The macroscale model in turn will assess the electrochemical/thermal/aging/safety behavior of the full cell and allow the design optimization through parametric study thanks to the reduced time calculation that it offers. In addition, the macroscale model will help to fit cell to system level simulation.

Figure 18 - Macroscale modelling approach interaction with the other WP.

3.2.4 System modelling approach interaction

Within WP7, the system modelling (AIT) will mainly interact with the macroscale modelling (IFPEN). The requirements defined in T2.1, T2.2 and T2.3 will drive the conceptual system design for the automotive and aeronautic use cases. Information about the pouch cell design from WP5 and pouch cell testing data from WP6 are needed.

4 Risk register

Table 16 - Risk Register

Risk No.	What is the risk	Probability of risk occurrence ¹	Effect of risk ²	Solutions to overcome the risk
7.2.3	Impossibility to create feasible for DFT calculation periodic interface model. Section 2.1.1.2	1	2	Simulation of non- periodic interface model
WP 7.2 and 7.4	Computational costs for a detailed optimization (PGV, manufacturing process)	2	1	Modelling of the experimental values in WP 3 and 4 will be ensured plus advice for an optimization
WP 7.4	Modelling CAM and SE in a common DEM model	2	1	Two separate DEM models for CAM and SE: Void space represents the other missing component.
WP 7.2 and 7.4	Intrinsic material properties as input parameter for microstructural model cannot be predicted in atomistic model or be found in the literature	2	1	Input parameter can be generated by powder measurements and subsequent calibration of the microstructural model.
WP7.3	IFPEN EC/thermal model too complex or computationally too demanding to be applied for large system simulations.	2	2	To mitigate this risk, (a) a fast EEC-LT model will be derived from testing the electrochemical model in a virtual environment, and (b) the level of system granularity can be adapted.
WP7.2.3	phase-field method : difficulty to evaluate the relevance of the prediction of the model (Li plating/crack)	2	1	Confrontation with some observation on the electrolyte at the same model scale
WP7.2.3	phase-field method: difficulty to select appropriate inputs to feed the phase-field model from	2	1	update the model to facilitate the scale change based on the

¹ Probability risk will occur: 1 = high, 2 = medium, 3 = low

² Effect when risk occurs: 1 = high, 2 = medium, 3 = low

	the ouput of the differents models developed at the others scales			knowledge gained at the time of the study
WP7.3.1	A lack of input parameters from WP3, WP4, WP5 and WP6 Not relevant estimation of some parameters expected from the downscale models	2	1	Use parameters available in the litterature
WP7.4	Unavailability of cell 1-10Ah or no sufficient time project to perform aging tests and validate the full cell model	1	1	If possible, use results from litterature or from other Europeen Project which are studing ASSB (example MODALIS ²)

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Project partners

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1	CICE	CENTRO DE INVESTIGACION COOPERATIVA DE ENERGIAS ALTERNATIVAS FUNDACION, CIC ENERGIGUNE FUNDAZIOA	Spain
2	AIT	AIT AUSTRIAN INSTITUTE OF TECHNOLOGY GMBH	Austria
3	SGR	SAINT GOBAIN RECHERCHE SA	France
4	UMI	UMICORE	Belgium
5	LV	LIONVOLT B.V.	Netherlands
6	TNO	NEDERLANDSE ORGANISATIE VOOR TOEGEPAST NATUURWETENSCHAPPELIJK ONDERZOEK TNO	Netherlands
7	FHG	FRAUNHOFER GESELLSCHAFT ZUR FOERDERUNG DER ANGEWANDTEN FORSCHUNG E.V.	Germany
8	CCI	CUSTOMCELLS HOLDING GMBH	Germany
9	RWTH	RHEINISCH-WESTFAELISCHE TECHNISCHE HOCHSCHULE AACHEN	Germany
10	MIMI	MIMI TECH GMBH	Germany
11	IFPEN	IFP ENERGIES NOUVELLES	France
12	PVS	PIPISTREL VERTICAL SOLUTIONS DOO PODJETJE ZA NAPREDNE LETALSKE RESITVE	Slovenia
13	LDO	LEONARDO - SOCIETA PER AZIONI	Italy
14	FEV	FEV EUROPE GMBH	Germany
15	EDLP	FEV eDLP GmbH	Germany
16	ZAB	ZABALA INNOVATION CONSULTING, S.A.	Spain

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