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## ASTRABAT Deliverable D2.4

### Test specifications

#### WP2, T2.4

##### Technical references

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## Glossary

Term	Definition
ASSB	All solid-state battery
RRT	round robin star test

### Disclaimer

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## Abstract

The ASTRABAT project main goal is to develop a new generation of batteries for electric vehicle battery storage with a solid electrolyte.

This report describes the protocols for material characterization (polymers, ceramic, electrolyte), and electrochemical test validation (comprising safety tests) that will be used in ASTRABAT to characterize materials and their formulation for the development of All Solid State Battery (ASSB). The protocols reported allow obtaining the data required for modeling the optimal ASSB technology. Furthermore, protocol for post mortem analysis of the cell is reported. The characterization will be the support of a whole approach of the cells' safety, safety by design development, and recycling approach.

In this deliverable, the reported test specification protocols will be implemented to deeply characterize the material and the interfaces allowing a judicious choice of the upcoming steps in each WPs of the ASTRABAT project.



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# 1 Material characterization

For modeling aspect carried out in the ASTRABAT project, some physical and electrochemical parameters of the electrodes, active materials and electrolyte must be determined. For electrolyte, conductivity properties in full range of usage temperature and the lithium transportation properties are required for models. These properties will be measured in the same scale of lithium salt concentration that is used in cell testing. The active materials properties which do not depend on the electrolyte (equilibrium potential, diffusion coefficient) will be measured with liquid electrolyte. The insertion kinetics will be measured in both liquid and solid electrolytes. The characterization of electrode porosity and tortuosity, and the ionic conductivity determination are required to determine the properties of lithium transportation through the different layers. The determination of these parameters will allow obtaining accurate and reliable model for the systems studied during the project.

## 1.1 Microstructural characterization

The microstructural characterization of the cell component's architecture will be performed, to deliver physical and chemical information needed for modelling. For this purpose, ToF-SIMS, SIMS tomography at CEA and SEM characterizations at IRCER will be done.

### 1.1.1 ToF-SIMS and SIMS tomography

In situ characterization via Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) will provide valuable information about the interface behavior under operating conditions.

#### Description of the experimental approach

Time of Flight Secondary Ion Mass Spectroscopy (SIMS) allows the characterization of elemental and molecular composition of the surface of a material with a satisfactory lateral resolution (some  $\mu\text{m}$  down to 50 nm when the best conditions are combined). This technique combines sensitivity (down to some ppm in the best cases) to good lateral resolution, while being sensitive to the first nm of the analyzed material.

Nevertheless, though primarily being a surface sensitivity technique, ToF-SIMS is thoroughly used to probe the bulk of materials. This can be achieved by alternating sputtering of the surface by using a secondary ion gun (typically  $\text{Cs}^+$  or  $\text{Ar}^+$ ) with its analysis with the primary ion source (e.g.  $\text{Bi}^+$ ). This setup is described on Figure 1Figure 1.



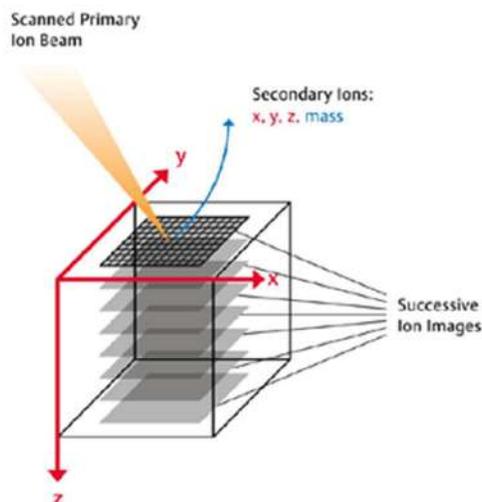


Figure 1 – 3d reconstruction based on profiling analysis by using ToF-SIMS (courtesy of Ion ToF<sup>1</sup>)

This approach allows providing 3D reconstructions of the analysis, as shown on Figure 2 for a biological sample [2].

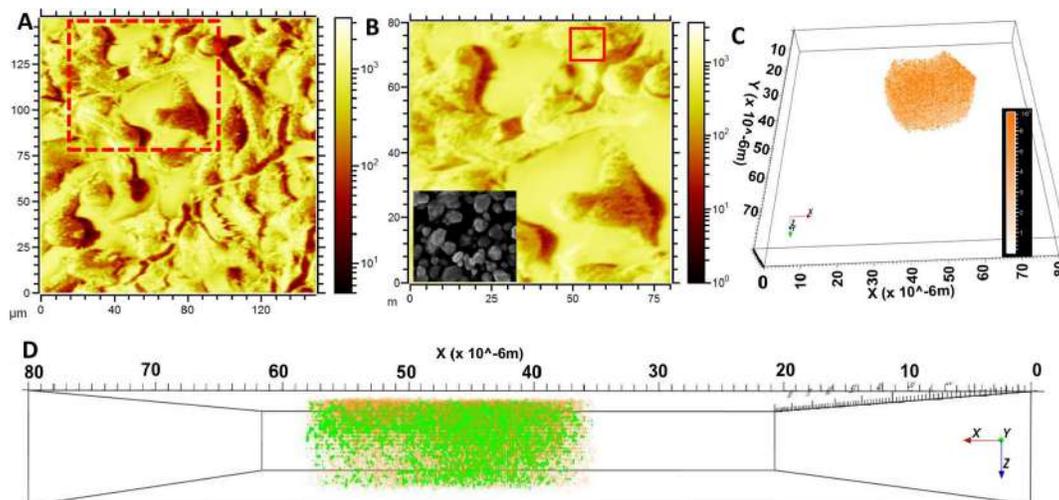


Figure 2 - Reconstructed ion image revealing quasi spherical Au-NPs with increasing Au ions to 1 mM Au ions [2]

However, such approach can sometimes lead to artifacts related to the selective pulverization of elements generated by the sputtering process. It is well-known that elements have different sputtering yields related to the element itself, the incident ion beam energy, the matrix effect etc.

Thus, another approach has been developed in the last years to overcome these issues. It is based on the implementation of a focused ion beam (FIB) column on the analysis chamber of the ToF-SIMS instrument. Such implementation allows generating cross section in the material to be achieved *in situ*, avoiding chemical evolution or contamination of the sample during transfer between dedicated FIB instrument and ToF-SIMS spectrometer.



The respective geometry of the FIB column and the primary ion beam source (the liquid metal ion source or LMIG) must be installed in a way that the FIB cut can be alternated with the analysis of the cross section. This is a similar setup as developed in FIB-SEM approach. Such setup is described on Figure 3.

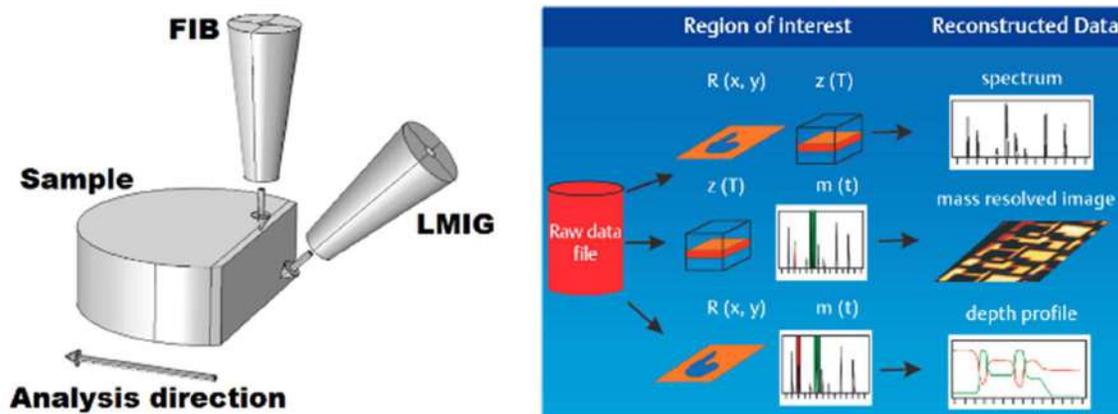


Figure 3 – Typical SIMS tomography setup<sup>3</sup>

The 4d-data obtained from a SIMS tomography allow extracting several kind of information (Figure 3, to the right). Each voxel contains spectroscopy information. It is thus possible to extract spectroscopy information, mass resolved images or depth profiles from the dataset.

### Example and requirements for the samples being analyzed

Preliminary tests have been achieved at CEA on a LCO//LLZO system in order to map Co diffusion in LLZO after a thermal treatment necessary to stick both materials together (Figure 4). 3D mappings of Co, La and Li could be achieved in the analyzed region.

In order to achieve these analyses, it may be necessary to transfer samples by using airtight vessel. The sizes of the samples must be adapted to the instrumentation: in particular to the sample holders, airtight vessel etc. Typically, samples should be extracted from the electrodes and should be of a reasonable size of less than 10mm in diameter. The thickness should be of less than 1mm. The analysis will be achieved on the surface of the sample. Thus, in order to analyze the cross section of an electrode, it will be necessary to extract a sample, which will be representative of the region to be analyzed. In case the sample would have to be protected from ambient air, it will be necessary to develop adapted sample holder, which will allow to characterize its cross section without any extraction process.

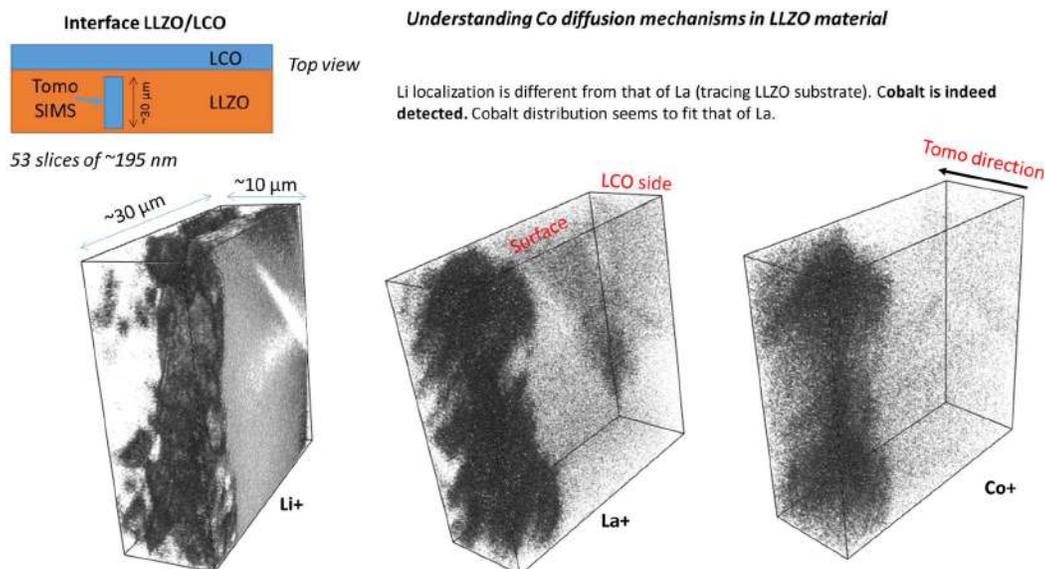


Figure 4 – Preliminary results obtained by using SIMS tomography on LCO/LLZO material

Both approaches (sputtering and FIB-cut) will be considered in order to compare their respective strength and issues. Also, as they remain destructive techniques it cannot be carried out on the same region. However, the combined information provided may be complementary. The chemical information provided will bring complementary information to FIB-SEM characterization achieved in the project.

### 1.1.2 Environmental SEM

The IRCER laboratory of UNILIM involved in ASTRABAT will use environmental SEM (ESEM) for standard analyses of the microstructure of the various components of the cells. Both morphological and chemical analyses (e.g. EDX mapping) will be performed in order to establish relationships with the upstream shaping and consolidation processes used as planned in ASTRABAT. Cell components will be first analyzed separately and then in association. When associated, a specific attention will be paid to the interfaces between the components. It must be noticed that the advantage of using ESEM is the possibility to adjust the atmosphere, especially the water content, as well as to set up an internal heating stage, to assess in real-time the combined influence of humidity traces and temperature on the overall stability of the microstructures of the cell components as well as the interfaces and interphases between them. The data will be treated if needed through digital image correlation to further improve the analytical resolution and to quantify the potential evolution of the microstructure upon the combined influence of the atmosphere and temperature.



## 1.2 Chemical and Physical Characterization

In order to assess their functionality and to derive the required physical parameters needed for the simulations and multi-scale modelling fully characterization of the components will be performed also at chemical and physical level.

### 1.2.1 Polymer Characterization

Polymers will be analyzed and characterized by basic physicochemical methods: NMR and IR spectroscopy will be performed, and ionic conductivity investigated through Electrochemical Impedance Spectroscopy (EIS). Also, thermal (TGA, DSC) thermomechanic (Dynamic mechanical analysis (DMA)) and rheological properties (viscosity) will be assessed.

#### H NMR and IR Spectroscopy

##### ORMOCER®

At FhG ISC the final ORMOCER® resin (not-cured polymer material) is characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR. NMR spectra were obtained with a Bruker Avance spectrometer (frequencies: 400 MHz ( $^1\text{H}$  NMR), 100 MHz ( $^{13}\text{C}$  NMR), 79 MHz ( $^{29}\text{Si}$  NMR)). Deuterated solvent used was  $\text{CDCl}_3$ .

Starting from alkoxyated silane precursors the polymer is formed via sol-gel synthesis (hydrolysis / condensation). Hydrolysis reaction was monitored by  $^1\text{H}$  NMR spectroscopy. Condensation and content of water can be monitored either by the combination of  $^1\text{H}$  and  $^{29}\text{Si}$  NMR or by IR spectroscopy (Nicolet iS5 spectrometer, quipped with a Specac Quest single reflection ATR accessory (diamond crystal), medium infrared region (MIR) 4000-400  $\text{cm}^{-1}$ ).

##### Fluorocarbon-based polymer

IR spectrophotometry is performed at DAIKIN with IR-Tracer 100 (Shimadzu) equipped with a single reflection ATR accessory (diamond crystal, 10.000 - 40  $\text{cm}^{-1}$ ). NMR spectra are obtained with a Bruker Fourier 80 spectrometer (80 MHz homonuclear  $^1\text{H}$  or heteronuclear  $^1\text{H}/^{13}\text{C}$  FT-NMR).

#### Electrochemical Impedance Spectroscopy (EIS) (Ionic conductivity)

##### ORMOCER®

At FhG ISC, the ionic conductivity of the polymer was determined with the help of impedance spectroscopy. Impedance measurements were performed with EL-ECC® cells and with a Biologic VMP300 potentiostat in a frequency range of 7 MHz to 100 mHz and a AC amplitude of 10 mV. A symmetric cell with stainless steel as working and counter electrode was



assembled and placed in a climate chamber (Vötsch). Impedance measurements were performed at different temperatures starting from 25 °C. Heating and cooling curves have been set as follows: 45 °C, 60 °C, 80 °C, 60 °C, 45 °C, 25 °C, 15 °C, 0 °C, -20 °C, 0 °C, 15 °C, 25 °C. In between temperature changes the cells have been tempered for 4 hours to ensure a constant temperature within the cell.

The bulk resistances of the electrolytes were calculated by reproducing the impedance spectra through equivalent circuit models. Once obtained the bulk resistances, the conductivities were obtained by correcting the inverse of the resistances for the geometrical constant of the cell. The latter was determined by measuring the electrode-electrolyte contact surface and the distance between the electrodes with a micrometer.

#### Fluorocarbon-based polymer

At Daikin, the ionic conductivity of the polymer is determined by electrochemical impedance spectroscopy. Impedance measurements are performed with a Biologic VMP3 potentiostat in a frequency range of 1 MHz to 100 mHz in the potentiostatic mode with an amplitude of 10 mV. Symmetric cells with stainless steel as working and counter electrode will be tested in the Microcell HC (rhd instruments) at different temperatures e.g. 45 °C, 60 °C, 80 °C, 60 °C, 45 °C, 25 °C, 15 °C, 0 °C, -20 °C, 0 °C, 15 °C, 25 °C. To ensure homogenous T-distribution within the cell, a wait step of at least 2 h will be applied.

The bulk resistances of the electrolytes were calculated by reproducing the impedance spectra through equivalent circuit models. Once obtained the bulk resistances, the conductivities were obtained by correcting the inverse of the resistances for the geometrical constant of the cell. The latter was determined by measuring the electrode-electrolyte contact surface and the distance between the electrodes with a micrometer.

### **Dynamic mechanical analysis (DMA)**

#### ORMOCER®

DMA will be used for determination of complex Young's modulus at FhG ISC. DMA measurements will be performed with a dynamic mechanical analyzer in single cantilever mode at 1 Hz and 10 µm amplitude. An upwards temperature ramp of 2 K/min is applied in the defined temperature range. The exact sample geometry needs to be measured and used for evaluation of each individual measurement. DMA results will be obtained in the form of temperature-dependent storage modulus  $E'$  (elastic proportion) and loss modulus  $E''$  (viscous proportion).

#### Fluorocarbon-based polymer

DAIKIN will perform Temperature-dependent dynamic mechanical analysis (DMA) on the Fluorocarbon-based polymer. DMA is used for determination of complex Young's modulus. DMA measurements are performed with a dynamic mechanical analyzer (MCR702, Anton Paar) in single cantilever mode at 1 Hz and 10 µm amplitude. An upwards temperature ramp



of 2 K/min is applied in the defined temperature range. The exact sample geometry needs to be measured and used for evaluation of each individual measurement. DMA results are obtained in the form of temperature-dependent storage modulus  $E'$  and loss modulus  $E''$ .  $E'$  and  $E''$  stand for the elastic and the viscous portions of  $E$ , respectively.

### Rheological Properties (Viscosity)

#### ORMOCER®

Rheological analyses were performed using an Anton Paar MCR 502 rheometer equipped with a PP-25 measuring system (parallel plate, 25 mm diameter). To characterize the viscoelastic properties of the cured hybrid polymer electrolytes, a frequency sweep oscillatory method was used. For this measurement a 750 mg polymer pellet is prepared using aluminum mold (25 mm diameter). The pellet is placed between the parallel plates and a normal force of 5 N is applied. The platter oscillates with an amplitude of 0.18 mrad and a frequency varying from 0.1 Hz to 100 Hz. This experiment is performed over a temperature range from -20 °C to 80 °C in temperature steps of 10 °C under a constant flow of dry air.

#### Fluorocarbon-based polymer

Rheological measurements are performed at DAIKIN using a stress-controlled rheometer (MCR702, Anton Paar) with a cone-plate geometry with a diameter of 50 mm. All measurements are performed at 25°C. In the viscosity measurement, pre-shear of 0.1 s<sup>-1</sup> for 200 s is set to the slurry for good reproducibility, afterwards the shear rate is logarithmically increased from 0.1 to 1000 s<sup>-1</sup>. Viscosity at each shear rate is obtained after reaching constant shear stress or the set pre-shear condition on the viscoelastic measurement was reached for a defined time.

Storage and loss moduli at various frequencies and strains are measured with strain sweep test, in which strain is changed logarithmically from 0.01 to 100% at constant frequency of 1 Hz, in order to check constant elastic moduli in a small strain region. Or frequency sweep test to see the frequency dependence of elastic moduli at constant strain.

### Thermogravimetric Analysis (TGA)

#### ORMOCER®

The thermal stability of the ORMOCER® formulations will be determined by thermogravimetric analysis (NETZSCH STA 449 C). The dynamic TGA measurements will be performed in between 30 and 900 °C with a heating rate of 10 K min<sup>-1</sup>. The onset of the thermal decomposition will be determined as the onset of the peaks in the first derivative of the weight loss curve.

#### Fluorocarbon-based polymer



In order to check the thermal stability range of fluoro-polymers, Thermogravimetric Analysis (DISCOVERY TGA 5500, TA Instruments) of polymer and/or polymer electrolyte are performed with argon carrier gas and a heating rate equal to  $10 \text{ K min}^{-1}$  within room temperature- $400^\circ\text{C}$  range.

## Differential Scanning Calorimetry (DSC)

### ORMOCER®

The thermal phase transitions will be determined by DSC measurements (NETZSCH DSC 204F1) at FhG ISC and will be carried out in between  $-120$  and  $150^\circ\text{C}$  with a cooling/heating rate of  $(-)/2 \text{ K min}^{-1}$ . The glass transition temperature will be reported as the midpoint of the secondary (step) transition. The melting point and any other endothermic or exothermic events will be reported as onset temperatures

### Fluorocarbon-based polymer

At DAIKIN, the structural changes during solvent based processing of the fluoropolymer and the impact of salt and plasticizers on the fluoropolymer are studied, providing information about the changes in the crystalline fraction, DSC measurements (DISCOVERY DSC 2500, TA Instruments) are performed in hermetic sealed pans at a heating rate of  $10 \text{ K min}^{-1}$  in a defined temperature range.

## 1.2.2 LLZO Characterization

Besides multistructural characterization (1.1), LLZO-powders will also be subjected to other physical-chemical characterizations at FhG IKTS, namely of phase purity by X-ray diffraction (XRD) and ionic conductivity (Electrochemical Impedance Spectroscopy (EIS)).

### **X-ray diffraction (XRD)**

The Al-doped LLZO powder is synthesized by solid state reaction. The starting materials  $\text{La}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{Li}_2\text{CO}_3$  and  $\text{Al}_2\text{O}_3$  are mixed in water-free isopropanol, and calcined multiple times with subsequent milling. The LLZO powder is analyzed regarding its phase purity with XRD. The particle distribution is measured without dispersing agent in isopropanol.

### **Electrochemical Impedance Spectroscopy (EIS) (Ionic conductivity)**

To determine the ionic conductivity pellets of the powder are pressed and sintered. The pellets with a density of  $> 90\%$  theoretical density are analyzed by impedance spectroscopy with blocking electrodes in the frequency range of  $100 \text{ mHz}$  to  $1 \text{ MHz}$ . The measurement is conducted in EL-ECC® cells with a Biologic potentiostat VMP3.



### 1.2.3 Lithium Salt Characterization

Synthesis and characterization of salts will be performed by WUT. All salts will go through basic spectral analyses (Li NMR, C NMR, F NMR) to confirm the product purity. Along with this, the thermal stability range of the salts alone, in solution and of the membrane is investigated via Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC) respectively. The viscosity of the Li salt solutions will be studied as well together with its ionic conductivity and Lithium cation transference number (Electrochemical Impedance Spectroscopy (EIS)).

Salts before use are dried in vacuum oven at 130°C, below 1mbar for 24 hours. Solutions, membranes and samples prepared/assembled in argon-filled glovebox with <1 ppm H<sub>2</sub>O and <1 ppm O<sub>2</sub> content.

#### **<sup>7</sup>Li NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR**

To investigate purity <sup>7</sup>Li NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR of lithium salts solutions in acetonitrile-d<sub>3</sub> are performed to check if corresponding to the structure and no additional signals detected by means of NMR.

#### **Thermogravimetric Analysis (TGA)**

In order to check the salt thermal stability range, Thermogravimetric Analysis (TGA) of lithium salts are performed with argon carrier gas and a heating rate equal to 10 K min<sup>-1</sup> within room temperature-400°C range.

#### **Differential Scanning Calorimetry (DSC)**

The thermal stability range of the salt solutions and membranes are also probed through Differential Scanning Calorimetry (DSC) lithium salts solutions in EC:DMC mixtures and lithium salts in polymer membranes in hermetic pans with a heating rate equal to 10 K min<sup>-1</sup> within -80°C to 200°C range.

#### **Rheological properties (Viscosity)**

Measured for lithium salts solutions at 20°C (thermostated with precision of 0.1°C) in rheometer with cone-plate system. 0.4 ml volume is used for 40mm diameter with 47 µm gap. Measurement performed in shearing rate range of 10 to 1000 s<sup>-1</sup>.

#### **Electrochemical Impedance Spectroscopy (EIS) (Ionic conductivity and Lithium cation transference number)**

Ionic conductivity: Electrochemical Impedance Spectroscopy (EIS) measurements with temperature varied from -10°C to 50°C in 10°C increments (with precision of 0.1°C,



stabilized for at least 45 minutes before each measurement) within 500 kHz-1 Hz frequency range with 10 points per decade and 5 mV AC signal amplitude. Liquid electrolyte samples assembled in micro conductivity cells with cell constant values of 0.3-0.7 cm<sup>-1</sup> calibrated with precision of 0.3%. Solid electrolyte samples of 12 mm diameter are assembled in Swagelok™-type cells between stainless steel punches. Measurements are repeated three times for each electrolyte composition for higher data consistency.

Lithium cation transference number: DC polarization with Bruce and Vincent correction method using the following equation:  $T_+ = (I_s (\Delta V - I_0 R_0)) / (I_0 (\Delta V - I_s R_s))$ , where  $\Delta V$  is the polarization voltage equal to 20 mV;  $I_0$  and  $I_s$  are the initial and the steady-state current during said polarization, respectively;  $R_0$  and  $R_s$  are resistances of the solid electrolyte interface (SEI) measured immediately before and after the polarization, respectively. Samples are assembled in the Li | electrolyte | Li system in the Swagelok™-type cells between stainless steel punches. Electrochemical Impedance Spectroscopy (EIS) is used to obtain  $R_0$  and  $R_s$  with 5 mV amplitude over the 500 kHz-100 mHz frequency range with 10 points per decade.



## 2 Electrochemical test validation

Full electrochemical characterization will provide data about the electrochemical behavior and materials degradation. All of this knowledge will be integrated in the multi-scale modelling and in the definition of actions to improve material and harmonies them in the cell.

### 2.1 Electrochemical characterization dedicated to model development

The development of the simulations and multi-scale modelling in ASTRABAT requires a whole characterization of the components in order to assess their functionality and to derive the required physical parameters.

All parameters that are required for active materials, electrolyte, electrodes and separator are listed in the table below. Note that the electrode tortuosity parameter will be a result of the model but could be also experimentally evaluated for validation. The separator parameters are noted in the table but will be of course not applicable for solid state design.

CEA will focus more particularly as specified in the technical proposal on active materials characterization (GITT, EIS). A temperature range is not specified at this stage but will have to be defined.

Table 1 – List of the active materials, electrolyte, electrode and separator parameters for modelling

Parameter	Symbol	Technique
Active Material		
Particle radius	$R$	Laser granulometry
<b>Equilibrium potential</b>	$E^{eq}(x_{Li}, T)$	<b>GITT in half coin cell</b>
<b>Specific capacity</b>	$q$	<b>Galvanostatic measurement at low C-rate (reversible capacity)</b>
Density	$\rho$	Helium pycnometry
<b>Li diffusion in particle</b>	$D_s$	<b>indirect via GITT relaxation phase</b>
<b>Insertion kinetics</b>	$k$	<b>EIS measurements in pouch-cell with a third reference electrode</b>
Electrolyte		
<b>Conductivity at 298 K</b>	$\kappa_0(c)$	<b>EIS measurements at 298K in symmetric SS/SS cell (SS: Stainless steel disc)</b>
<b>Activation energy related to conductivity</b>	$E_a$	<b>EIS measurements at 1mol/L at different T</b>
Salt diffusivity	$D_l$	Concentration cell



<b>Transference number</b>		$t_0^+$	<b>Potentiostatic polarization in symmetric Li/Li cell</b>
Reference concentration	lithium salt	$c_{l,ref}$	1 mol/L
Electrode			
Thickness		$L$	Measured digital micrometer
Porosity		$\epsilon$	Deduced from mass measurement
Total active material fraction in solid phase		(%wt)	Provided by formulation
Fraction of each active material		(%wt)	Provided by formulation
Effective electric conductivity		$\sigma_s^{eff}$	Estimation via formula or 4-point measurement
Separator (if present)			
Porosity		$\epsilon_{l,sep}$	Data sheet
Length		$L_{sep}$	Data sheet
<b>Mac Mullin Number</b>		$N_m$	<b>EIS in symmetric cell</b>

A large part of this assessment is performed by carrying out electrochemical tests (in bold in the Table 1) and the cell design will depend on the parameter to be determined.

- Equilibrium and diffusion coefficient measurement by GITT

For example, equilibrium potential and diffusion coefficient will be characterized by GITT in half-coin cell. Slow rate such a C/50 and C/100 to characterize anode with high Si loading will be also performed in half-coin cell. Electrochemical Impedance Spectroscopy (EIS) will be used to measure the insertion kinetics into the electrode materials in reference electrode instrumented full pouch cell. All these electrochemistry tests will be made on the electrode materials with liquid electrolyte in first step to limit the impact of the solid electrolyte. In the second step, these electrochemistry characterizations will be reproduced with solid electrolyte that could implicate to adapt the test conditions (see Deliverables D D4.1, D4.2, D4.5).

It is noteworthy that the electrodes must be previously formed. The formation protocol has to be defined carefully especially for the Anode-Si based electrode. That will allow to properly design the full pouch-cell, considering the irreversible capacity that depends on the electrolyte composition, electrode formulation and formation protocol.

For active materials:

The half-coin cell design is used to perform slow rate measurements that consists of a charge/discharge cycle at C/50 and C/100 and GITT measurements. GITT test consists of a series of current pulses applied to the cell, each followed by a relaxation period. Table below show the half-coin cell configuration for testing electrode materials with liquid electrolyte in a first step to characterize the electrode materials. In a second step, solid electrolyte



material will be tested in the same stacking configuration with replacement of the liquid electrolyte and separator stack by solid electrolyte material.

**Cell design: half-coin cell (CR2032)**

**Positive electrode:  
SiC based anode  
or NMC based cathode**

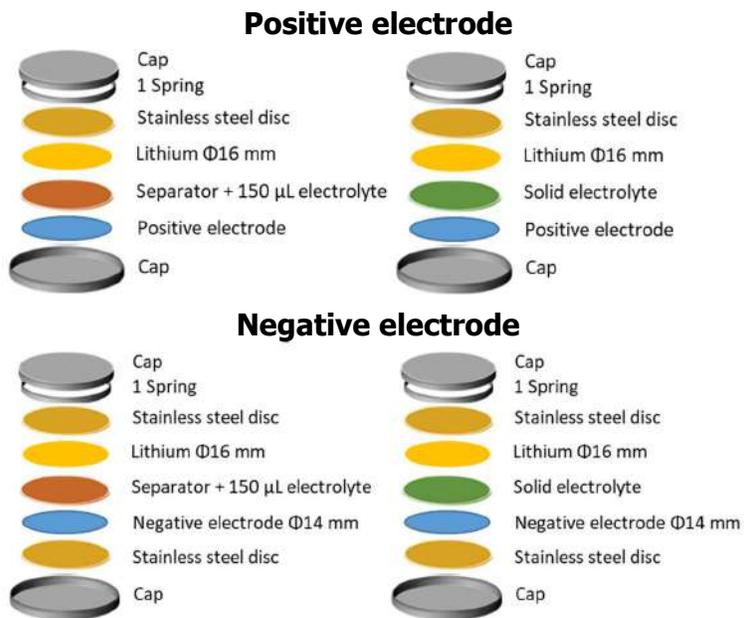
**Negative electrode:  
Lithium**

**Conditions:**

**-Current rate: C/50 to C/100**

**-Pulse time: 12 min**

**-Relaxation period: 4h**



Note: The current rate and the rest time duration applied are in accordance with the conditions test given in literature <sup>4</sup>.

To calculate the diffusion coefficient, analytical formulas are proposed in the literature depending on if the response to short times or to long times during the current pulse is considered <sup>4</sup>.

- Insertion kinetics

The insertion kinetics can be evaluated by EIS measurements performed on an instrumented full pouch cell. The configuration below is given for the first step with liquid electrolyte and separator configuration for testing electrode material. The reference electrode is electronically isolated from both electrodes by the cell separator for one side and by another small squared piece of separator for the other side. The electronic isolation of the reference electrode will have thus to be achieved in accordance with the solid-state design.



**Cell design: Pouch-cell**

**Positive electrode:  
NMC based cathode**

**Negative electrode:  
SiC based anode**

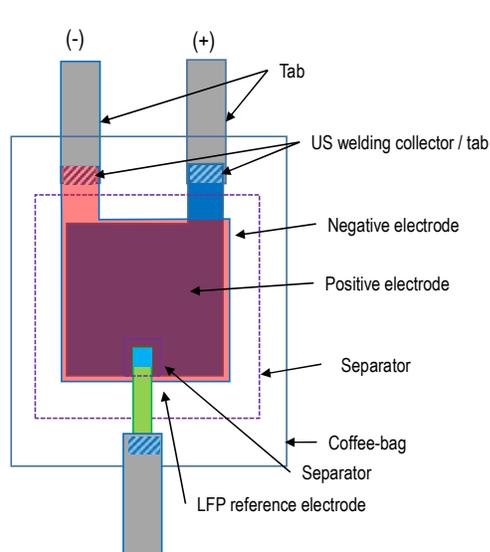
**Reference electrode: LFP**

**EIS Conditions:  
Frequency sweep from 200 kHz to  
0.01 Hz  
Voltage perturbation:  $\pm 5\text{mV}$**

**Current rate: C/50 to C/100**

**Rest: 1 hour**

**EIS measurement every 5%SOC**



Note: The EIS conditions are those used in the literature <sup>5</sup>.

From the kinetics parameters obtained by fitting the EIS spectra with a suitable equivalent circuit, the exchange current density can be calculated: the equation used is given in the literature <sup>6</sup>.

For electrolyte:

The ionic conductivity of the liquid electrolyte and the electrolyte-separator system is obtained by performing EIS measurement in symmetric coin-cell as specified below. We assume that the same cell design that the cell built for the characterization of liquid electrolyte-separator system could be used for solid electrolyte system. But some adaptations or the use of more specific removable and reusable cells could be required.



**Cell design: symmetric coin-cell (CR2032)**

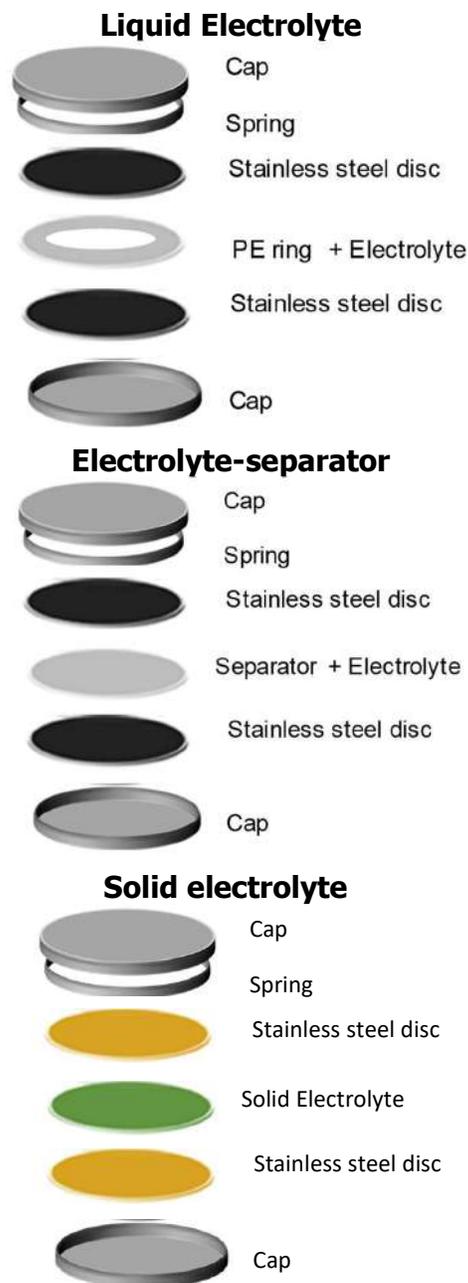
**Stainless steel disc is used as electrodes**

**Conditions:**

**Frequency sweep from 200 kHz to 1 Hz**

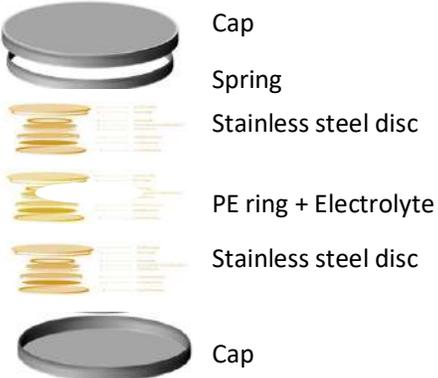
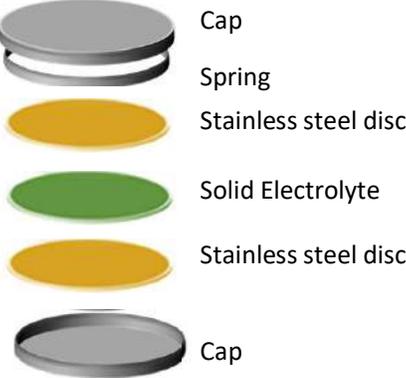
**Voltage perturbation :  $\pm 5\text{mV}$**

**Or Current perturbation :  $\pm 0.8\text{mA}$**



The transference number of the liquid electrolyte is obtained by performing EIS measurement in symmetric coin-cell. Similarly, as that is indicated above, an identical assembly or specific reusable cells could be used to characterize solid electrolyte material.



<p><b>Cell design : symmetric Li/Li coin-cell (CR2032)</b></p> <p><b>EIS: Frequency sweep from 200 kHz to 1 Hz</b></p> <p><b>Current perturbation: <math>\pm 0.8\text{mA}</math></b></p> <p><b>Conditions:</b></p> <p><b>1 - Rest 1h</b></p> <p><b>2 – EIS measurement</b></p> <p><b>Go back to 1 - 10 times</b></p> <p><b>3 – Rest 1 h</b></p> <p><b>4- Polarization: +5 mV during 30 min (1 point/0.05s recorded)</b></p> <p><b>5 - Rest 1h</b></p> <p><b>6 - EIS measurement</b></p>	<p style="text-align: center;"><b>Liquid Electrolyte</b></p>  <p style="text-align: center;"><b>Solid Electrolyte</b></p> 
---	---

Note: The equation to calculate the transference number is given in the literature <sup>7</sup>.

For electrode:

Inside the electrode, the transport properties of the electrolyte (conductivity, diffusivity, noted  $\psi$ ) are modified by the microstructure of the electrode. The effective properties of the electrolyte at the macroscopic scale,  $\psi^{\text{eff}}$ , can be related to their bulk counterpart using the porosity of the electrode,  $\varepsilon$ , and its tortuosity,  $\tau$  <sup>2</sup>:

$$\psi^{\text{eff}} = \psi \frac{\varepsilon}{\tau}$$

Electrode tortuosity can be determined by EIS measurement in symmetric cell: Positive/Positive or Negative/Negative electrodes in blocking configuration: pristine electrodes will be used. The corresponding Nyquist plot reduces to a vertical line toward low frequencies, while at high frequencies, the Nyquist plot displays a 45° slope. These tortuosity measurements at the electrode scale) are interesting to do because this will

<sup>2</sup> Johannes Landesfeind et al 2016 J. Electrochem. Soc. 163 A1373

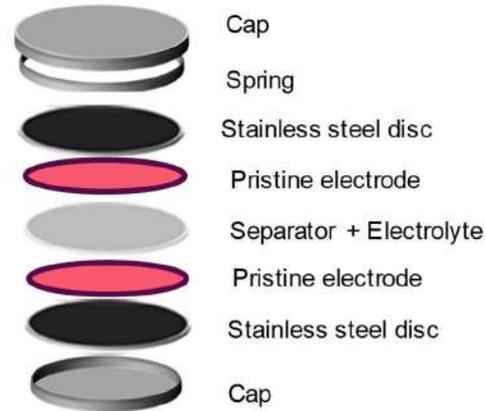


validate the developed microstructure models). They have to do on some systems and electrodes as what will be developed in the WP3, WP4 and WP5.

**Cell design: symmetric  
Pristine/Pristine electrodes coin-cell (CR2032)**

**EIS: Frequency sweep from 200 kHz to 10 MHz**

**Current perturbation:  
±0.8mA**



The equations used to determine the electrode tortuosity are the following Landesfeind et al. 2016.

The effective ionic resistance of the electrolyte, noted  $R_{ion}$  is extracted from the Nyquist plot *via* linear extrapolations of the low and high frequencies regions to the x-axis, which provides respectively the high frequency resistance  $R_{HF}$  and the extrapolation of the low frequency branch,  $R_{EL \rightarrow low}$ . The equation below is used to estimate  $R_{ion}$  <sup>8</sup>

$$R_{EL \rightarrow low} = \frac{R_{ion}}{3} + R_{HF}$$

The electrode tortuosity is then calculated by rearranging Ohm's law. If the effective ionic resistance  $R_{ion}$  through a cross-sectional area  $A$  of a material with porosity  $\varepsilon$  and thickness  $d$ , and if the conductivity of the electrolyte  $\sigma_l$  is known, the tortuosity  $\tau$  can be calculated by:

$$\frac{\tau}{\varepsilon} = \frac{R_{ion} A \sigma_l}{d}$$

Validation of the model:

Model validation requires to test the full cell by using electrochemical cycling at different C-rate (charge and discharge) and by hybrid pulse power characterization (HPPC) test. Because such tests must be performed in the other WP, they could be used to validate the developed models



## 2.2 Post-mortem study

Post-mortem studies will be performed to characterize the internal components after formation and after cycling. Such study implicates a set of methods of electrochemical, physicochemical and structural characterization of materials and components (positive and negative electrodes, separator, electrolyte) at different scales to identify precisely the mechanisms which are involved and which cause degradation<sup>9</sup>. Figure 5 illustrates the different techniques of characterization that are performed for each of the bulk or surface components. Note that separator is specified to generalize to all systems but is not to be considered for solid state.

It is the complementarity of the information obtained with these techniques that helps to understand the origin of the degradation and the resulting performance losses.

Method	detection of Li	depth profiling	sensitivity	Electrode / separator degradation					Material degradation					
				growth of films on electrodes	clogging of pores	delamination of electrode or separator	cracks in electrode coating	deformation of electrodes	changes/films on particle surfaces	particle cracks	exfoliation	dissolution/migration of transition metals	electrolyte degradation	
optical microscopy	no	no	surface	yes	limited	no	no	no	no	no	no	no	no	no
SEM	no	no	surface	yes	yes	no	no	no	no	no	no	no	no	no
TEM	no	no	surface	no	no	no	no	no	no	no	no	no	no	no
EDX	no	no	surface	yes	yes	no	no	no	no	no	no	no	no	no
XPS	yes	limited	surface	yes	no	no	no	no	no	no	no	no	no	no
ICP-OES	yes	no	bulk	limited	no	no	no	no	no	no	no	no	no	no
GD-OES	yes	yes	surface/bulk	yes	no	no	no	no	no	no	no	no	no	no
FTIR	no	no	surface/bulk	yes	no	no	no	no	no	no	no	no	no	limited
SIMS	yes	limited	surface/bulk	yes	no	no	no	no	no	no	no	no	no	no
NMR	yes	no	bulk	limited	no	no	no	no	no	no	limited	no	no	no
XRD	no	no	bulk	limited	no	no	no	no	limited	no	limited	no	no	no
GC-MS	no	no	electrolyte	no	no	no	no	no	no	no	no	no	no	yes

yes
limited
no

Figure 5 - Physicochemical characterization techniques and phenomena they are able to detect. Green, orange, and red colors indicate good, limited, and no capability for detection of a specific aging mechanism, respectively<sup>9</sup>.

The preparation of the samples requires the dismantling of cell in a glove box in an inert atmosphere (with argon to obtain low levels of H<sub>2</sub>O and O<sub>2</sub>). Thus, the internal components are not in contact with the air, thus preserving their condition as it was in the cell after operation. The cell is always dismantled at a fully discharged state, on the one hand for safety reasons, and on the other hand to characterize the cells at an identical state of charge between fresh and aged electrodes.



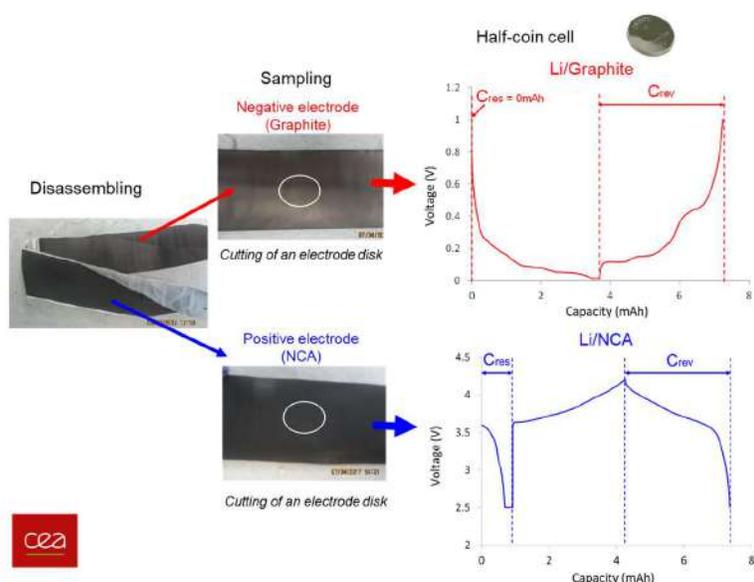


Figure 6. Electrochemical test in half-coin cell for measuring, after aging, the reversible capacity and the residual capacity of the electrodes of a Graphite / NCA cell.

The electrode microstructural and physicochemical characterization is most often coupled with an electrochemical characterization to control the lithiation state of each electrode and to measure their insertion capacity. For example, to measure residual capacity (initial capacity in lithiation for the positive electrode and in delithiation for the negative electrode) and total reversible capacity of an electrode, half-coin cell are reconstructed from the dismantled components as shown in Figure 6. Samples are taken from the negative and positive electrode of a cell. They are cut as a pellet and then assembled in half-coin cell facing negative lithium metal electrode. The electrode and solid electrolyte sampling will certainly have to be adapted to solid state depending on how they could be separated from each other's.

Electrochemical tests are usually performed on the half-coin cells to obtain the residual and reversible capacities of each electrode. In this example, the residual capacity of the half-cell measured after aging can be compared with the residual capacity obtained in the fresh state. The difference in capacity can be directly related to the loss of exchangeable capacity lost by irreversible consumption of lithium ions. Thus, some of the loss of capacity observed in the complete cell can be associated with a loss of exchangeable lithium ions, consumed by parasitic reactions, associated with the growth/reformation of the surface interfacial layer of graphite particles (SEI), the deposit of metallic lithium on the same electrode under certain operating conditions, or the loss of electronic connection of lithiated particles. Reversible capacity represents the complete electrode insertion capacity that may have been degraded after operation (e.g., electro-disconnection of lithiated or delithiated particles, degradation of insertion structures). Depending on the extent of these degradations, this may have had an impact on the capacity of the entire cell (in capacity or power at high current).

Once the performance loss has been quantified, the origin of the performance loss should be investigated by implementing internal component-level characterizations.



## 2.3 Electrochemical tests characterization

In ASTRABAT the reproducibility of performances and assessment of the reliability of the different cells architectures will be performed. These tests will be carry out on 10 mAh cells capacity.

A round robin star test (RRT) method will be used to compare the ASSB cells. The reference cells will be tested in electrochemistry in CR2032 coin cell and small 500 mAh pouch cell to select the best electrode and electrode process manufacturing technology, then the larger cells will be assessed.

It is important to note that whilst the values given below are intended to serve as a guide, it should be understood that they are subject to change if valid reasons are provided by consortium partners and are dependent on the technological developments that occur throughout the project

The RRT will be used as a reference for partner leading in-house electrochemical and thermal assessments in the framework of the project. The test following 3 phases:

### **Phase 0 : Baseline Materials and cell testing:**

- (i) Reference non solid-state system: Si-C based anode / Liquid electrolyte / NMC-based cathode
- (ii) Reference solid-sate system: SiC-(ORMOCER LLZO doped) / LLZO doped polymeric electrolyte / NMC-(fluorocarbon polymer LLZO doped)
  - a. component one by one (coin cell, half-cell), to measure the stability and full characterization
  - b. to test cell components together (full cell)

### **Phase 1 and Phase 2 will be done to compare the 2 new generations of ASTRABAT cell architectures. The tests is performed by testing :**

- i) component one by one (coin cell, half-cell), to measure the stability and full characterization (energy, power, cycle at room temperature)
- ii) to test cell components together through 500 mAh-pouch cell performances assessment (energy, power, cycle at room temperature)



Table 2 - Test system for ASTRABAT **full cell** electrochemical characterization:

Cell Type	Materials & Testing	
	COIN CELL	POUCH CELL
Mechanical	CR2032-Type coin cell 2 stainless steel caps and a silicone joint 20mm Dia x 3,2mm	-----
Mechanical	2 springs	External pressure to be defined
Mechanical	1 spacer	-----
Electrolyte	LP30 (EC: DMC 1:1 +1M LiPF <sub>6</sub> ), LiTDI (EC: DMC 1:1 or 1:2 + 0.6M LiTDI), LiPCP (EC: DMC 1:2 + 1M LiPCP)	
Test	<p><u>To check cycle life:</u></p> <ul style="list-style-type: none"> <li>- Temp: 20 °C</li> <li>- 30min OCV</li> <li>- E window: 2.7 V - 4.3V</li> <li>- Continuous 100% DOD.</li> <li>- C/10. till 80% BoL</li> </ul> <p><u>To check performance:</u></p> <ul style="list-style-type: none"> <li>- T: 20 °C</li> <li>- 30min OCV</li> <li>- Continuous 100% DOD.</li> <li>- C-rate tests (10 cycles each, Charge: Discharge): C/10:C/10, C/5:C/5, C/2:C/2, C:C, 2C:2C, C/10:C/10</li> </ul> <p><u>Other tests:</u></p> <p>EIS 4.10E5 to 1.10E-1 Hz ±10mV at 50% SOC, before and after cycling</p>	

For **half-cell** characterization (coin-cell type):

Anode	Materials & Testing	
	Separator*	Lithium Chip 99,9%
E window	Celgard 2400 16mm Diam	
	Si-based electrodes: E window: 0.1 V - 1 V (vs Li/Li <sup>+</sup> )	NMC-based electrodes: 0.6 V - 3V (vs Li/Li <sup>+</sup> )

\*For Phase 0 reference cell is : Si-C based anode / Liquid electrolyte / NMC-based cathode



## 2.4 Safety tests

Safety is a key criterion in current EV batteries and battery cells must be ready to face disruptive scenarios such as the accidental or intentional crash or firing of the vehicle. Therefore, it is important to evaluate the safety performances of the system in the operating range but also beyond, and to be aware of the consequences. For this reason, safety assessments will be conducted to complete the performance evaluation.

Electrical, mechanical and thermal assessment will be realized at pre-prototype level including safety abuse tests during the different stages of the battery life such as operating, storage exposure to shocks, temperatures, and vibrations and transport condition. A certification of safety will be done at M28 (MS5) of the project.

### 2.4.1 Hazard Level Testing including abuse tests

The part of the document presents the abuse tests that will be performed in ASTRABAT. Overcharge, Nail penetration, Short-circuit and Thermal runaway will be applied on two cells for each test. Tests results will be assessed by assigning a hazard severity level score based on EUCAR hazard levels. In addition, CEA will perform two tests with gas analyses, so a minimum of 10 cells is necessary for this subtask. In all cases, the temperature of the cell's surface as well as the tab temperature will be monitored together with the current and the voltage profile.

Experimental conditions of abusive tests:

#### 1. Overcharge

This test reproduces an equilibration fault or a charger fault in which the maximum allowable charge voltage threshold is exceeded. The test consists of applying a constant voltage and a constant current between the tabs of the cell to study its electrochemical behaviour. The cell shall be charged using a constant voltage power supply. The test temperature is 20°C and the cell is fully charged (SOC of 100%)

A safety machine will be used for this test. The test conditions for the overcharge test, in accordance with the standard UN38.3 rev6, will be the follows:

- Start the acquisition devices
- Verify that the temperature of chamber is 20°C ± 5°C
- Continue charging the cell beyond the 100% SOC. In the ASTRABAT context, the current of overcharge will be defined according to the electrical specification of the cell generation developed. The overcharge voltage its limited then its reaches twice the maximum voltage specified by the manufacturer. The overcharge test shall be discontinued when the quantity of electricity applied to the cell reaches 200% SOC equivalent, or catastrophic event occurs.
- Check the sample external aspect, the temperatures and the voltage.

After overcharge test the cell will be observed until the cell temperature is below 40°C, or during 2 h.



## 2. Nail penetration

Piercing the battery across the casing with a conducting element simulates an internal short-circuit. Safety machine will be used for this test, Figure 7.



Figure 7: Safety machine for nail penetration tests

The cells will be pierced at a SOC of 100% using a sharp conducting nail with a 3 mm diameter and a 30°-point angle. The temperature of the test is 25°C. The cell will be placed on an electrically isolated plate. The movement, provided by a pneumatic cylinder, will be vertical, uniform and rotation-free. The cell will be held in such a way as to remain fixed, but without stress. The battery will be pierced in the centre, perpendicular to the electrodes with a penetration rate of 8 cm/s.

After nail penetration test the cell will be observed until the cell temperature drop down to 40°C, or during 2 h.

## 3. Short-circuit

The test consists of applying an external short circuit on to the terminals of the accumulator, to reproduce a handling fault or a management failure. The test temperature is 20°C and the cell is fully charged (SOC of 100%). A safety machine will be used for this test. The test conditions for the short circuit test, in accordance with the standard UN38.3 rev6, will be the follows:

- The cell to be tested shall be heated homogeneously at 57°C ±4°C (skin temperature)
- Start the acquisition devices
- Applied to short circuit to the cell terminal, with a total resistance of less than 0.1 Ohm. (The resistance will be adjusted in function of sample resistance, minimum limit of 0,005 Ohm). Maintain the short circuit during one hour after the sample skin temperature decrease down to 57°C, or catastrophic event occurs.



- Check the sample external aspect, the temperatures and the voltage.  
After short-circuit test the cell was observed during the cell temperature is below 40°C, or during 2 h.

#### 4. Thermal stability:

The Accelerated Rate Calorimeter EV ARC from THT, see Figure 8, will be used for the thermal abuse tests, in order to determine the temperature at which the cell becomes unsafe. The tests will be performed on cells previously fully charged, according to a standard charging procedure defined by the Partner in charge of the cell manufacturing.



Figure 8: Photographs of the calorimeters used at CEA to perform thermal runaway tests

Thermal runaway tests will be performed in a pseudo-adiabatic calorimeter, following the “Heat-Wait-Seek” protocol: from an ambient temperature called **start temperature**, the temperature is raised for a given **temperature step**, then stabilized until an exothermal reaction of the cell is detected in less than 30 minutes. If not, a new **temperature step** is done. An exothermal reaction is considered when self-heating is higher than the **temperature rate sensitivity** measured at skin level. When detected, this temperature level is recorded and called the **onset temperature**. Then, the temperature keeps on rising until the **end temperature** threshold is reached, or if the maximum temperature rise criterion called **end temperature rate** is reached. The Figure 9 below gives an illustration of the process:



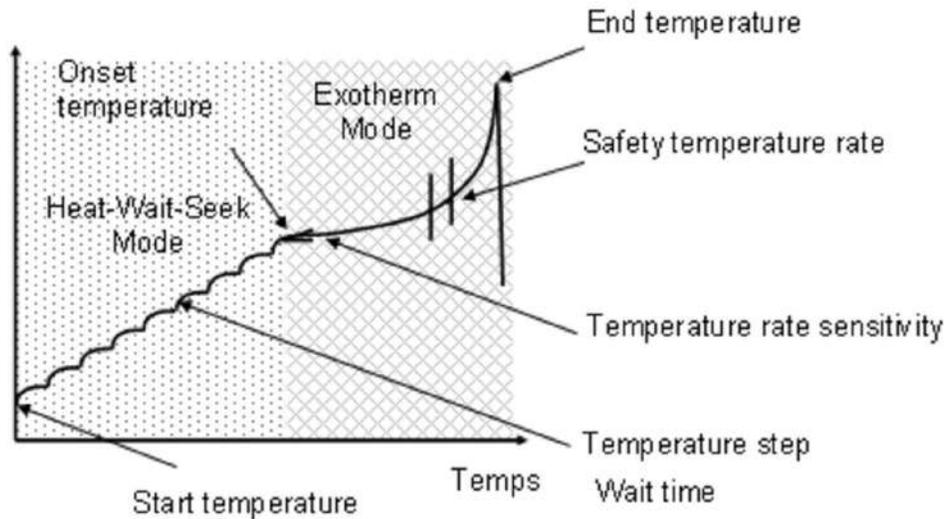


Figure 9: Heat-Wait-Seek process during a thermal runaway test

The setup proposed for ASTRABAT project is:

- Start temperature: 30°C
- Temperature step: 5°C
- Temperature rate sensitivity:  $>0.02^{\circ}\text{C}/\text{min.}$  = thermal runaway
- End temperature: 200°C → test stop
- End temperature rate: 3°C/min. → test stop

#### Annex: EUCAR Hazard levels

External influences, such as	Impacts on the lithium battery	Internal events, such as	Hazard Level	Description	Classification Criteria & Effect
			<ul style="list-style-type: none"> <li>• External heating</li> <li>• Overcharging</li> <li>• Deep discharge</li> <li>• Excessive charging current</li> <li>• External short-circuit</li> </ul>	<ul style="list-style-type: none"> <li>• Electrode-electrolyte reactions</li> <li>• Electrochemical reactions</li> </ul>	0
			1	Passive protection activated	No defect; no leakage; no venting, fire or flame; no rupture; no explosion; no exothermic reaction or thermal runaway. Cell reversibly damaged. Repair of protection device needed.
			2	Defect / Damage	No leakage; no venting, fire or flame; no rupture; no explosion; no exothermic reaction or thermal runaway. Cell irreversibly damaged. Repair needed.
			3	Leakage $\Delta \text{mass} < 50\%$	No venting, fire or flame*; no rupture; no explosion. Weight loss $< 50\%$ of electrolyte weight (electrolyte = solvent + salt).
			4	Venting $\Delta \text{mass} \geq 50\%$	No fire or flame*; no rupture; no explosion. Weight loss $\geq 50\%$ of electrolyte weight (electrolyte = solvent + salt).
			5	Fire or Flame	No rupture; no explosion (i.e., no flying parts).
			6	Rupture	No explosion, but flying parts of the active mass.
			7	Explosion	Explosion (i.e. disintegration of the cell)

\* The presence of flame requires the presence of an ignition source in combination with fuel and oxidizer in concentrations that will support combustion. A fire or flame will not be observed if any of these elements are absent. For this reason, we recommend that a spark source be used during tests that are likely to result in venting of cell(s). We believe that "credible abuse environments" would likely include a spark source. Thus, if a spark source were added to the test configuration and the gas or liquid expelled from the cell was flammable, the test sample would quickly progress from hazard level 3 or 4 to hazard level 5.



## 2.4.2 UN38.3 Lithium battery cell transportation

ASTRABAT project will evaluate cells following transport regulation (road, maritime and air transport). Safety tests will be performed at LEITAT (to a large extend) and CEA.

40 pouch cells (500 mAh) will be required to fully assess the UN38.3 according to the Table 3:

Table 3 - UN38.3 lithium battery cell transportation tests

Order	Test	Ref.	Type	Beneficiary	SOC [%]	Cycle	Cells required
n°1	Vibration	UN38.3-T3	As received	CEA	100	1	10
n°2	Shock	UN38.3-T4	As received	CEA	100	1	10
n°3	Altitude simulation	UN38.3-T1	As received	LEITAT	100	1	10
n°4	Thermal test	UN38.3-T2	As received	LEITAT	100	1	10
n°5	Short circuit	UN38.3-T5	Destructive	CEA	100	1	10
n°6	Impact/crush	UN38.3-T6	Destructive	LEITAT	50	1	5
n°7	Overcharge	UN38.3-T7	Destructive	LEITAT			5
n°8	Forced discharge	UN38.3-T8	Unusable	LEITAT	0	1 & 50	20

The 6th edition of "Recommendations on the Transport of Dangerous Goods" Amendment 1, which is in force since 1st of January 2019, where each test procedures and cell requirements can be accessed is available under following links:

<http://www.unece.org/trans/areas-of-work/dangerous-goods/legal-instruments-and-recommendations/un-manual-of-tests-and-criteria/rev6-files.html>

<http://www.unece.org/trans/areas-of-work/dangerous-goods/legal-instruments-and-recommendations/un-manual-of-tests-and-criteria/amend-to-rev6.html>



### 3 References

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