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SPICY Deliverable D6.7

Post-mortem analysis protocols

WP	6	Test and Li-ion, assessment
Task	6.5	Post-mortem analysis

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3	14.10.2015	E. Paillard, A. Moretti, V. Sharova	1st version by KIT, 2nd version by FZJ, 3rd version by FZJ taking feedback into account (from CIDETEC, KIT)
4	11.11.2015	E. Paillard	4th Revision considering feedback from coordinator and further inputs from CIDETEC and KIT + deliverable 6.2 'Test plan for ageing and modelling'
5	18.11.2015	W. Porcher	Revision
6	06.01.2016	E. Paillard	Revised version after further discussion with all WP6 partners (2 phone conferences) to discuss the sample flow for the first cells and the location of the opening of the cells.
7	22.01.2016	E. Paillard	Revised by CEA. Changes in the sampling area definition, correction in table 3.

[1] Dissemination level: **PU** = Public, **PP** = Restricted to other programme participants (including the JU), **RE** = Restricted to a group specified by the consortium (including the JU), **CO** = Confidential, only for members of the consortium (including the JU)

[2] Nature of the deliverable: **R** = Report, **P** = Prototype, **D** = Demonstrator, **O** = Other

[3] Creation, modification, final version for evaluation, revised version following evaluation, final

Deliverable abstract

The present deliverable describes the procedures that will be applied to GEN0, GEN1, GEN2 and GEN3 cells after the ageing tests described in D6.2. Post-mortem (and in some cases ante-mortem) analysis includes the safe opening of batteries, the separation/extraction of the different cell components (electrodes, separators, and electrolyte) and their sampling within the whole batteries for analysis by different partners.

Different techniques will be used for the observation (SEM, SEM-FIB) and analysis of bulk materials (XRD, NMR) and interfacial layers (XPS, RAMAN, EDX) to understand (and minimize) the degradation phenomena occurring within the batteries (Electrolyte degradation, cathode dissolution, aluminium corrosion, pore clogging within separator and electrodes, loss of electrode cohesion, particles cracking …) depending on the cell design and test conditions.

Finally, if the electrode cohesion allows it, lab-scale cells (half-cells and full Li-ion) will be assembled using aged electrodes samples from different sampling areas. Their electrochemical characterization, using fresh electrolyte and separator, will provide similar parameters to those acquired during the ageing tests for the modelling task and allow, in addition, a rough mapping of electrode performance decay within the cells.

Deliverable Review

	Reviewer #1: Willy Porcher			**Reviewer #2: .....**		
	Answer	**Comments**	**Type***	**Answer**	**Comments**	**Type***
1. Is the deliverable in accordance with						
(i) the Description of Work?	☒ Yes ☐ No		☐ M ☐ m ☐ a	☐ Yes ☐ No		☐ M ☐ m ☐ a
(ii) the international State of the Art?	☒ Yes ☐ No		☐ M ☐ m ☐ a	☐ Yes ☐ No		☐ M ☐ m ☐ a
2. Is the quality of the deliverable in a status						
(i) that allows it to be sent to European Commission?	☒ Yes ☐ No		☐ M ☐ m ☐ a	☐ Yes ☐ No		☐ M ☐ m ☐ a
(ii) that needs improvement of the writing by the originator of the deliverable?	☐ Yes ☒ No		☐ M ☐ m ☐ a	☐ Yes ☐ No		☐ M ☐ m ☐ a
(iii) that needs further work by the Partners responsible for the deliverable?	☐ Yes ☒ No		☐ M ☐ m ☐ a	☐ Yes ☐ No		☐ M ☐ m ☐ a

* Type of comments: M = Major comment; m = minor comment; a = advice

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1. Introduction

This deliverable aims at describing the procedures and tests, which will be performed on aged SPICY cells of successive generations, developed within WP2, WP3, WP4 and WP5 and aged within WP6 (task 6.3) to understand the degradation mechanisms at the origin of performance decay. Post-mortem analysis consists in analysing the cell components (electrodes, separator and electrolyte) after the ageing tests (described in D 6.2), performed under different C-rates, states of charge and temperature conditions, to assess how the cycling conditions, as well as the cell chemistry and design, affect the ageing of the batteries. In particular, the effects of the different ageing cause summarized in Table 1 will be investigated using a variety of analytical techniques described in this deliverable. Comparison will be done with pristine components but also components extracted from 'fresh' cells (i.e. ante-mortem analysis of cells only subjected to formation cycle(s)).

Table 1. Ageing mechanisms in Li-ion batteries

Ageing causes	*Enhancing factors*	*Impact*	*Observable effects/Techniques*
Electrolyte			
Electrolyte decomposition (Main ageing cause in conventional Li-ion batteries)	High T	Capacity, safety, power	Decomposition products dissolved in electrolyte (NMR, ICP-OES) Solid deposits on electrode surface and porosity and separator (SEM-EDX, XPS, NMR, IR, RAMAN)
Carbon and Si/C anodes – electrode/electrolyte interface			
Electrolyte decomposition (side reaction at low rate)	High T, high SOC	Capacity, power	Accelerates electrolyte decomposition (thickening of solid deposits layers and increase of dissolved decomposition products)
Solvent co-intercalation, gas evolution, cracking of particles	Overcharge	Capacity, power	Exfoliation of graphite (SEM), cracked Si particles (SEM), accelerated electrolyte decomposition
Changes in porosity due to volume changes, SEI formation and growth	High C-rate and high SOC, High T	Power	SEM, SEM-FIB Rebuilding of cells and rate performance.
Contact loss of active material particles due to volume changes during cycling	High C-rate, High DOD	Capacity	Re-building of half-cells Adhesion test (90°C peeling)
Decomposition of binder (and contact loss)	High SOC (high voltage) and high T	Capacity, Power safety	Re-building of half cells Adhesion test

Current collector corrosion	Overdischarge, low SOC, High T, water traces in electrolyte	Power	Corrosion (SEM, after removal of coating), ICP-OES for dissolved copper, EDX and XPS for detecting possible redeposit.
Metallic lithium plating and subsequent electrolyte decomposition by metallic Li	Low T, High C-rates, poor cell balance, geometric misfits	Capacity, (Power) Safety (shorts)	Accelerated ageing of electrolyte.
Oxidation of conductive particles	High T, water traces in electrolyte	Power	Increase of surface group onto carbon surface (RAMAN, IR)
$LiMFeMnPO_4$ Cathode			
Dissolution of transition metal ions	High voltage, temperature, high dielectric constant solvents	Capacity, power	ICP-OES (Electrolyte), XPS (on anode to see whether metals are deposited), EDX.
Accelerated electrolyte ageing	High potential, small particle size, presence of transition metal oxides	Capacity, Power	Increase of electrolyte decomposition (thickening of SEI (anode also) and solid deposits and increase of dissolved decomposition products)
Irreversible phase transitions (bulk and layers)	Voltage range	Capacity, power, voltage	Loss of capacity and/or variation of insertion/desinsertion voltage if new phase are active (XRD, if phase are crystalline, XPS might be limited by C-coating on cathodes)
Current collector corrosion	Use of stable organic Li salts, high voltage	Power	Pitting corrosion (SEM)
Separator			
Separator clogging	Electrolyte degradation	Power	Deposited products (SEM, NMR after rinsing). Rate tests after re-assembly for assessing the power loss associated. MacMullin numbers.
Separator degradation	Temperature	Power	SEM

2. Protocol

2.1. Battery disassembly and components sampling (FZJ, CEA):

Figure 1 shows image of the packaging that will be used within SPICY for GEN0, GEN1, GEN2 and GEN3 Li-ion batteries which will be subjected to ageing tests under different conditions prior to the present post-mortem analysis protocol.

Figure 1. *Picture of the four types of cell packaging that will be produced within SPICY. From Left to right: Cylindrical hard casing 17 Ah (PROLLION), Prismatic hard casing 17 Ah (CEA), Prismatic hard casing 5 Ah (TUM), and prismatic soft packaging (pouch Bag) 17 Ah (CEA).*

The cells will be discharged to Vmin, using a CCCV (C/2, 10h-C/50), to limit reactivity of the electrodes in case of accidental short-circuit during disassembly. Cells will be opened under inert gas atmosphere (Ar) to reduce further the risk and avoid contaminating the samples.

2.1.1. Electrolyte recovery

The first step will be the electrolyte recovery. It is known to be the most challenging, as the electrolyte is consumed during battery ageing and thus, the batteries at their end of life might appear rather 'dry' at their opening. In addition, most electrolytes comprise volatiles components, which evaporate quickly and makes it difficult to assess precisely the composition of the aged electrolyte. The separation of the electrolyte is a complex task. Indeed, part of the electrolyte evaporates making complicated the quantitative analysis. Grützke *et al.*[4], for example, used super critical carbon dioxide for electrolyte extraction. They were able to extract solvents and some solvent degradation products. However, the lithium salt ($LiPF_6$) was only recovered in traces. Stiazny *et al.*[5] obtained the electrolyte of the aged cells by leaching it out with dichloromethane, but the method used tend to impact the results

[4] Grützke, M., et al., Supercritical carbon dioxide extraction of lithium-ion battery electrolytes. The Journal of Supercritical Fluids, 2014. 94 (0): p. 216-222.

[5] Stiaszny, B., et al., Electrochemical characterization and post-mortem analysis of aged LiMn2O4–NMC/graphite lithium ion batteries part II: Calendar aging. Journal of Power Sources, 2014. 258(0): p. 61-75.

Thus, two different approaches will be tested:

a. Direct recovery:

For this, a hole will simply be drilled through the packaging (a priori through the 'up' side, but to be defined when cell drawings become available or when the first empty cells will be received (January 2016)) so that to collect directly the electrolyte. However, this approach might not be sufficient, as it is likely that only low amounts of electrolyte can be recovered this way. In addition, the volatile components are then, even partly, lost (depending on the time for extracting significant amount of electrolyte). However, it gives a good picture of the electrolyte composition, **in particular for soluble degradation products.**

b. Evaporation/condensation of volatile products and flushing the cell with solvent.

Another approach, **to collect a maximum amount of the volatile components**, would consist in placing first the full battery in a vacuum chamber (such as a large vacuum desiccator) after drilling a hole so that the electrolyte volatile components can be recovery with a cold solvent trap.

Then, the salts and less volatile compounds will be partly recovery by flushing the cell with DMC. The cells will simply be filled fully with DMC (no vacuum applied), let to rest for 30 minutes and then the DMC will be recovered by simply pouring it out (this will be repeated 2 times). An issue that might arise is that the more polar components of the electrolyte (EC for instance) might also evaporate during the evaporation stage under vacuum and DMC alone might not be able to sufficiently dissolve all the ionic species present in solution, given its low dielectric constant. However, using solvents with higher dielectric constant might lead to dissolution of solid deposits. Higher dielectric solvent (such as acetonitrile) will be used on smaller samples rather than the full battery in attempts to dissolve deposited products for analysis of both dissolved products (NMR) and cleaned interfaces (XPS). However, solid deposits will be, in the general case, analysed together with the components they are deposited onto.

2.1.2. Cell opening

The cells will be disassembled inside a glove box under inert atmosphere, either at CEA, for the stainless steel packaging from CEA and Prollion, or at FZJ for the other designs. The cuts will be done so that the electrode roll or stack is kept intact when cutting through the packaging. The specific technique used will be adapted to the packaging of the different cells (scissors/scalpel for pouch bags or small circular diamond coated rotating disk (Dremel™) for hard casing). The exact cut will be decided in January when non-activated cells and empty packaging will be made available at FZJ. Ideally, the cuts should avoid electrical connectors and allow removing the electrode roll or stack without damaging it.

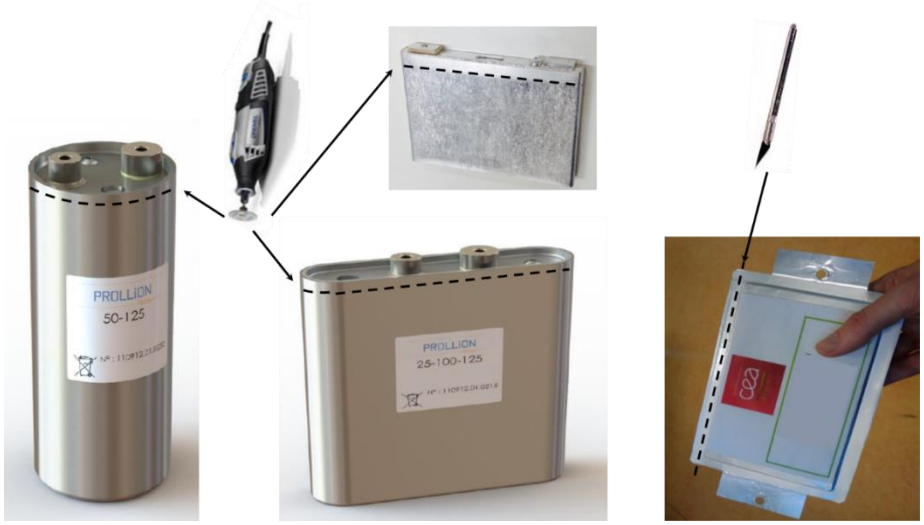

Figure 2. *Sketch of opening cuts (precise cuts to be defined in [January - March] 2016)*

2.1.3. Sampling of used components

The full electrodes, after visual analysis and acquisition of photos (to archive visible inhomogeneity for further analysis), will be cut in pieces for further analysis with samples taken from different locations on the electrodes, in order to study the influence of design on ageing. Different types of cells (wound and stacked) will be autopsied, thus sampling will be done differently, whether the electrodes are continuous or split in tabs. Thus, we describe here a rather extensive way of sampling that defines a very large quantity of samples. However, at first, the tests will start with only few sampling areas, as far apart as possible within the cells, and depending on the results and the monthly discussions within WP6, more samples might be analysed to realize more precise 'mapping' on selected cells (and for selected experiments).

An example of sample flow is given in part 3 for the first two cells to be autopsied (it proposes to sample and analyse four sampling areas: one at each electrode tab and two in the middle of the electrode tab, in addition to analysis on specific area, according to visual observation of the electrodes). Based on the first feedback from experimentalists, a running excel sheet (sample flow) will be prepared for each batch of cells available, taking into account practical considerations such as time for the experiments and experiment preparation, the number of sample to screen for each cell, which will be agreed during WP6 monthly meetings).

In any case, it is of primary importance to define precisely the samples positions within the cells so that the information concerning the location of the samples within the battery is not lost.

<u>Wound cells</u>

Figure 3 shows how the sampling areas will be defined for wound electrodes. The width will be split in three, and the length (for rolled electrodes), every 15 cm in the length direction.

To avoid mixing the sides, a mark (**small cut in the top right corner**) will be done on each sample.

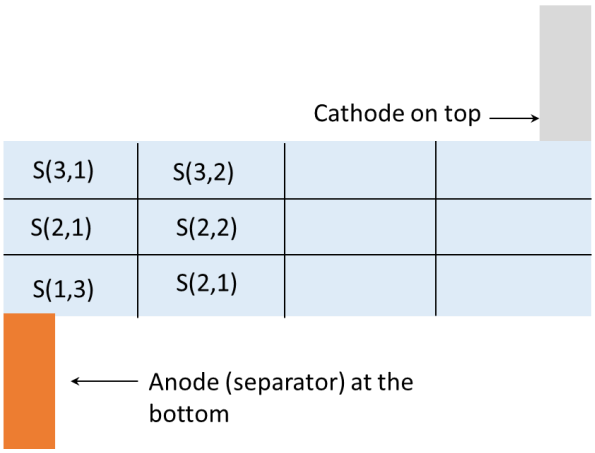

Figure 3. *Example of sampling zones S(x,y) that can be defined for a given electrode stack design for continuous electrodes (length of electrode not representative).*

Within each sampling zone, samples will be cut according to partner needs for their experiments and the location within the sampling zone archived as well (see part 3 for an example).

Stacked cells

In this case, the successive 'cells' (one 'cell' being considered as (separator)/anode/separator/cathode will be numbered (x) from bottom (anode) to top and sampling areas will be defined by one additional coordinate (y) in the width direction (three sampling area per electrode tab).

Cleaning of samples

Even though some cells will be flushed with DMC (BASF, Selectilyte, < 20ppm H_2O) for electrolyte extraction, another rinsing step with DMC will be added for each (solid) sample before sending it to the partners to be sure to remove deposited Li salts. Each sample will be dipped in a (relatively) large volume of DMC at room temperature for 30s. (For instance, a 1.13 cm^2 sample will be dipped in 5-10 mL of DMC).

The samples will then be dried under vacuum for at least 30 minutes at room temperature.

For each sample, the following table will be filled to be able to compare with pristine components and components extracted from 'fresh cells' (formation cycle(s) only). For increasing the precision on the surface area, a precision electrode puncher will be used to punch 1.2 cm diameter disk probes (within each sample). For thickness, 5 measurements will be taken for each sample with a micrometric gauge (+- 0,002 mm).

Table 2*. Physical parameters of separator, positive and negative electrode*

Sample name	

	Mass (g) (+- 0.1 mg)
	Diameter (cm) (+- 0.01 mm)
	Area (cm^2) (+- 0,02 cm^2)
	Thickness (µm) (+- 0.002 mm)
	(Opt.) Mass of active material (g)[6]
	Density (derived from mass and thickness)[6]

2.2. Physical, chemical and morphological characterization of the aged components (all partners)

Visual characterization (FZJ, CEA)

Changes in colour, cracks within the (whole) electrodes, will be assessed first by visual characterization to orient further tests (restricted by the techniques to smaller surface area) on selected areas of electrodes and separator. Pictures of the whole electrode surfaces will be taken (and the corresponding sampling zone identified, when features are observed).

The electrodes and separators once dried will be subjected to the different analytical techniques listed below. Component of 'fresh' cells (i.e. assembled and not aged after the formation step) will be analysed too, as well as pristine components (never assembled) for comparison. Ideally, for each technique (within the limit of equipment availability, budget and time), three samples will be analysed from three different sampling areas (two sampling areas at the current collectors and one in the middle). Additional samples will be analysed when judged necessary (depending on visual observation and feedback from the sampling zones analysed first).

SEM + EDX (KIT, CEA, CIDETEC)

The parameters of interest include particle size and, especially for Si containing anodes, particle cracking (if SEI are thick enough their thickness could be estimated). The inspection will cover the surface of the electrode from the rim of the coating toward the inner part of the electrode to investigate possible packaging effects and from one electrode tab to the other to observe effects in current density inhomogeneities at high current rates.

The same magnification as those described in D1.7, will be used for surface analysis (cracks, homogeneity) (in-lens SE modes):

- Anode: 200X, 500X, 1000X, 2KX, 5KX, 10KX

- Cathode: 200X, 500X, 1000X, 2KX, 5KX, 10KX, 20KX

[6] Error to be determined according to the error on current collector homogeneity regarding weight

EDX (including mapping) will allow detecting possible metal dissolution and deposition at the anode. The analysis of the cathodes will be performed as well. SEM imaging will give a good idea of porosity changes within the electrode, using FIB (focused ion beam) at KIT to realize a cross-cut and investigate the bulk of the electrodes. The state of the current collector can also be analysed by FE-SEM. Some electrodes will be scraped from the current collector for assessing the corrosion of aluminium.

XRD (KIT, CEA)

Samples of positive and negative aged electrodes will either be scraped from the current collector and the resulting powder analysed by X-ray diffraction or placed directly in the X-ray beam to investigate structural changes in the (crystalline) bulk material consequent to the aging. The typical range for XRD measurements is: 10-80º; 1s/0.02º.

Adhesion test (CIDETEC)

Part of the electrodes will be sent to CIDETEC to measure the adhesion strength of the electrodes on the current collector. A 90º peel test is carried out at 20mm/min crosshead speed on 20x90mm (WxL) electrode samples to obtain a peeling strength value ($N \cdot m^{-1}$). 6 different samples will be analysed for each sampling area.

This test will allow following the loss of interfacial adhesion strength and will be cross-analysed with the loss of active materials, deduced from low rate capacity of the aged electrode after their re-assembly in fresh half-cells.

XPS (FZJ)

XPS will be used to characterize the surface of aged electrodes (and separator) to investigate the surface layer(s) (deposited organic and inorganic products (including SEI) and possible surface phase change within the active materials at the interface with electrolyte). All the relevant spectra will be acquired, depending on the composition of the electrolyte and electrodes (Si2p O1s, P2p, C1s, F1s, Li1s, B1s, N1s…). The XPS equipment that will be used by FZJ is equipped with a small antechamber, allowing limiting atmospheric exposure when loading samples.

Although XPS analysis of organic compounds within the SEI is not trivial, the technique allows probing specifically the outer layer of the particles and should bring valuable information on the species formed, in combination with other spectroscopic techniques (IR, Raman, NMR). XPS offers also the possibility of realizing a depth profile, by etching the surface by Argon beam, which could also allow reveal information on the ‘inner part of the SEI’, at the contact with the anode active particles (by comparison with spectra acquired on other cell components having solid deposits onto their surface (such as the separator), that do not include any SEI.

RAMAN, IR (KIT)

Spectroscopic techniques such as RAMAN and IR will be used for characterizing the nature of the carbon coating and of carbonaceous materials, as well for characterizing the surface groups, before and after the aging. Both for RAMAN and IR, the electrode, previously washed as indicated above, can be directly used.

Raman measurements will be performed with a confocal InVia Raman microspectrometer with a 633 nm laser (Renishaw). IR spectra will be collected from 400 cm^{-1} to 4000 cm^{-1}. These techniques might also allow getting a better picture of the SEI composition, combined

with XPS and NMR as none of the technique alone allows full determination of its composition.

Some attempts can be done on the electrolyte analysis to gain additional information on its decomposition under severe conditions. The measurements are done using glass capillaries thus only few microliters of sample are necessary.

Elemental analysis and ICP-OES (KIT)

ICP-OES allows analysing the elemental composition of electrodes (after dissolution) as well as the presence of chemicals in trace amounts within the aged electrolyte (metal ion dissolution from cathode or current collectors). For ICP-OES, at least 120 mg of sample is needed to make two repetitions of the analysis. The powder will be treated with a mixture of HNO_3 and HCl ("acqua regia"), and heated until the boiling point is reached. The digestion of the sample last few minutes. Afterward the diluted solution (up to 200ml with ultrapure water) will be analysed (focusing on Fe, Ni, Co, and Mn emission lines but spectra screening for possible contaminates can be done when necessary). Calibration curve using standard solutions will be built for quantitative determination.

The analysis of the electrolyte typically requires at least 3 ml of sample. To perform an accurate quantitative analysis the "standard addition" methodology will be used for the calibration curve. If the minimum quantity of sample is not available only qualitative analysis can be perform.

Elemental analysis will be used to determine the amount of carbon in the electrode to reveal possible graphite migration. Only few milligrams of sample are necessary.

NMR (FZJ)

Electrolyte will be analysed by ^{1}H, ^{13}C and ^{19}F NMR. Solid deposit will be (tentatively) dissolved in more polar solvents than DMC (such as acetonitrile or DMF) for NMR analysis.

2.3. *Electrochemical characterization of aged electrodes (KIT, FZJ, CIDETEC)*

As mentioned earlier, decay of performance depends on many factors. A main factor is the electrolyte degradation (for conventional Li-ion batteries), which results in both an increase of cell internal resistance (ESR) due to electrolyte loss, but also an increase of diffusion related transport limitations due to the deposition of degradation products within all the pores of the battery (electrodes and separator) and as layers at the interfaces electrode/electrolytes. Thus, reassembling cells with fresh electrolyte and separator allows suppressing some causes of capacity decay and assess more precisely the contribution of each factor. In addition, in this case also, electrodes can be washed with higher polarity solvents, for removing part of deposited products.

This will allow useful comparison between performance of the full Li-ion cells (large cells, but also and lab-scale cells, similarly built for comparison), performance of the pristine

electrodes in half-cells, performance of 'fresh' electrodes (formation cycle done) in full and half-cells and finally aged electrodes in half and full-cells.

The cycling of half-cells will allow checking the integrity of the electrodes (active material loss, electrical insulation or degradation of active materials), and assess the effect of the clogging of the pores of the electrode on the rate performance.

The cycling of full Li-ion cells, will allow performing the 'check-up' procedures, described in the annex of D6.2, that are tests that are periodically done on the batteries during ageing and that allow harvesting parameters for the modelling task. Finally, by assembling cells with samples from different sampling area, it will allow a rough mapping the ageing of the electrode within the full batteries.

Galvanostatic cycling of aged electrodes (half-cells)

Parts of cycled electrodes will be re-assembled in fresh (lab-scale) half-cells (coin cells at CIDETEC and swagelok 3-electrode cells at FZJ and KIT) with fresh electrolyte and thick non-woven mats separators (or stack of separators, for limiting shorts due to dendrites on the Li metal anode). Similar cells will be assembled with pristine or 'fresh' electrodes for comparison. The half-cells will be assembled in coin (Half-cell:16.6 mm diameter disk Full-cell: 16.6/17.7mm at CIDETEC) or swagelok cells (12 mm) with single sided electrodes (one side being scrapped using the slurry solvent: NMP or water). The electrodes will be cycled using the same voltage limits as described in D1.7 so that to compare results with pristine electrodes and between partners (0.01-1V for anodes,3.65-2.5V for LFP 4.5V- 2.5V for LFMP).

After a first discharge (CCCV at C/20, C/40) to determine the lithium repartition between the electrodes, the cells will then be cycled at low discharge rates to define the capacity fading caused by the active material loss or increase of the internal resistance (C/30, CCCV, 1 cycles).

A C-rate test will then be performed (in discharge only, for limiting dendrites on the lithium electrode, charge being kept slow (Cf. D1.7: 3 cycles at C/10, C/5, C/2, 1C, 2C, 3C, 10C, 20C, with one C/10 cycle in between) as described in D1.7 for assessing the rate performance of the electrodes after electrolyte replacement and washing of some of the electrolyte degradation products (to be compared with half-cells made with pristine and 'fresh' electrodes in the same conditions). This would allow assessing the rate capacity loss due to active materials versus electrolyte degradation and separator pore clogging. In case SEI (and other solid degradations products present within the electrode pores) can be dissolved with higher polarity solvents (acetonitrile), electrodes washed this way will also be used for cell reassembly.

Electrochemical testing of harvested electrodes can be completed by Galvanostatic Intermittent Titration Technique (GITT), which consists on charging and discharging the half-cell applying a series of current pulses, each followed by a relaxation time and monitoring the potential drop. From the GITT measurements, some thermodynamic and kinetic parameters of the electrode can be calculated, such as the chemical diffusion coefficient of lithium and equilibrium potentials. This test will however be done only on selected samples, considering the time required for experiments and analyses.

Electrochemical impedance spectroscopy (EIS) on half-cells

EIS will be done on reassembled cells, to study the SEI and charge transfer resistances (vs fresh electrodes and vs measurements done during ageing tests). EIS spectra will be acquired at different potential (defined as every 20% increase of SoC for 'fresh' cells at C/25).

Three electrode cells and measurement conditions will be similar to those reported in **D1.7** for half and full-cell testing.

Galvanostatic cycling of full Li-ion cells

Electrode samples from different sampling area will be used for assembling full Li-ion cells of small surface area (coin cells), as well as pristine and 'fresh' electrodes.

The same separator as for the large cells they originate from will be used so that to be able to harvest parameters directly comparable to those obtained during ageing tests while substracting the influence of separator clogging and electrolyte loss. The 'extended check-up procedure' (ECU), described in D6.2 annex will be used, slightly modified. Indeed, as small cells require less intense current for a given C-rate, the C-rate test will be augmented by 3C, 5C, 10C. 15C and 20C. The ECU also includes DST cycles and electrochemical impedance spectroscopy for a full investigation of the cell state of health.

By this, we will obtain a rough 'mapping' of electrode performance decay within the cells (three sampling zones for each cell to start with, as described in 3. for the first set of fresh cells). Following the first results, discussion will take place during monthly phone conference, to decide on further tests using archived samples and to define the tests for the next batches with at the light of the first results.

3. Sample flow description

For each generation of cells, many samples will be harvested for each cell that will arrive at FZJ or CEA for post-mortem analysis. If some measurements will be done extensively, such as thickness, loading and density, some other cannot be extended for a deep screening of each cells. Moreover, if most measurements require only small amounts of sample, others, such as adhesions tests, require sample larger than the defined sampling area. Thus, for each batch of cell a document including a table will be prepared after discussion with all partners involved in task 6.5 (post-mortem) and WP6 leader. Thus, for each batch of cell a document including a table will be prepared after discussion with all WP2 partner, similarly to table 3, which describes the sample flow for the two first 'fresh' cells to be open at FZJ in January-February 2016.

The two first GEN0 cells will be sent to FZJ in January 2016, one prismatic 17 Ah and one prismatic 5 Ah. 2 others GEN0 cells will be opened to CEA. They will be the first cells (after the dummy cells used for training for the opening) to be open. The electrolyte recovery will be attempted with different techniques for each model of cells (as electrolyte analysis is made in bulk and most likely not much design dependent, at least for 'fresh cells').

These cells will serve as reference for all the techniques used to tune the protocol. Also, following the analysis of this first set of fresh cells, partners will have a clearer idea on the time taken for experiments and exploitation of results, which will serve as a base for planning the analyses of aged cells, which will be decided for each cell in monthly conference calls.

Definition of samples within and outside main 'sampling zones'

After their autopsy and splitting into samples, the different partners will perform the measurements described in part 2. While the most basic measurements (thickness, weight) will be performed extensively in all sampling zones, three sampling zones will be selected for analysis with most of the techniques mentioned (except for porosity measurement and peeling tests, which requires larger surface areas of samples):

1. The sample area the most central in the electrode tab (half width and half length) ('Central zone')
2. A second sampling zone, next to the 'central zone', but rinsed with acetonitrile for comparison 'Central Zone AN'
3. The sample area the closest to the anode current collector tab ('Anode tab zone')
4. The sample area the closest to the cathode current collector tab ('Cathode tab zone')

Size of samples:

Most techniques necessitate only small surface area of components (SEM, SEM EDX, RAMAN-IR, ICP-OES, XRD, XPS). Thus, an (minimal) area of 7 * 2.76 cm will be reserved for these analyses. (See figure 4)

The reassembly of cells will necessitate 1.2 cm disks for half-cells and 1.77 cm disks at max for full Li-ion cells (for anodes). Thus, the electrodes of another area of 8 cm * 2.76 cm will be scrapped on one side for assembling cells with single coated electrodes. If more sample are requested by partners, areas next to the zones will be used.

Figure 4 describes how the samples will be harvested out of each sampling zone.

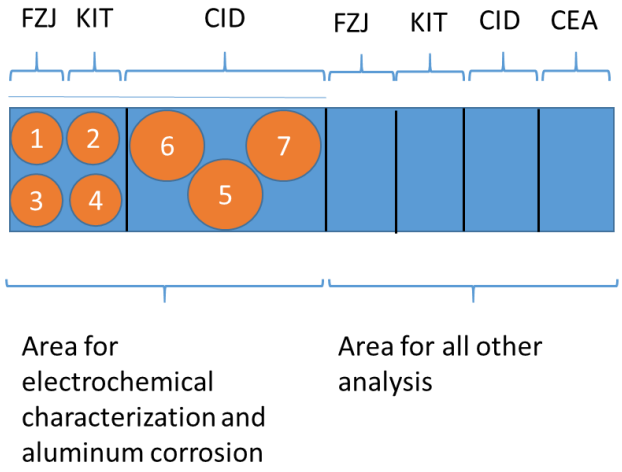

Figure 4. *Description of the sampling within each 'main' sampling zone (square samples will be sent to partners as indicated above.*

However, some measurements will require more sample surface area. In particular, the measure the porosity using a mercury porosimeter requires a larger surface area than the sampling areas defined. Thus, the measure of porosity change will be done on a single sample area (c.a. 300 cm^2 needed, excluding the sampling zone(s) used for other analyses). The sample for the peeling test should be 90 * 20 mm, so for this measurement, sample will be taken as a strip of 2 cm*10 cm. ICP-OES test require 120 mg of electrode, corresponding to between 8 and 17 cm of (single sided) electrode, thus, 20 cm^2 areas (2 *10 cm) will be harvested next to the sampling zones for these analyses as well.

Table 3 describes the sample flow for the two first GEN0 cells that will be autopsied at FZJ and CEA. It also includes an extra 'zone' next to the central area, which will be rinsed using acetonitrile, to see if it is possible to remove more of solid deposits, while keeping an active

SEI. The rinsed electrodes (depending on the effect of the rinsing), will then be subjected to similar analyses to compare the results. The part soluble in AN will be analyzed as well after acetonitrile evaporation.

Table 3. *Sample flow for the first 2 fresh cells to arrive at FZJ in January-March 2016*

Bulk samples	Samples needed per zone	Recipient	Measurements	n° of samples (per cell)
1* Electrolytes	-	KIT	ICP-OES	1
1* Electrolyte	-	FZJ	NMR, MS…	1
1* 300 cm2 separator	-	FZJ	mercury porosimetry	1
1*300 cm2 cathode (double sid	-	FZJ	mercury porosimetry	1
1* 300cm2 anode (double side	-	FZJ	mercury porosimetry	1
Sampling zones (rinsed DMC or AN)				
4 sampling zones	3 * 1.77 mm anodes (Full Li-ion)	CID		
	3* 1.66 mm cathodes (Ful Li-ion)	CID	3 full Li-ion per zone	12
	2* 1.2 mm anodes (half-cells)	KIT		8
	2*1.2 mm cathodes (half-cells)	KIT	4 half-cells per zone	8
	2* 1.2 mm anodes (half-cells)	FZJ		8
	2*1.2 mm cathodes (half-cells)	FZJ	EIS	8
	1* separator	CEA	SEM, SEM-EDX	4
	1*separator	FZJ	XPS	4
	1*cathode	FZJ	XPS	4
	1*anode	FZJ	XPS	4
	1* separator	FZJ	Mac Mullin number	4
	1* anode (120 mg)	KIT	ICP-OES	4
	1* cathode (120 mg)	KIT	ICP-OES	4
	1* anode (1*1 cm)	KIT	RAMAN-IR	4
	1* cathode (1*1 cm)	KIT	RAMAN-IR	4
	1* anode (1*1 cm)	CEA	SEM, SEM-EDX	4
	1*cathode (1*1 cm)	CEA	SEM, SEM-EDX	4
	1*anode (1*1 cm)	KIT	SEM-FIB	4
	1*cathode (1*1 cm).	KIT	SEM-FIB	4
	1* anode (1*1 cm)	CID	XRD	4
	1*cathode (1*1 cm).	KIT	XRD	4
	1* rinsing solution (AN)	FZJ	NMR..	1

4. Conclusion

This deliverable has been extensively discussed during several telephone conference since its first submission to the coordinator and is thus submitted with some delay (but before the first cells are available for autopsy). Indeed, assessing the influence of the cells design on the ageing of the batteries is one of the targets. However, as the number of samples that the autopsy of cells will produce exceed by far the possibilities of analysis, the precise number experiments for each cell must be discussed, with the light of the data already acquired and thus, monthly phone conference will take place for sharing results and deciding on further experiments and/or focusing on techniques that lead to the most valuable information.

Analyzing cells aged in different conditions will allow assessing the influence of test conditions and design. For selected cells (following ageing conditions), the influence of the design will be more precisely screened in attempts to ‘map’ the ageing of cells.

Finally, the reassembly of half and full Li-ion cells and their subsequent electrochemical testing will provide quantitative parameters to feed the modelling tasks, similarly to what will be done on the cells during the ageing tests, with again, more extensive mapping within cells for selected cells(ageing conditions).