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NETWORK OF RESEARCH PILOT LINES FOR LITHIUM BATTERY CELLS

D4.1 Round-robin protocol

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Executive Summary

The overall objective of the LiPLANET project is to create a European innovation and production ecosystem by forming a network of Lithium cell pilot lines that integrates industrial stakeholders and establishes unique selling propositions towards EU industry in support of its market access within the cell manufacturing ecosystem. Moreover, reinforcing the position of the European Union (EU) in the Lithium cell manufacturing market will be further achieved by exploiting synergies between pilot line operators, identifying knowledge and equipment gaps, creating common training and standardization initiatives, and ultimately jointly developing strategies for scaling up the impact of the network.

Standardization initiatives include the definition of an operational protocol to implement the battery cell production process. The protocol will be validated by the execution of a round-robin inter-laboratory (inter pilot line) test that is performed independently by the different pilot lines in the consortium. Thus, the five pilot line partners of LiPLANET project constitute the so called Working Group (WG).

The WG is in charge of defining and providing the standard protocol to be implemented. This should serve as reference test for the qualification of EU-wide battery cell pilot lines, providing comparable results and the basis to analyze the sensitivity of cell properties to production effects.

As known, each pilot line owner has different electrode dimensions and cell formats and, consequently, different energy storage capacity. It has been found that the most comparable is a cell with the same number of electrodes (*i.e.* same stack thickness) rather than a cell with the same energy storage capacity (or same electrode surface area). In that regards, each pilot line should **manufacture cells with the same number of electrodes** to assess the inter-pilot line cell manufacturing reproducibility.

The round robin test will be then performed to determine the reproducibility of those parameters identified as crucial within the lithium battery cell manufacturing process. Independently of the pilot line configuration, they are recognized as key parameters that might influence the final battery cell characteristic. The WG has defined the electrode loading and densification as the standard electrode characteristics to fulfill by a close control of the parameters identified as crucial within the cell manufacturing process.

This preliminary protocol is a living document that will be assessed, revised and updated, if necessary, by an appointed leading pilot line (WG member) before to be implemented as a round-robin protocol.

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1 Introduction

1.1 LiPLANET in brief

The overall objective of the LiPLANET project is to create a European innovation and production ecosystem and reinforce the position of the European Union (EU) in the Lithium battery cell manufacturing market. LiPLANET plans to build a more competitive lithium battery cell manufacturing ecosystem and increase the production of lithium-based cells towards industrial scale, by bringing together the most relevant European Li-ion cell pilot lines and the main stakeholders of the battery sector. The project LiPLANET lays the foundation for a network of battery cell pilot lines in Europe. This network allows exploiting synergies between pilot line operators, identifying knowledge and equipment gaps, organize joint trainings as well as, favor collaboration with industry and academia, and facilitate the access to market.

For this purpose, different activities are followed throughout the project:

- ✓ mapping of the European lithium cell pilot lines and implementation of a network,
- ✓ creation of a standardized legal framework and a data exchange platform for the cooperation between industry, academia and pilot lines,
- ✓ round-robin test to compare qualification methods,
- ✓ development of a roadmap for joint strategies of the network towards industrial scale battery cell production in Europe.

1.2 Scope and objective of this deliverable

The objective of this deliverables is to provide the agreement on the operational protocol for the execution of a round-robin inter-pilot lines test that is to be performed after independent validation by the different pilot line members of the LiPLANET network.

This operational protocol will serve as reference test for the qualification of EU-wide lithium battery cell pilot lines, providing comparable results and the basis to analyze the sensitivity of cell properties to production effects.

The reference operational protocol is consolidated contemplating the

1. Steps of the pilot line production process.
2. Relevant parameters to be measured and controlled.
3. Absolute and relative tolerances to fulfill.

Considering the pilot line production process defined and described in deliverable D1.1 (*Pilot line definitions and terms of reference*) and the capabilities of the pilot lines involved in the round-robin test, the current deliverable provides details about the reference operational protocol to be validated and implemented.

2 General Statements

2.1 Round Robin Test

The scope of the round robin test is the agreement of a working group (WG) constituted by the five pilot lines owned by partners of LiPLANET consortium. They are CIDETEC, TUBS, AIT, CEA and ABEE. All five pilot lines will participate in the implementation and validation of the round robin test.

The round robin test will be performed to determine the reproducibility of those parameters identified as control steps within the lithium battery cell manufacturing process. The key parameters are identified independently of the pilot line configuration, machinery, overall facilities and the manufacturing procedure established by the pilot line operators.

The test will be based on an operational protocol designed and conducted to understand and quantify the possible variations in those key parameters. Besides, it would allow identifying the sources of those variations for optimizing the operational protocol. In that regard, pilot lines might therefore be requested to provide additional information about their facilities and cell manufacturing steps.

The most essential information gather from the round robin test is whether the results achieved in the pilot lines fall within the limits set by the WG, and whether the reproducibility of results is in the satisfactory range for the LiPLANET network.

The goal of this internal operational protocol (round robin test) is then to guarantee reproducibility of lithium battery cell characteristics and, measurements of those relevant control parameters carried out by different lithium battery cell manufacturing pilot line operators belonging to LiPLANET network.

2.2 Definition of process and target parameters

As defined and described in deliverable D1.1, a lithium cell R+D pilot line is capable of developing, testing and optimizing materials and the manufacturing process to properly adapt those to requested electrodes profiles and cell formats fulfilling industrial usual procedures.

The R+D pilot line could be though as a flexible semi-automatic sequential production process where the manufacturing of the lithium battery cell consists basically of **three key manufacturing processes**, namely:

1. Electrode manufacturing
2. Cell Assembly
3. Cell Finishing

Each of the key manufacturing processes is constituted by several sequential steps (definitions can be found in Section 4.4 in deliverable D1.1) which can be controlled by a relevant parameter among others (depending on the quality control implemented by each pilot line operator).

Table 1. Key manufacturing process steps and their corresponding parameters

Process	Step	Parameters
Electrode Manufacturing	Mixing	Mixing time (h) Viscosity (Pa.s) Temperature (°C) Atmosphere (vacuum, clean room, etc.)
	Coating	Coating speed (m/min) Coating width (mm) Coating accuracy (± mm) Production (m/ day)
	Drying	Drying speed (m/min) Length (m) Temperature profile (°C) Air flow (convective direct/diffuse)
	Calendaring	Line pressure (N/mm) Calendaring speed (m/min) Roll temperature (°C)
	Slitting	Cutting speed (m/min) Cutting width (µm)
	Post-Drying	Batch (e.g. vacuum oven)/Continuous (e.g. IR) Pressure (mbar) Drying time (h/batch) Drying temperature (°C)
Cell Assembly	Separation	Cutting/pouching speed (sheet / min) Separation time (s/sheet)
	Stacking (pouch)	Z-folding & single-sheet stacking (cycles s/sheet) Stacking accuracy (µm)
	Winding (prismatic/cylindrical)	Machine throughput (cells / min.) Winding speed
	Electrolyte filling	Dosing method Working pressure (mbar) Consistent, continuous or cyclic filling Control of the electrolyte quantity
Cell Finishing	Roll pressing (pouch)	Pressure (mbar) Process time (s / cell)
	Formation	Process duration (h) Resistances (Ohm) Capacity (Ah)
	Aging	SOC at the beginning (%) Aging time (days) Temperature range (°C) Internal resistance (Ohm)

Those steps should be controlled to assure and guarantee internal / inter-pilot line reproducibility. That control is done by measuring a parameter identified as relevant for quality control. Thus, conducting the internal operational protocol will enable defining the key parameter(s) which can affect the final characteristics of the lithium battery cell. Furthermore, it will prove the importance of round robin tests for the battery quality improvement and comparison of the qualification of the lithium cell pilot line process properties and performance.

It is worth to mention that during the data sharing for checking the inter-pilot line reproducibility, information on type of machinery and the corresponding producer might be required. This information would help to compare the results among pilot lines.

2.3 Relevant steps and parameters to be controlled

Among all steps and parameters described above in Table 1, the WG has appointed few of them as relevant to measure and carry out a close control during the manufacturing process. Those selected parameters will serve as internal control and as inter-pilot line comparative.

Based on their potential effect on the final cell characteristics, the relevant steps and parameters selected are described in Table 2.

Table2. Key parameters to be measured and controlled

Step	Control	Tolerance
Mixing	Viscosity (Pa.s) Solid content (wt. %)	≤ 5 % ≤ 1 %
Calendaring	Thickness before / after (µm) Porosity (%) Degree of densification (g/m^3)	3 – 4 / 1.5 – 2 ≤ 2 % ≤ 3 %
Stacking	Electrodes alignment (mm)* Stack thickness (mm)	≤ 0.3 ≤ 0.1
Electrolyte filling**	Weight (before vs. after) (g) Resistance (Ohm)	≤ 0.2 g ≤ 2 %
Formation	Capacity (Ah) Resistance (Ohm) OCV (V)	≤ 2 % ≤ 2 % ≤ 2 %

(*)*Visual inspection of tab and separator alignment control through periodic intervals will be adequate since the assembling unit should be accurate enough.* (**)*Electrolyte storage period must be controlled and reported. An amount of 5 ml/Ah is recommended.*

The control of these parameters will help to meet the standard characteristics defined for the positive and negative electrodes; they are the electrode loading and densification (Table 3).

Table 3. Targeted electrode characteristics

Standard Characteristics	Positive Electrode	Negative Electrode	Tolerance
Loading (mAh/cm^2)	3	3	≤ 5 %
Densification (g/m^3)	3.1	1.4	≤ 3 %

3 Methodology of the operational protocol

3.1 Conduct, sample handling and consumables

All tests must be conducted in strict accordance with the operational protocol procedure and must be completed within the time frame specified by the WG. Any additional instructions from the WG related to the particular round robin must be followed. All tests at a particular pilot line shall be conducted by the same operator(s) using the same equipment.

All the pilot lines must use identical batches of key materials (*viz*. active materials and electrolyte). Those materials that are expected to be stable may be stored, subdivided and distributed by the appointed responsible. However, less stable materials like the electrolyte may be obtained directly from the supplier, but care must be taken to ensure that all pilot lines use the same batch during test validation.

Less crucial materials like the conductive agents, binders, solvents, current collectors, structural materials for the cell manufacture (*e.g*. housing, tabs, alf, etc.) could come from different manufacturers or from different batches. Such consumables may vary from pilot to pilot line and even, over the course of time, within a pilot line. Therefore, pilot lines remain free to use different manufacturers and batches of those materials.

3.2 Implementation of the protocol

In order to analyze the capacities and the reproducibility of the cells manufactured at the different pilot lines, the chemistry and the format of the cells is pre-defined, with the constraint of selecting non-competitive technologies, so that all gained results of the round robin tests are free for being published and accessed with no restrictions of the involved parties.

Preventively the LiPLANET consortium has agreed to focus on one chemistry, Generation 2b NMC 622, and three cell formats:

1. Coin cells or single-cell pouch cells (for comparing the electrodes and in particular the cathodes manufactured in the different pilot lines).
2. Cylindrical cells (as a representative industrial format).

3. Pouch cells (as a representative industrial format).

The pre-selected cylindrical format for the cell is 18650.

Each pilot line has to produce 5 coin cells, 20 pouch cells, and (when possible) 20 cylindrical cells.

The pouch or cylindrical cells have to be produced in two trials of 10 cells each to assess internal reproducibility. Each trial includes from slurry preparation to cell formation.

In order to assess the inter-pilot line cell manufacturing reproducibility, each pilot line should **manufacture cells with the same number of electrodes** (*viz*. same final stack thickness), regardless the capacity of the final cell.

In order to harmonize the cell manufacturing and facilitate the assessment of the inter-pilot line reproducibility, the following guidelines must be followed:

1. **Materials**: key materials have to be purchased from the same provider and batch. Appointed providers will be selected by the WG. New members of LiPLANET network shall validate the key material prior to use. Other materials, although they could come from the same provider, can be acquired independently by each pilot line owner.
    a. **Key Materials:**
        i. Cathode active material: **NMC622**
        ii. Anode active material: **Artificial graphite**
        iii. Electrolyte formulation: **EC:EMC 3:7, 2%VC**
    b. **Other Materials:**
        i. Cathode binder: **Solef 5130**
        ii. Cathode conducting agent: **C65 + SFG6L**
        iii. Cathode current collector: **Aluminium 15 µm**
        iv. Anode binder: **CMC/SBR (2:1)**
        v. Anode conducting agent. **C45**
        vi. Anode current collector: **Copper 12 µm**

2. **Slurry preparation**: Independent of the mixing device characteristics owned by each pilot line, the solid content (wt. %) and the slurry viscosity (Pa.s) will be the parameters to be

measured by each pilot line operator. If needed, this data will be provided for future correlation among the pilot lines.

a. **Electrode formulation:**

   i. Anode formulation: **94 – 3 – 3**

   ii. Anode solvent: **water**

   iii. Cathode formulation: **95 – 2.5 – 2.5**

   iv. Cathode solvent: **NMP**

b. **Controlled parameters**:

   i. Solid content (wt. %): ≤ 1 %

   ii. Slurry viscosity (Pa.s): ≤ 5 %

3. **Electrode coating and Calendering:** Coating parameters like gap, coating speed or drying temperature, will be controlled by each pilot line based on its own manufacturing procedure. Each pilot line has to be able to coat a continue electrode with the same loading (mAh/cm^2), thickness and degree of densification (see Tables 2 and 3 above).

   a. **Electrode characteristics:**

      i. Anode loading(mAh/cm^2): 3 ± 5 %

      ii. Anode densification (g/cm^3): 1.4 ± 3 %

      iii. Cathode loading(mAh/cm^2): 3 ± 5 %

      iv. Cathode densification (g/cm^3): 3.1 ± 3 %

   b. **Controlled parameters:**

      i. Thickness before/after (μm): 3 – 4 / 1.5 – 2

      ii. Porosity (%): ± 2 %

      iii. Degree of densification (g/cm^3): ± 3 %

4. **Cell assembly**: each pilot line may have different electrode dimensions and cell format. That means that each electrode has different energy storage capacity. In order to assess the cell manufacturing reproducibility and compare among pilot lines, the **WG has agreed to manufacture cells with the same number of electrodes**, regardless the capacity of the

final cell. It has been found that the most comparable is a cell with the same number of electrodes (*i.e.* same stack thickness) rather than a cell with the same energy storage capacity (or same electrode surface area).
Structural materials (*viz*. housing: tabs; separator like2325/2320 Celgard or FS3011 Freudenberg; alf; etc.) for cell manufacturing will be selected by each pilot line. Nevertheless, for protocol validation, the separator to be used will be initially CELGARD 2325.

a. **Defined formats:**

i. Cylindrical format : 18650

ii. Pouch format: 10 cathodes

b. **Controlled parameters**:

i. Electrodes alignment (mm):	≤ 0.3
ii. Stack thickness (mm):	± 0.1

5. **Electrolyte filling**: each pilot line may have a different electrolyte filling procedure. During this step, a distinction must be made between the sub-processes *filling* and *wetting*. To achieve a maximal wettability, it is important that the electrolyte completely permeates and fills the pores in the separator and electrode. The calendering step will inevitably influence the wettability because it alters the porosity and particle distribution. However, control of the weight (before/after filling) and internal resistance will be performed and reported. **(*)** ***Initially an amount of electrolyte of 5 ml/Ah is suggested***.

a. **Electrolyte*:**

i. EC:EMC 3:7, 2 % VC

b. **Controlled parameters**:

i. Electrolyte quantity (g):	± 0.2
ii. Resistance (Ohm):	± 2 %

6. **Formation**: It will describe the first charging and discharging processes of the battery cell. There are different procedures for the formation depending on the cell manufacturer and on cell application. Care must be taken since the procedure applied may impact highly the cell performance. **(*) In order to validate the operational protocol, the WG has agreed to set one preliminary standard protocol**.

a. **Preliminary set protocol*:**

   i. Capacity: @ C/2 to 2.7V cutoff. Charge: CC @ C/3 at RT to 4.2 V; CV to C/30 cutoff current. Rest: 15 min.

   ii. Resistance: 10s discharge @ 2C starting at 3.6V during the C/2 discharge above.

   iii. Formation: 2x full cycles between the nominal cutoff voltages of 2.7 V and 4.2 V with C/20, for both charge and discharge at RT without CV phase and without rest time in between cycles.

b. **Controlled parameters**:

   i. Capacity (Ah)
   ii. Resistance (Ohm)
   iii. OCV (V)

3.3 Data transfer

The WG will provide a data entry spreadsheet which is designed to collect and analyze easily the results from the different pilot lines. Nevertheless, close attention must be paid to how data is presented, including, *e.g*. machinery; cell code; date; time; etc.

The pilot line operators would provide its results as follows:

Supply to WG database responsible the complete set of test results generated during the round robin via the spreadsheet within an agreed time scale.

All requested information must be provided and all problems both in individual tests and overall shall be recorded.

Pilot line operator identifies their own results, in line with the data confidentiality rules established by LiPLANET consortium (WP2).

4 Final Statements

The above described protocol is a living document. It will be initially implemented by the appointed leading pilot line. Based on the outputs, the protocol would be updated, optimized and validated. Therefore, above-mentioned suggested parameters to control and measure might change during protocol validation.

To implement this operational protocol to all pilot line members of the LiPLANET network, this preliminary protocol will be validated by the partners of the LiPLANET project.

Initially, the appointed project leading pilot line will conduct several times the protocol to validate the results and ensure its internal reproducibility. If the reproducibility of the results is not achieved, the operational protocol must be revised and updated, accordingly. In case of reproducible results, the definition of the operational protocol can be set and then, transferred to the other pilot line partners for implementation and validation.

Future members of LiPLANET network will be asked to carry out the operational protocol for at least one cell format.