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Interim results of the H2020 3beLiEVe project: battery material selection, cell prototyping, battery module and pack design and manufacturing process modelling for Generation 3b LNMO cells

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Abstract

This paper presents selected interim results of the H2020 project 3beLiEVe, which aims to deliver next-generation Lithium-Nickel-Manganese-Oxide (Generation 3b) battery cells for automotive applications, encompassing research activities across three pillars: (i) Selection and optimisation of the cathode (LNMO) and anode (Si/C) materials, as well as the high-voltage electrolyte, (ii) development and integration of cell-internal and external sensors, and demonstration at cell, module and pack level, (iii) demonstration of large-scale manufacturing capability and compatibility with a circular economy. This article shows selected results of the project achieved so far in these three pillars, aiming to inform the scientific community about some of the latest achievements of European research on Generation 3b Li-ion batteries.

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Keywords: Generation 3b; LNMO; Li-ion battery cell, module, pack; battery sensors; battery manufacturing;.

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Nomenclature

AM	Active Material
C65	SUPER C65 conductive carbon black powder
CMC	carboxymethyl cellulose
CMU	Cell Management Unit
EBS	External Body Sensor
EES	External Electrode Sensor
LFP	Lithium Iron Phosphate
LiBOB	Lithium bis(oxalato)borate
LiFSI	Lithium bis(fluorosulfonyl)imide
LNMO	Lithium-Nickel-Manganese-Oxide
NMP	N-Methyl-2-pyrrolidone
PVDF	polyvinylidenefluoride
SBR	Styrene-Butadiene Rubber
Si/C	Silicon-graphite (composite)
SLM	SENSIPLUS Learning Machine

1. Introduction

Road transport can play a key role in the urgently needed decarbonisation of transport. More than some other sectors, it has the potential for quick carbon reduction by 2050. Light duty vehicles are already well on their way to electrification, with most of the European brands offering a wide range of hybrid and fully electric vehicles among their fleets, with increasing shares of electric models expected across the portfolios. Research and innovation continue to bring forth improvements in all technological areas of the automotive sector. Among these, batteries are a field where major improvements are expected, increasing energy and power density of the upcoming Li-ion generations, while decreasing manufacturing costs and ultimately increasing affordability of electric vehicles.

3beLiEVe (EU Commission CORDIS, 2021) is a research and innovation project funded under the topic H2020 LC-BAT-05-2019 (EU Commission, 2019). It aims to deliver next-generation Lithium-Nickel-Manganese-Oxide (LNMO) cells, in line with the performance objectives of the "generation 3b" Li-ion battery cells, as per EU SET-plan Action 7, (EU Commission, 2022). The project is executed by a consortium of 21 European partners from 9 different EU member states plus an associated country, receiving an EU contribution of approximately 10.8 million €. The project is built around three technical pillars:

- development of a next-generation 3b material formulation consisting of a LNMO cathode combined with a high voltage electrolyte and a 10-20 wt.% Si/C anode;
- engineering and delivery of cell-internal and external sensors to monitor relevant electric, thermal, and mechanical cell parameters, used to enable advanced diagnostic and operational functions in the battery management system (BMS) and govern the adaptive liquid cooling system of the battery pack;
- development of battery technology to be compatible with a circular economy, encompassing the material selection, the cell and battery large-scale manufacturing processes, optical in-line quality inspection of coated electrodes, battery testing in first and second life, and its dismantling and recycling phases.

The 3beLiEVe cell technology aims to achieve gravimetric and volumetric energy densities of 300 Wh/kg and 750 Wh/l respectively, combined with the capability of 2,000+ deep cycles of which 10% at 3C+. A production cost of approximately 140 €/kWh (calculated based on production at scale above 10 GWh/year by 2030) is targeted at cell level, to be reduced to 90 €/kWh by factoring-in the residual value coming from the cells' second life application and the material recycling. Concerning end-user applications, the 3beLiEVe technology primarily addresses the automotive sector, with applications for light and heavy-duty vehicles.

3beLiEVe is, at present, in its third project year. This paper presents selected interim results under the three technical pillars above and as per first quarter of 2022.

2. Results of 3beLiEVe pillars

1.1. Pillar-1: Material selection, upscaling and delivering of the 3beLiEVe prototype cells

Several LNMO cathodes (Lithium-Nickel-Manganese-Oxide), Si/C composite anodes and high voltage electrolyte candidates have been screened as part of the 3beLiEVe activities under Pillar-1, with the aim of selecting the best performers against the project targets. The preliminary LNMO cathode selection was performed based on chemical/structural analysis as well as electrochemical performance vs. Li/Li^+ at materials level. In addition, NMP and water-based slurries, and electrodes with high active material loading were prepared with representative formulations for subsequent scale-up and large cell assembly using selected LNMO candidates. Electrodes with >3 mAh/cm^2 were achieved for the selected LNMO cathode, reaching 300 cycles with more than 80% of capacity retention. The most suitable anode was selected based on the cycling performance at half-cell level of several carbon-based composites containing 15-to-40 % of Si, varying the microstructure and the dopants of the compounds. As a compromise between high capacity and long-term stability, a candidate with 15 % Si-composite was selected. Finally, the addition of LiBOB additive (Lithium bis(oxalato)borate) to the high-voltage electrolyte containing LiFSI (Lithium bis(fluorosulfonyl)imide) showed a significant improvement in the cycling stability of the LNMO||Si/C cells.

Several LNMO cathode candidates have been screened, namely LNMO #1, LNMO #2 and LNMO #3. According to phase structure and microstructural analysis, the main differences between the three LNMOs are the structural ordering as well as the morphology of the components. LNMO #1 and LNMO #2 crystallize in the disordered spinel phase in which the transition metal cations are randomly distributed on the transition metal atomic sites of the structural framework, while LNMO #3 shows an ordered spinel phase, where Mn and Ni predominantly occupy distinct, specific sites. In terms of morphology, LNMO #2 differs strongly from LNMO #1 and LNMO #3, which have spherical polycrystalline particles with an average diameter of 10 µm. LNMO #2 is composed of single crystals of 3 µm.

The cycling performance of the three LNMO candidates was evaluated in CR2032-type coin cells vs Li^+/Li using LP30 electrolyte. A rate capability test up to 3C was performed before the cycling stability test at 1C in a voltage range between 3.5 and 4.8 V (5.0 V in the case of LNMO #3 due to the slightly higher charge plateau of this component, as per Figure 1-(a)).

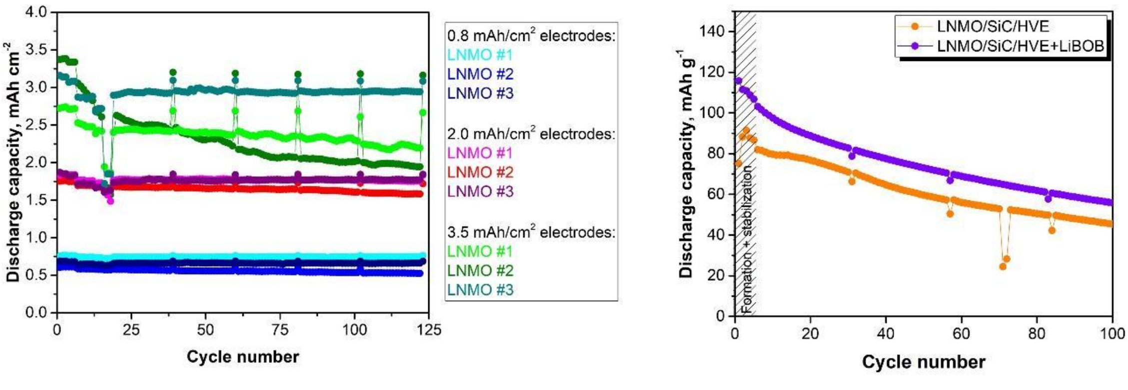


Figure 1. a) rate capability and cycling stability test for LNMO #1, LNMO #2 and LNMO #3. Color code: blue (0.8 mAh/cm^2 electrodes), pink (2.0 mAh/cm^2 electrodes) and green (3.5 mAh/cm^2 electrodes); b) cycling performance of LNMO||Si/C cells with LiFSI (orange) and LiBOB (violet) additive containing high voltage electrolytes.

NMP-based electrodes prepared with high AM and solid content (ca. 93% AM and 70% solid content) with AM loadings of ca. 0.8, 2.0 and 3.5 mAh/cm^2 were tested. All the laminates showed the characteristic voltage profile of LNMO with initial discharge capacity values above 130 mAh/g irrespective of the LNMO type and AM loading. LNMO #2 exhibited higher rate capability characteristics. However, for highest-AM-loading electrodes, the cycling stability deteriorated. Specifically, the capacity retention after 100 cycles of the low-AM-loading electrodes was

81-91%, that of the intermediate-AM-loading electrodes was 88-94% whereas that of the high-AM-loading electrodes was 68-75 %. The capacity retention after 100 cycles of the LNMO #3 was close to 100% irrespective of the AM loading. Similarly, the capacity retention of the LNMO #1 was close to 100% for low and intermediate AM loading electrodes while it decreased to 79-90% for high AM loading ones. Going one step further, LNMO #1 electrodes with >3 mAh/cm^2 reached 300 cycles with more than 80% of capacity retention. Moreover, for intermediate AM loading electrodes (ca. 2.5 mAh/cm^2), aqueous formulation-based electrodes showed approximately 225 cycles of stable performance before starting to fade. Similar to the cathode candidates, the Si/C composite anode active materials with 15 and 30% of Si content were subjected to an exhaustive material characterization. The Raman spectra of the two candidates show that the presence of highly crystalline Si is salient, reflected by the sharp spectral feature at 516 cm^{-1}. The powder morphology shows random particle shapes of graphite with average size of 5-30 µm decorated with smaller Si-rich particles of around 10 µm. With the aim of optimizing the cycling stability, the anode material with 15% of Si was selected for slurry and electrode fabrication optimization. Those electrodes provided initial capacity of 500 mAh/g and ca. 100 cycles with capacity retention >80% at C/10 when cycled in half cell configuration vs Li^+/Li using the LiFSI containing electrolyte. To assess the cycling stability of the full cells, selected LNMO and Si/C were coupled in single-layer pouch cells with an electrolyte containing LiFSI, as well as an alternative one containing a LiBOB additive. An improvement in the discharge capacity was observed with the addition of the LiBOB additive (Figure 1-(b)), based on the improved initial capacity value from 90 to 115 mAh/g, while no significant effect on the cycling stability was detected.

The scale-up activity to pouch cell level was performed in overlap with the material selection. For this scale-up, a fourth LNMO (LNMO #4) was selected. It is morphologically nearly identical to LNMO1 and exhibited very similar electrochemical and processing (coating) properties. The scale-up process was validated in 7-layer pouch cells consisting of 3 cathodes and 4 anodes with a double-sided coated area of 7 cm × 10 cm, resulting in a nominal capacity of approximately 1Ah. To achieve the target volumetric energy density of 750 Wh/liter, and given the final cell format, the required stack properties were calculated. It calls for electrodes with 4 mAh/cm² loading in 77 Ah cells. It should be noted that for manufacturing reasons, the project has opted for a final cell capacity in the order of 30Ah, i.e. a smaller stack but with same electrode properties. On the pre-production pilot scale, the electrochemical tests with this loading in a 7-layer pouch cell, after formation and at 0.5 C, exhibited a specific first-cycle discharge capacity of approximately 65 % of the expected one. The reversible specific discharge capacities for LMNO #4 cathodes and Si/C anodes were measured in half cells and were 135 mAh/g and 550 mAh/g respectively, and were used to calculate the areal loading. It is assumed that the high areal loading leads to conductivity problems within the cathode, especially at C-rates higher than 0.2 C (Li & Al, 2020). To test this assumption, electrodes with 2.5 mAh/cm² were coated and tested for comparison. Measurements showed that the reduction of areal loading resulted in a significantly higher specific discharge capacity and improved the capacity retention over 200 cycles at 0.5 C, as depicted in Figure 2.

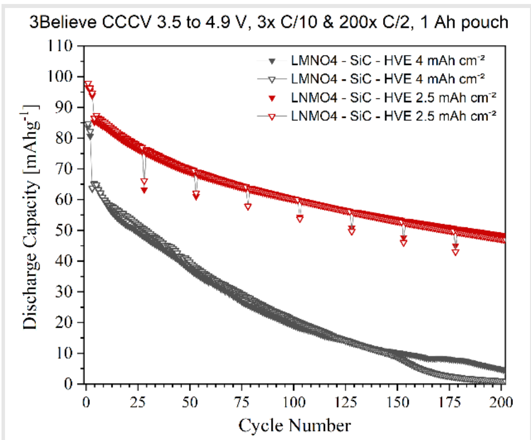


Figure 2. Comparison of specific discharge capacities measured in LMNO #4//Si/C 1Ah pouch cells with 2.5 mAhcm^{-2} and 4 mAhcm^{-2} areal loading, N/P 1.0. Constant current and constant voltage (CCCV) capacity retention test with 3 cycles 0.1C and 200 cycles 0.5C, cells with low loading were additionally cycled at 1C every 25th cycle.

Although the energy density of high-loaded cathodes is intrinsically higher on a theoretical basis, the results show that reducing the areal loading led to an energy density increase in practice, caused by a significant increase in specific discharge capacity. Therefore, electrodes with 2.5 mAh/cm² loading are used to achieve the energy density target. Pouch cells with 1 Ah capacity were assembled to determine the current progress in electrochemical performance. Double-sided electrodes were used, which were successfully scaled up from lab parameters to a 1.5 litre batch size processed in a planetary mixer. The best-performing cathodes used the formulation 93:4:3 [wt%, LMNO #4:C65:PVDF] whereas the optimum found for anodes was 94:2:2:2 [wt%, SiC:C65:CMC:SBR]. With those components, preliminary values of 450 Wh/l were achieved, calculated based on a nominal voltage of 4.75 V and the stack volume. Two reproducible cells were cycled over 200 cycles at 0.5 C; their volumetric energy density and columbic efficiency are plotted in Figure 3. The initial energy density of 400 Wh/l at 0.5 C decreased to 225 Wh/l after 200 cycles, showing a continuous capacity decrease. The columbic efficiency above 99.5% over 200 cycles indicates a stable cell performance. The discharge rate capability was investigated at 1 C every 25th cycle and indicates good usability for automotive applications. An increase in cell performance is expected with a new electrolyte formulation on which the 3beLiEVe consortium was working at time of writing.

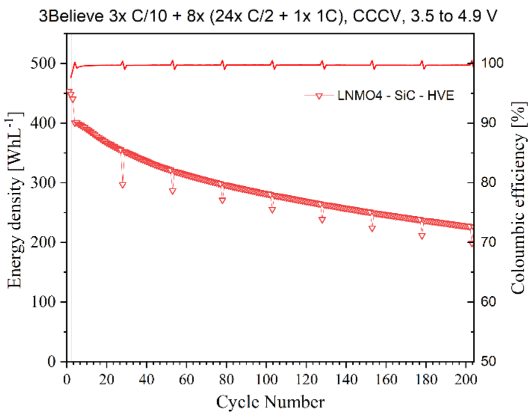


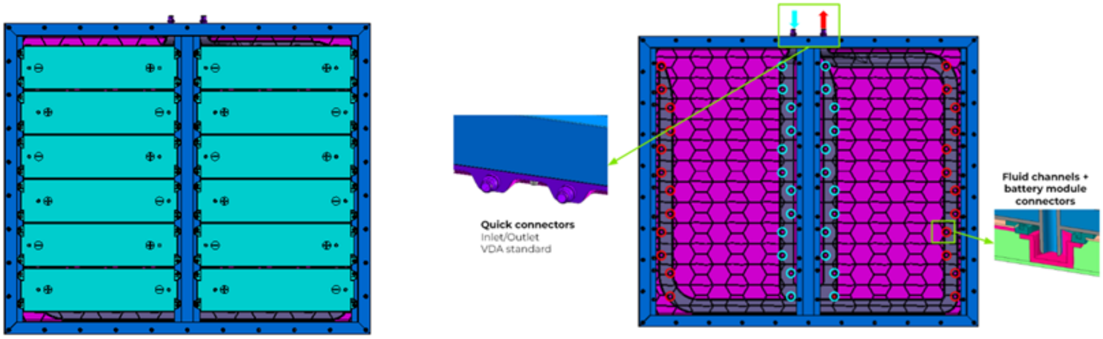
Figure SEQ Figure * ARABIC 3. Volumetric energy density and columbic efficiency of a represantative 1Ah LMNO4//Si/C pouch cell with 2.5 mAhcm⁻², N/P 1.0. CCCV retention test with 3 cycles 0.1C and 200 cycles 0.5C, 1C every 25th cycle. REF _Ref103147014 \h Table 1 shows the values for energy density calculations.

Table 1. Values for energy density calculation

Stack area	70 cm²
Cathode thickness	173 µm
Anode thickness	93 µm
Separator thickness	20 µm

1.2. Pillar-2: Battery module and pack design, including sensors

The 3beLiEVe module and battery pack are designed to achieve high integration and efficient thermal management, while reducing the weight and improving ease of disassembly and subsequent recyclability.

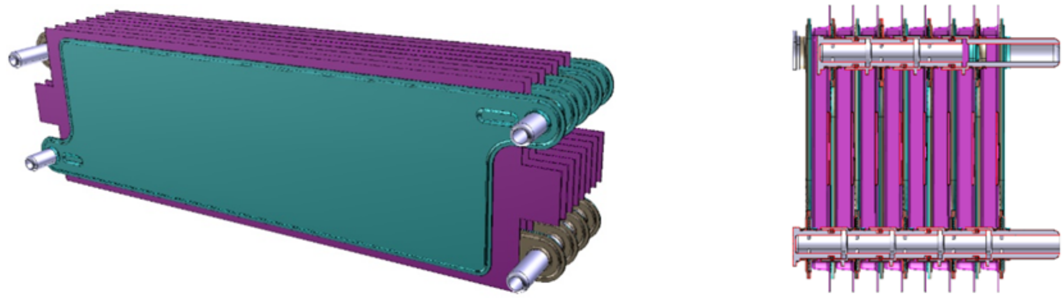


(a) (b)

Figure 4. a) battery pack layout overview; b) integration of the coolant distribution.

The design activities encompass the development of new materials and manufacturing processes, employing thermoplastic organosheet composites strengthened with an integrated aluminium frame, and the integration of the cooling system in the battery case, allowing for the direct “plug-and-play” of the modules in the pack. The layout of the battery pack and of the coolant distribution is depicted in Figure 4, and it is based on an 8S (eight cells in series) module architecture, selected based on the best compromise with the envisaged cooling system. Organosheet composite covers allow for a smart and compact integration of the several fluid cooling lines and connections required for each battery module, while offering the required protection against stone impact and road debris and a weight reduction of approximately 10% compared to a conventional aluminium battery pack. Given the 3beLiEVe pouch cells are natively designed with a silicon anode, swelling is expected to occur. Preliminary estimations indicate an increase of the cell thickness up to 7% in operating conditions. The cooling system is designed to tolerate this effect, while sustaining constant contact strength and retaining its thermal exchange performance.

The concept allows for a degree of freedom between each cooling plate in the transversal direction. A tensor system is integrated at each side of the cell stack, while the coolant leakage risk is limited with the use of dual static joins to connect the cooling plate nozzles between them. Cooling plate parts, male and female nozzles, plates, and internal fins are brazed together to simplify the manufacturing. The system is depicted in Figure 5 and it can tolerate a cumulative swelling for the eight-cell stack of ± 4.5 mm.



(a) (b)

Figure 5. a) cooling system overview for 1 module; b) Cooling system flexibility overview.

3beLiEVe also encompasses development activities on three types of sensors: (i) the NXP MC 33775A chip (external), (ii) the Insplorion internal opto-electronic sensor and (iii) the Sensichips SENSIPLUS chip (external). The Insplorion sensor consists of a light source and a receiver integrated in a PCB, connected via an optical fibre shaped in a small loop. The fibre is placed between electrode layers and the PCB is sealed into the cell’s pouch foil on one edge. First sensor integration tests showed that PCBs can be integrated in an industry-oriented manufacturing process. Using optical fibres integrated in pouch cells, approximately 1,000 hours of optical data was gathered in four different LMNO//Graphite pouch cells. The Sensichips SENSIPLUS consists of an on-cell chip-based cell management unit (CMU) capable of multiple in-operando measurements. A complete system composed of the CMU, two external electrode sensors (EES) and an external body sensor (EBS) mounted on a 5Ah pouch cell is depicted in Figure 6.

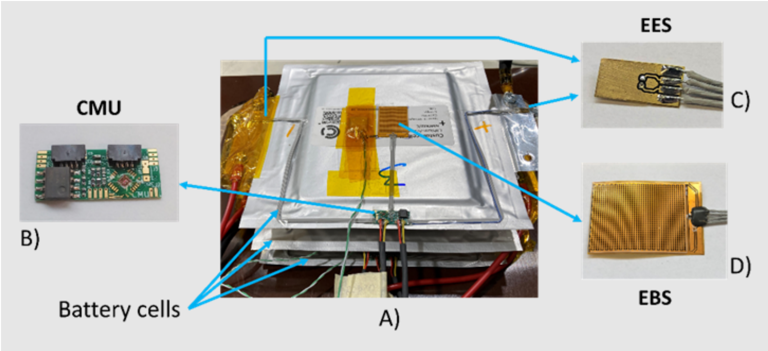
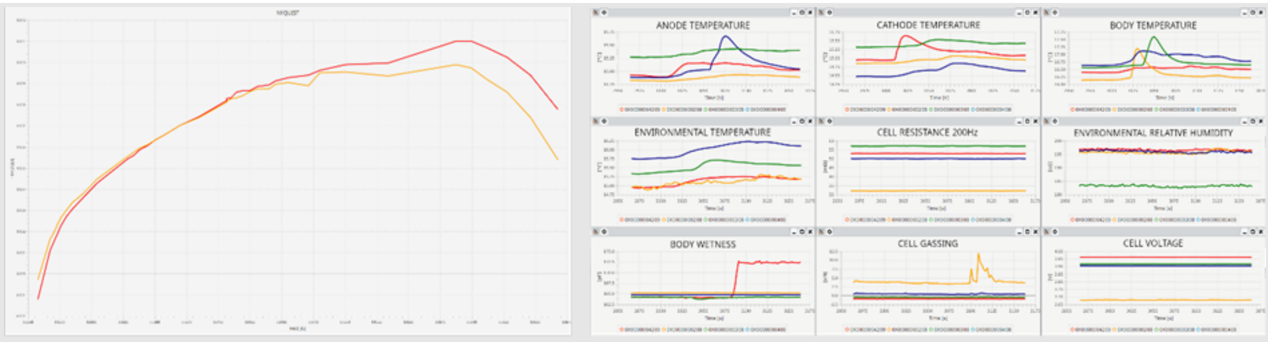


Figure 6. a) Sensiplus complete system, including b) CMU, c) external electrode sensors (EES), and d) external body sensor (EBS).

The EBS is composed of a commercial negative-temperature-coefficient (NTC) resistor (Panasonic ERT-JZEV104F) and a custom comb-finger capacitor used to detect moisture. Two EESs must be used with the CMU: one is soldered to the cathode tab and the other to the anode tab. They provide the supply voltage to the CMU electronic circuits and are used to measure the electrodes' temperatures (thanks to the same NTC used on the EBS) and the internal cell impedance. The CMU is based on the SENSIPLUS microchip, which includes an electrochemical impedance spectrometer with lock-in amplifier, a potentiostat/galvanostat along with on-chip sensors for temperature, relative humidity, and gassing. Multi-sensor measurements are cross-correlated by the SENSIPLUS Learning Machine (SLM) and streaming minimal processed data to the battery management system (BMS). A proprietary software allows easy control of the collected output data with a simple graphical interface for both Microsoft Windows and Linux-based systems. For example, Figure 7-(a) shows the internal cell impedance Nyquist graph in the range 5Hz – 20kHz, but the chip can acquire a spectrum from 100mHz to 2.5MHz. Figure 7-(b) represents a screenshot of nine different, simultaneous measurements. In both cases, each graph shows the output data of multiple CMUs operating concurrently, represented by different line colours. The CMU is chemistry independent; it can be used with various Li-ion chemistries, supercapacitors and fuel cells.



(a) (b)

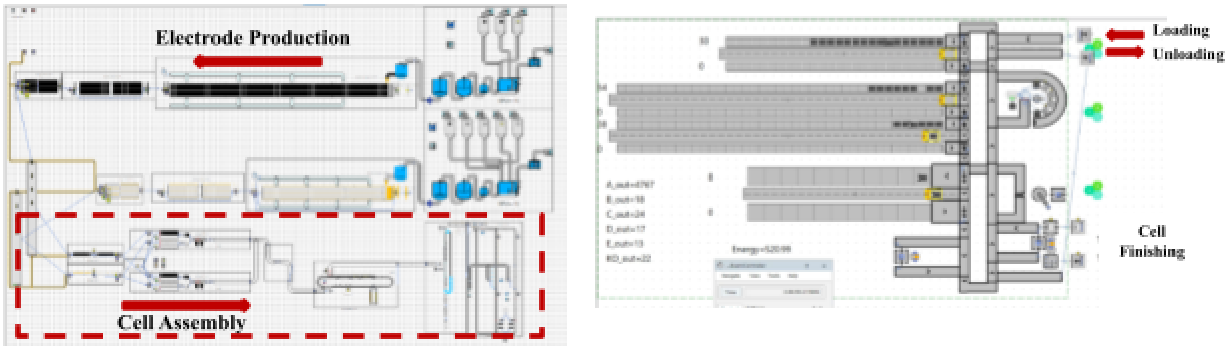
Figure 7. (a) internal cell impedance Nyquist graph in the range 5Hz – 20kHz performed on two cells simultaneously; (b) screenshot of nine different measurements (four temperatures, internal cell impedance at 200Hz, relative humidity, body wetness, cell gassing and cell voltage) performed on four cells simultaneously.

1.3. *Pillar-3: Design and simulation of the large-scale manufacturing process (gigafactory level)*

To understand the requirements for and implications of gigawatt-hour-scale factory production of the developed technology, 3beLiEVe encompasses the design and simulation of LNMO cells at a "gigafactory" level as an integral part of its research activities. Here, the manufacturing processes and methods for electrode production, cell assembly, and finishing have been simulated using the Tecnomatix Plant Simulation 15 software, virtualizing a 10

GWh/year gigafactory based on 3beLiEVe cell chemistry via an appropriate process chain model. In the first phase, a single production line was devised that includes all units required for 3beLiEVe cell production. Once the single production line has been defined and validated, additional production lines will be placed in parallel to achieve the targeted capacity of 10 GWh/year. The model includes essential machine parameters controlling the process flow by considering the intermediate product parameters at each step. The production lines were assumed to be operative 300 days/year in three shifts. The model enables the definition of logical material flows inside each unit based on 3beLiEVe cell requirements and calculates in real-time the energy consumption of existing units in the cell production lines while also incorporating randomly distributed machine failures. The model enables understanding of the complex interactions between different units in a gigafactory environment, managing the resources, increasing the machine throughputs, optimizing the layout of the factory, and improving the material flow while eliminating jams and reducing scraps. Three main production zones of the factory producing the 3beLiEVe pouch cells are depicted in Figure 8.

The electrode production area comprises mixing, coating, drying, calendaring, and slitting processes (Figure 8-(a)). The mixing unit was modelled via a smart dosing system, mixers with a total capacity of 750 litres, and buffering tanks to guarantee continuous feeding of the coating process. A portioning system was devised to resemble the slot-die coating of the electrode slurries at the beginning of the coating and hot-airflow drying process. A coil width of 1,450 mm was chosen for both anode and cathode.



(a) (b)

Figure 8. Production areas of 3beLiEVe battery cell manufacturing: (a) electrode production and cell assembly lines; (b) cell finishing.

This choice enables us to extract four slit coils out of each master coil and minimizes the scrap rates. Cell assembly processes take place inside the dry room atmosphere, denoted by dashed lines in Figure 8-(a). Technical input data were derived from Manz automated machines. A roll-to-roll mechanical notching machine with a maximum speed of 1 m/s was used to notch the slit coils. The lamination and stacking machines equipped with auto-splicing units were followed to produce axial monocells with a maximum speed of 800 mm/min. The stacked cells were fixed in a taping machine followed by a tab trimming and welding process. The deep-drawn pouch foils accommodate the electrode stacks in the packaging unit; the resulting packaged cells are then sealed and trimmed. The electrolyte filling machine can fill twelve cells at a time in two parallel lines with a buffering capacity of six cells. The electrolyte-filled cells are transferred to the cell finishing area inside formation trays. The cell finishing area consists of tray exchange, high-temperature aging, room-temperature aging, pre-charge and formation, degassing, and cell grading processes (Figure 8-(b)). A smart conveyor system connects these processes. The aging areas were simulated as high-bay warehouses where stacker cranes moving on rails pick each tray at the entrance and place it on the corresponding rack and, based on the demand by other units, deliver the tray to the conveyor system.

3. Conclusion and future works

This paper presents a selection of the interim results of the H2020 project 3beLiEVe across its three pillars of activities. These findings are not intended to be conclusive, given that the project is scheduled to complete its activities in the course of 2023. Rather, the manuscript provides a snapshot of the 3beLiEVe research activities on the materials, cells, sensors, modules, packs, and manufacturing process modelling, with the aim of informing the scientific community about some of the latest achievements of European research on generation 3b Li-ion batteries and on the common effort of the 3beLiEVe partners towards strengthening the European battery manufacturing industry.

Acknowledgements

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