CELL-INTEGRATED SENSING FUNCTIONALITIES FOR SMART BATTERY SYSTEMS WITH IMPROVED PERFORMANCE AND SAFETY

GA 957273

D 2.3- DEVELOPMENT OF ELECTRICAL CONNECTIONS

LC-BAT-13-2020 - Sensing functionalities for smart battery cell chemistries

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Summary

The following deliverable D.2.3 "Development of electrical connections" describes the activities related to the Task 2.3 of the WP2. More specifically, Task 2.3 focused on the use of the reference electrodes printed on separator Celgard 2500, as described in D2.2, in pouch cell configurations.

To take full advantage of the flat, non-bulky geometry of created printed reference electrode, flat-flex wires assembly and sample wiring have been specifically developed. This approach enabled the novel self-sensing pouch cell prototypes integrating printed reference electrodes for in-situ and in-operando Electrochemical Impedance Spectroscopy (EIS) measurements and accurate monitoring of the cathode and anode potentials.

This deliverable and the related task do not include any deviation from the objectives and timings planned in the Grant Agreement of the SENSIBAT project.

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Abbreviations

Symbol / Abbreviation	
DEC	*Diethyl carbonate*
EC	*Ethylene carbonate*
EIS	*Electrochemical impedance spectroscopy*
LFP	*Lithium iron phosphate ($LiFePO_4$)*
NMC	$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$
PPSU	*Polyphenylsulfone*
WP	*Work Package*

1 Introduction

The main objective of Task 2.3 is to integrate printed reference electrodes, as developed in Task 2.2 onto porous Celgard 2500 separator, into the novel self-sensing pouch cell prototypes. The so-integrated printed reference electrodes enable the in-situ Electrochemical Impedance Spectroscopy (EIS) measurements and in-operando measurements of the electrolyte conductivity and its change during the Li-ion battery operation, as well as the monitoring of cathode and anode potentials, as specifically studied in Task 2.4 and Task 2.5 of the WP2.

The present deliverable describes the work performed in the frame of Task 2.3 regarding the incorporation of printed sensing/reference electrodes into pouch cell configurations through flat-flex wire assembly and wire connections, as also anticipated in deliverable D2.1. The pouch cell sealing avoids the electrolyte leakage during cell operation, while reference electrode must withstand the mechanical stresses occurring on them during cell assembly. The first examples of Li-ion battery pouch cell prototypes were therefore assembled using a NMC 622 cathode, a printed reference electrode on Celgard 2500 separator, $LiPF_6$ EC: DEC (1:1) 1 M commercial electrolyte and a graphite anode.

Preliminary electrochemical characterizations evidenced that the printed reference electrodes are stable in the electrolyte and therefore they do not need to be encapsulated. So, they can interact with the electrolyte to exhibit a controlled chemical state associated to stable and constant equilibrium potentials over times. To validate the reliability of our pouch cell assembly configurations, the performances of reference electrodes were preliminary evaluated through electrochemical analyses, as reported in Deliverable D2.1.

2 Cells assembly

Designing pouch cells is a challenging task that requires meeting simultaneously a set of requirements. Cell characteristics such as energy and power density, temperature range of cell, as well as cyclability and lifetime must be carefully considered for the final assembly. In addition, the assembly must guarantee safe cell operation, while minimizing manufacturing costs.

Pouch cell assembly refers to a proper positioning of the electrodes and the electrolyte into a coffee bag to isolate the internal cell (electrodes, electrolyte, etc.) from the outside (ambient atmosphere). The general requirements for assembling Li-ion pouch cells can be summarized as the following [1].

- High permeation barrier against liquid, vaporized electrolytes, as well as moisture and oxygen of the environment

- Mechanical stability and durability

- Good electrolyte resistance and chemical inertness

- Electrical insulation of the packaging

- Electrochemical stability of the cell during cycling

- Thermal resistance in Li-ion battery operation temperature range (-20/ 60 ˚C)

- Low manufacturing costs

- Easy processability and sustainability

In particular, Li-ion batteries, moisture leads to a reaction of electrolyte with water, forming corrosive and dangerous hydrofluoric acid. Therefore, Li-ion pouch cells must be properly sealed to avoid contacts of their components with ambient air (moisture, oxygen), while maximizing their electrochemical performances and lifetime.

2.1. Flat-flex wires assembly and sample wiring

Coffee bags were used as external packaging for our pouch cell assemblies. To achieve a proper sealing of the coffee bags, it is mandatory to develop flat, thin and flex connections that interfere as less as possible during cell packaging bonding. This process consists of the thermal bonding of the coffee bag edges under external uniaxial pressure, using a commercial bag-sealer. A rigid or too thick connection (i.e., a bulky wire) could cause partial sealing, inducing electrolyte leakage and moisture infiltration inside the cell, compromising cell stability and functionalities over time. Moreover, in some circumstances, connections must be properly insulated, except the terminals, to avoid unwanted electrical contacts when a full cell will be assembled.

To address the above requirements, 5x50 mm pure copper strips (with a thickness of 25 µm) were manually cut off from a commercial copper sheet and a set of 2 identical strips of 5x40 mm of 1-mil Kapton HN tape (polyimide sheet with a thickness of 20 µm) were bonded on the upper and lower surface of the copper strip to ensure electrical and chemical insulation from the surrounding environment (electrolyte) (**Figure 1**). The thickness of the whole assembly should be around 155 µm (65 µm for each Kapton tape and 25 µm for the copper layer), which is reasonable for the subsequent embedding in standard pouch cell bags during the sealing process. Then, the flat-flex wires were carefully aligned on the sensing electrodes printed on Celgard 2500 (see deliverable D2.2) and manually bonded using a layer of the same Kapton tape. A second identical layer of

Kapton tape was bonded on the opposite face of the Celgard separator, acting as stiffener to ensure proper electrical contact between the two parts (*i.e.*, to avoid the electrolyte permeating directly in the copper-printed layer junction causing connection failure). Finally, a piece of Celgard 2500 with the same dimensions of the sensing electrode-coated one was attached on the upper side of the whole assembly to simulate the real configuration in the cell. Upper Celgard was therefore used like an electrolyte-permeable electrical insulator to avoid the short circuit of the printed sensing electrodes within the cell electrodes. The assembly procedures were carried out manually. Therefore, slight differences between the assemblies were possible. Consequently, the process of wiring and assembly was repeated at least two times for each sample to check its reproducibility and reliability.

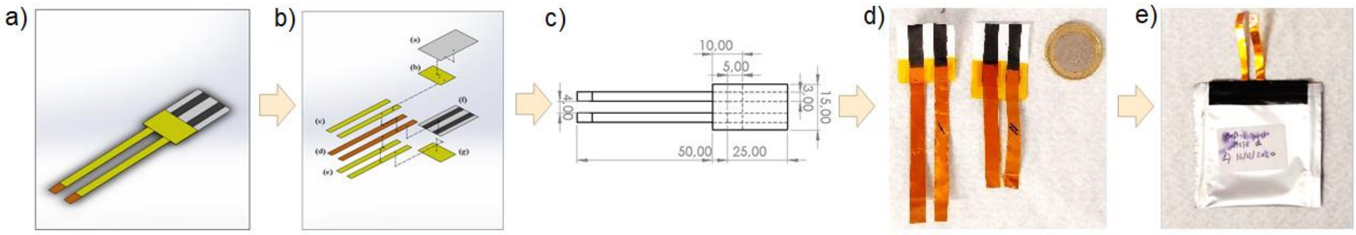

Figure 1. Scheme of the whole pouch cell-like assembly (dimensions are in mm).

2.2. Pouch cell assembly

The pouch cell assembly structure is based on a plastic laminate technology with the following properties:

- Moisture barrier properties to prevent the entrance of environmental humidity into the pouch cell, causing deleterious chemical reaction involving the electrolyte

- A high rupture strength to prevent cell rupture against pressure and strike during the cell assembly processes

- Impermeability to the electrolyte to prevent the leakage of the latter outside the cell

- Heat sealability, to avoid electrolyte leakages at joint points while permitting homogeneous pressure distribution over the cell components

The realization of the pouch-cell follows the key guidelines reported in deliverable D3.2 of WP3, in which baseline cells, without integrated sensor, were assembled and characterized to compare their electrochemical performance with those using integrated Level 1 and Level 2 sensors, as expected by the project. More in detail, 50×50 cm^2 aluminum/thermoplastic polymer composite bags that bonds themselves during heating under uniaxial pressure were assembled and sealed at the edges and borders through a thermal-pressure method. This process was carried out on two of the three sealable sides. On the flat-flex wiring side, additional layers of thermoplastic stiffener tape and thermo-bonding adhesive layers were used to ensure proper sealing. Then, the cell was dried at 80 °C in vacuum overnight to remove residual moisture. The anode/separator/cathode stack using flat-flex wire-connected electrodes was placed inside the pouch bag. In the preliminary test without cathode and anode, the separator with the printed sensing electrodes was rinsed with $LiPF_6$ EC: DEC (1:1) 1 M commercial electrolyte before its embedment in the pouch bag to ensure adequate pre-wetting. After filling the pouch bag with the battery electrolyte, the fourth edge of the bag was sealed avoiding gas trapping. In fact, a vacuum can be applied to the pouch cell immediately before the heat is applied to impregnate the electrode and separator pores with electrolyte.

In **Figure 2** is reported the scheme of the pouch cell assembly procedure. For the assembly of pouch cell, NMC 622 cathode and graphite anode were used according to project specifications (see also deliverables D1.1, D2.2 and D3.2). The whole assembly process was carried out in a dry environment (dry-room). The assembled pouch cells were kept for 24 hours at room temperature for efficient impregnation of electrolyte into the whole surface of the electrodes before electrochemical testing.

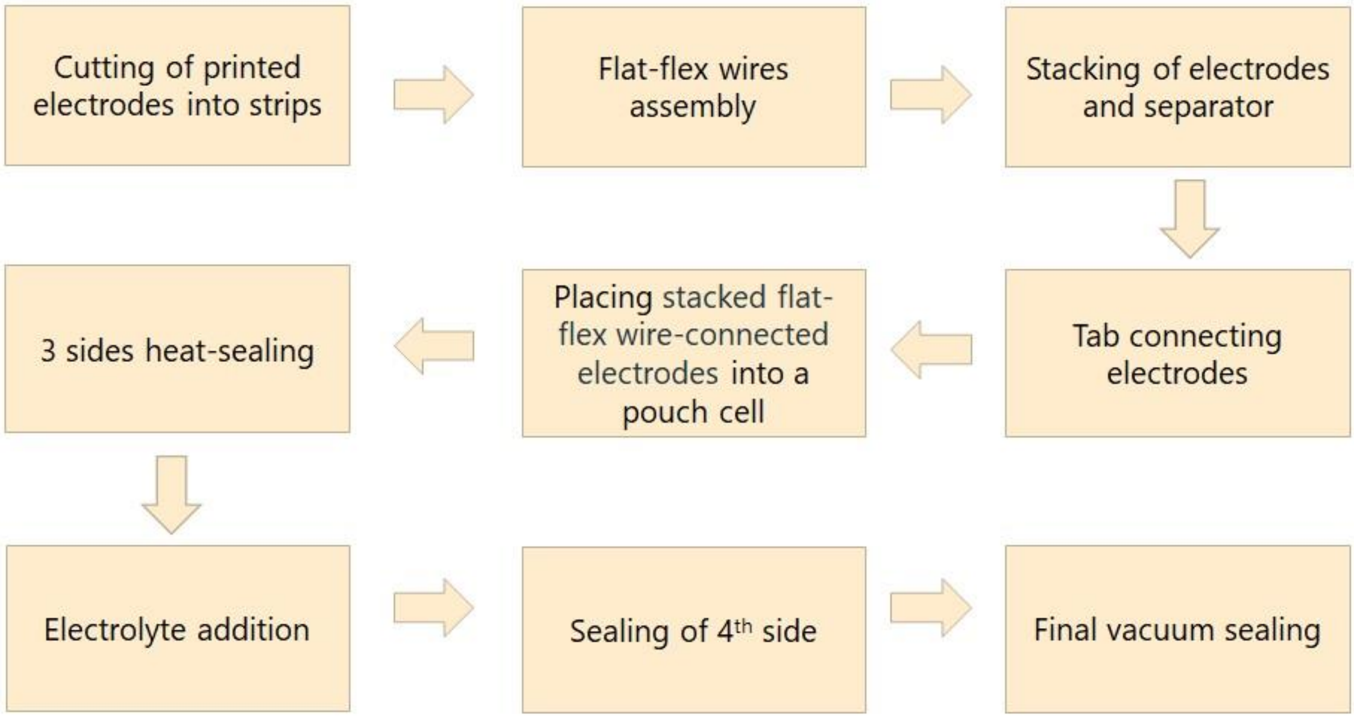

Figure 2. Schematic of fabrication of 5×5 cm^2 pouch cell.

Figure 3 shows the representative pouch cells including in three and four-electrode configurations (*i.e.*, cells including our printed sensing electrodes)

Figure 3. Pouch cells in three and four-electrode configurations, as resulting by the incorporation of sensing electrodes printed on Celgard 2500 separators.

3 Tests

3.1 Electrical resistance characterization of flat-flex wiring

A conventional laboratory multimeter (Keithley DMM 6500) with a simple two-wires probe was used to measure the electrical resistance of the extremes of each printed sensing electrode track (3 × 25 mm^2) before and after wiring. The length-normalized resistance of the flat-flex wire connected sensing printed sensing electrodes are reported in **Table 1**. The investigated samples were LFP-based reference electrodes with polyphenylsulfone (PPSU) binder, as described in deliverable D2.1. For each sample, two sub-samples were obtained. The electrical properties of the printed layers are dependent upon the thickness, their constituent compounds, film preparation method and post-deposition treatments [2]. Due to the negligible resistance of the Cu flat-flex wire (<0.002 $\Omega \cdot cm^{-1}$) compared to the printed sensing electrode, the whole obtained resistance was approximated to the resistance of printed electrodes. The obtained data indicated that the printed sensing electrodes are well connected and exhibit satisfactory electrical conductance, in agreement with the specification measured by four-probe measurements for printed sensing electrodes (see deliverable D2.1 and D2.2).

Table 1. Resistance values of electrodes and assembly electrodes/wires.

Sample	Track 1 R point to point (25 mm) (Ω cm^{-1})	Track 1 R point to point (25 mm) (Ω cm^{-1})	Track 1 printed-wire resistance (20 mm) (Ω cm^{-1})	Track 1 printed-wire resistance (20 mm) (Ω cm^{-1})
LFP-A 1	148	148	145	150
LFP-A 2	196	156	180	145
LFP-B 1	292	295	275	285
LFP-B 2	248	236	245	235

3.2 Sensing electrode/electrolyte compatibility

To guarantee a proper pouch cell assembly, the printed reference electrode must preserve its characteristics during electrolyte impregnation, without showing significant electrode lamination and swelling phenomena. Thus, printed reference electrodes on Celgard 2500 were immersed in a 1 M commercial $LiPF_6$ EC: DEC (1:1) electrolyte (Solvionic) for 30 min. **Figure 4** shows the photograph of a representative printed reference electrode (LFP-A) after electrolyte impregnation.

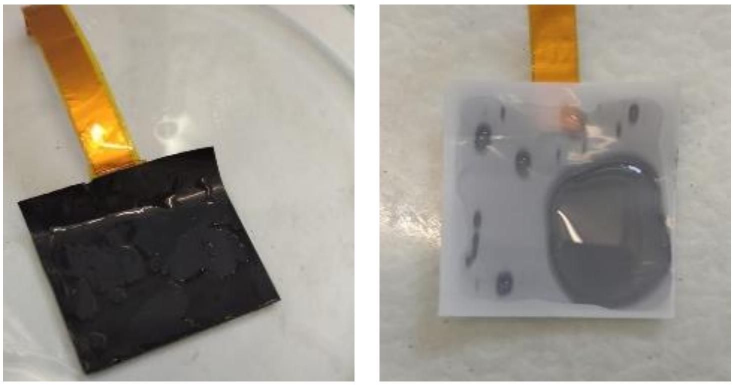

Figure 4. Photographs of a representative reference electrode (LFP-A) printed on Celgard 2500 after immersion in 1 M commercial LiPF6 EC: DEC (1:1) electrolyte for 30 min.

As already anticipated in deliverables 2.1 and D2.2, no significant swelling was observed after electrolyte immersion, validating further the formulation of the printed reference electrodes (additional details are discussed in deliverables D2.1 and D.2.2).

3.3 Electrodes evaluation after pouch cell assembling

The integrity of the LFP-A printed sensing electrodes on Celgard 2500 after assembling the pouch cell was evaluated by opening the pouch cell after 24 hours (**Figure 5).** The printed sensing electrodes preserved their initial condition after 24 hours without showing relevant geometric modifications. The produced pouch cell assembly configuration was therefore selected for the continuation of the project activities of Task 2.4 and Task 2.5, as well as the preliminary electrochemical characterization already reported in deliverable D2.2.

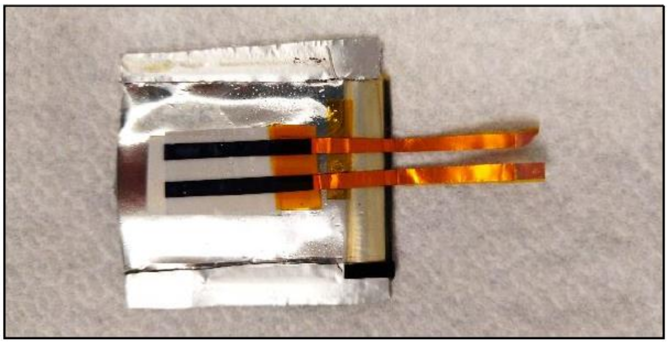

Figure 5. Photographs of printed sensing electrodes after opening the pouch cell.

4 Conclusion

This document describes the activities of Task 2.3 regarding the flat-flex wire connection of our printed sensing electrodes, as well as the pouch cell assembly procedure needed for the continuation of the activities of WP2 (*i.e.*, electrochemical configuration of printed sensing electrodes and pouch cells using integrated sensing electrodes).

The obtained results proved the successful realization of flat-flex wire connection of our sensing electrodes printed on Celgard 2500 separators. By following the general procedure reported for the realization of pouch cell assembly baselines (see Deliverable D3.2), pouch cells integrating our sensing electrodes were also successfully assembled.

While this document reports the retention of the geometric properties of the printed sensing electrodes during the pouch cell assembly procedure, previous deliverable D2.2 evaluated the resulting electrochemical performance.

The analysis of the functional capabilities of the proposed printed sensing electrodes will be continued during the activities of Task 2.4, aiming at proving in-situ EIS and in- operando electrolyte conductivity measurements, as well as the accurate monitoring of cathode and anode potentials during the pouch cell operation.

5 Risks

Risk No.	What is the risk	Probability of risk occurrence[1]	Effect of risk[2]	Solutions to overcome the risk
WP2.1	*Low stability of pouch cell*	*3*	*2*	*Improving the sealing/ encapsulation process and optimizing printed sensing electrode thickness*

[1] Probability risk will occur: 1 = high, 2 = medium, 3 = Low

[2] Effect when risk occurs: 1 = high, 2 = medium, 3 = Low

6 References

(1) Herrmann, M. Packaging - Materials review. AIP Conference Proceedings. 1597 (2014) 121.

(2) Hassanien, A. S.; Akl, A. A. Effect of Se addition on optical and electrical properties of chalcogenide CdSSe thin films. Superlattices and Microstructures. 89 (2016) 153-169.

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Project partners

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