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

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D3.5 – REPORT PROTOTYPING 1 AH CELLS WITH INTEGRATED LEVEL 2 SENSORS

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Summary

The deliverable D3.5 “Report prototyping 1Ah cells with integrated Level 2 sensors” summarizes the activities related to the Task 3.5 in the frame of work package 3.

Within this task, Level-2 sensors developed and prepared by BDM were integrated into prototype pouch cells with 1Ah of capacity by the responsible partners ABEE and VAR. These cells were electrochemically investigated with the aim to provide two different verifications.

On the one hand, the functionality of level 2 sensors in 1 Ah cells was verified. On the other hand, the absence of interferes with the battery cell’s performance was demonstrated by comparison to baseline cells.

In general - although long term measurements are not finished due to the timing of this deliverable - the report confirms for the 1 Ah stacked pouch cells the earlier reported results of Level 2 sensors (deliverable D2.5; M30).

The work is following established investigation routines also used in deliverable 3.3, that investigated cells of the same format with Level-1 sensors. In addition to the electrochemical behavior, focus of the investigation are related to the sensor integration process like the sealing at the position where the sensor exits.

This deliverable and the related task include a delay of one month, related to the close timing between development and production of the Level 2 sensor (reported in D2.5) and the schedule for the present deliverable. The resulting delay was carefully evaluated and will not lead to further delays in the SENSIBAT project.
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Table 1. Cell matrix according to DOW

Table 2. New cell matrix agreed by partners

Table 3. Ultrasonic Welding parameters used at ABEE
### Abbreviations

| Symbol / Abbreviation | Description |
|-----------------------|-------------|
| CMC                   | Carboxymethyl cellulose |
| DOW                   | Description of Work |
| LFP                   | Lithium-ion-phosphate |
| LTO                   | Lithium titanate |
| NMC 622               | LiNi0.6Mn0.2Co0.2O2 |
| NMP                   | N-Methyl-2-pyrrolidone |
| PAA                   | poly(acrylic acid) |
| PVDF                  | Polyvinylidene difluoride |
| SoC                   | State of Charge |
| SoH                   | State of Health |
1 Introduction

The present deliverable D3.5 provides information on the production of cells with integrated Level 2 sensors, describing the work performed in the frame of Task 3.5. The main objective of the task is the implementation of Level 2 sensors in 1 Ah pouch cell and the verification of the sensor functionality. The report is accomplished by the addition of first electrochemical data and the direct comparison of this electrochemical data to baseline cells (cells without sensors).

Table 1 and Table 2 summarizes in general the foreseen cell production matrix according to the DOW (Description of Work) and after rearrangement of the partners within the project. This deliverable considers the yellow highlighted cells with Level 2 sensor in Table 2, which are constructed by ABEE and VAR.

| Partner/cell type | Baseline cell | Cell with Level 1 sensor | Cell with Level 2 sensor | Total |
|-------------------|---------------|--------------------------|--------------------------|-------|
| VAR – 5Ah Cell    | 20            | 20                       | -                        | 40    |
| ABEE – 1Ah Cell   | 40            | -                        | -                        | 40    |
| AIT – 1 Ah Cell   | -             | 20                       | 20                       | 40    |

| Partner/Cell type | Baseline cell | Cell with Level 1 sensor | Cell with Level 2 sensor | Total |
|-------------------|---------------|--------------------------|--------------------------|-------|
| AIT – 5Ah Cell    | 20            | 20                       | -                        | 40    |
| ABEE – 1Ah Cell   | 10            | 15                       | 15                       | 40    |
| VAR – 1Ah Cell    | 10            | 15                       | 15                       | 40    |
2 Cell Design and Setup

2.1 Cell Formats
To ensure comparability of the baseline cells shown in this deliverable, ABEE and VAR used the same cell components, although the cell formats of the two companies were slightly different. This variation in the cell format and data regarding the used NMC 622 cathode and graphite anode have been reported within D3.2 “Report on prototyping baseline pouch battery cells”.

2.2 Sensor preparation
The partners received two different types of lithium-ion-phosphate (LFP)-based reference electrodes, i.e., Level 2 sensors, printed by BDM on Celgard 2500 by screen or stencil printing, as described in D2.5

To produce these reference electrodes, BDM used a) polyvinylidene difluoride (PVDF) binder for the formulation of N-Methyl-2-pyrrolidone (NMP)-based pastes for the printing of the first type of reference electrodes, and b) poly (acrylic acid sodium)-grafted carboxymethyl cellulose (PAA-grafted CMC) binder for the formulation of water-based paste for the printing of the second type of reference electrodes. Both types of reference electrodes were delivered to the corresponding partners. Additional details regarding the composition of the selected reference electrodes, as well as their printing and preliminary test in small-area (3 cm²) pouch cells, have been described in D2.5.

The received reference electrodes had a size of 5×0.8 cm². In a first step, ABEE and VAR used ultrasonic welding on the coated separator to attach an aluminium tab, as commonly used for the tabbing of the positive electrode. The process is shown in Figure 1. Further, ABEE reported the used welding parameters to ensure a sufficient connection, while avoiding the damage of the polymeric separator used as substrate for the reference electrodes (see Table 3). It must be mentioned that both companies had to repeat the welding step for several times (up to 7) to achieve a sufficient joining between the aluminium tab and the reference electrode directly printed atop the separator. Kapton tape (polyimide sheet with a thickness of 20 μm) was used to fix the reference electrodes. Granted, the chosen equipment is designed to weld metal to each other, but for the industrial deployment of such sensors, the connection of tabs to printed reference electrodes must be still optimized using either a different welding equipment or another design layout to ensure the technical readiness level for industrial cell production processes.
Figure 1: Ultrasonic welding of Al tab on the coated separator at VAR (left) and at ABEE (right)

Table 3: Ultrasonic welding parameters used at ABEE

| Parameter               | Value |
|-------------------------|-------|
| Delay Time (sec)        | 0.1   |
| Welding Time (sec)      | 0.06  |
| Take off Delay (sec)    | 0.05  |
| Take off                | 0.05  |
| Welding Amplitude       | 0%    |
| Layers                  | 8     |
3 Sensor Integration

In the following, the integration process of Level 2 sensors into 1 Ah pouch cells is reported. The integration procedure follows routines developed within D2.5, as the involved partners in this deliverable paved the way by integrating Level 2 sensors into smaller (3 cm²) pouch cells.

In alignment with the general aim of the task 3.5, the focus of the work was to minimize the influence of the reference electrode on the cell operation. Comparable to the integration of Level 1 sensors previously described in the project, a sufficient integration without changing the electrochemical behaviour of these cells compared to the baseline cells can be considered the necessary condition for the success of practical sensor devices.

3.1 Sensor positioning

The project partners decided to integrate the reference electrode in the middle of the stack, after the 4th of 8th anodes at VAR and the 5th of 9th anodes at ABEE. As described in D2.5, an additional separator layer (Celgard® 2500) was added to avoid potential short circuits between the separator and the cell electrodes. The welded tab on the reference electrode is lead outside the pouch bag. The feedthrough, causing major problems with Level 1 sensors (explained in D3.3), was unproblematic as the tab is of the same material used for the positive pole. The integration process of the Level 2 sensor in the pouch cell is visually displayed in Figure 2: Cell stack production with Level 2 sensor for both manufacturing partners.

Cell stack with integrated level 2 sensor during cell production

![Cell stack production with Level 2 sensor](image)

Figure 2: Cell stack production with Level 2 sensor
Next, the cell production process followed the routines described in D3.2 for baseline cells. Finally, the resulting cells were electrochemically investigated.

At the moment of writing this report, 7 out of 15 cells were constructed at VAR. Of these 7 cells, 5 are currently electrochemically evaluated - while 1 cell displayed a failure. This cell failure is associated with the manual stacking process and is likely not connected to the sensor integration. Besides, ABEE prepared 4 cells.
4 Electrochemical Measurements

The cells were electrochemically tested according to the protocols defined in deliverable D1.2. After the formation, a preconditioning step was integrated to bring the reference electrode to a stable equilibrium potential to provide reliable monitoring of the positive and negative electrodes potential. The preconditioning step was previously developed by BDM and POL and has been described in detail in D2.5.

4.1 Formation

As for the baseline cells (D3.2) and Level 1 sensor cells (D3.3), the produced cells initially underwent a formation procedure. Although the incorporated LFP-based reference electrode was not preconditioned to a stable potential in this initial formation step, the potentials vs. the negative/positive electrode were monitored (see Figure 4).

In this formation step, the presence of the Level 2 sensor has not led to detectable effects. Figure 4 shows voltage/potential (vs. reference electrode) profiles of the cell electrodes during the formation of a representative cell.

![Figure 4: Formation data of 1 Ah cell with Level 2 sensors produced at VAR (with applied jig)](image)

4.1.1 Comparison to baseline cells

The formation procedure revealed the charge/discharge capacity measured for the first 3 cycles. In this context, the capacity data were compared to those obtained for baseline cells.
Figure 5 displays that three cells with Level 2 sensors featured capacities comparable to the baseline cells. One cell exhibited a significantly lower capacity compared to baseline cell and was stopped because of its failure in the subsequent check-up cycling. As mentioned before, the reason for this cell malfunctioning is likely associated to the manual stacking process of these prototype pouch cells, as also observed for the evaluation of baseline cells in previous phases of the project.

The other three cells revealed a slightly lower capacity compared to baseline cells. Again, this may be result of the manual stacking process, but could also be associated to the presence of Level 2 sensor within the cell stack. Nevertheless, thanks to the porosity of the Level 2 sensors, their effect on the cell performance is marginal, which is consistent with the results shown in D2.5.

In general, it can be concluded that the three cells performed comparable to baseline cells and the incorporation of Level 2 sensor has not led to significant negative effects on the cell capacities.

### 4.2 Check-up Cycles

After the cells fulfilled the formation, a check-up procedure was performed according to the criteria defined in D1.2. This check-up procedure was used to compare the operating behavior of baseline cell with cells integrating Level 1 and Level 2 sensors.

In the third cycle, cell voltage values at different State of Charge (SoCs) (90, 50 and 10%) obtained for the Level 2 sensor-integrating cells matched those obtained by baseline cells (4.0, 3.7 and 3.4 V, respectively). In a final step, the cells were charged to 33% of SoC, (Figure 6). In addition, thanks to the functionalities of the Level 2 sensor.
sensor, the potentials of the anode and cathode were measured versus the potential of the (un-preconditioned) LFP-based reference electrodes.

Figure 6: Cell Voltage and electrode potential profiles of the SENSIBAT 1Ah pouch cell with Level 2 sensor (un-preconditioned) produced at VAR (with applied jig) during the check-up test

4.2.1 Comparison to baseline cells

Figure 7 shows the comparison between the cell voltage profiles measured for the Level 2 sensor-integrating cell and a representative baseline cell. The shift in the timeline is a consequence of the slightly different cell capacities. In general, the voltage profiles of the two cells were comparable, while Level 2 sensor allowed the positive and negative electrode potentials to be monitored.
Comparison of the Check-Up Cycle Voltage Profiles of Baseline cell and Cell with integrated level-2 Sensor.

Figure 7: Time-based comparison of check-up tests for an exemplary baseline cell and a level2 sensor (un-preconditioned)-integrating cell at VAR (with applied jig)
4.3 Preconditioning

The preconditioning procedure of the reference electrodes developed by BDM and POL, and described in D2.5, was partly followed, as a C-rate calculation mistake was accidently done. Consequently, the preconditioning of the reference electrodes was performed at higher C-rates, which, however, still resulted in a stable equilibrium potential of LFP-based reference electrodes. As foreseen, the cell voltage did not change during the applied procedure, which is consistent with the preliminary results shown in D2.5 for small-area (3 cm²) pouch cells. This, procedure will be used also for the evaluation of cells that will be produced within the project.

Figure 8: Exemplary voltage and anode potential profiles of a 1 Ah cell with level 2 sensor during the preconditioning of the reference electrodes at VAR
4.4 Cycling Tests

After finishing the formation, check-up and preconditioning procedures, the cycling of the cells was started. For this purpose, the performance routine described in D1.2 was used. The cell voltage and electrode potential profile vs. capacity measured for two cells incorporating a CMC-based, LFP-based Level 2 sensor are displayed in Figure 9. Minor differences in the obtained potential profiles were successfully monitored by means of the reference electrodes.

The data obtained for a cell incorporating a reference PVDF-based LFP-based level 2 are shown in Figure 10, where the cell voltage and electrode potential profiles are shown versus time. Unfortunately, a second cell displayed a failure, while a cell replica is currently under evaluation.

Nevertheless, the results shown in Figure 10, proved the electrodes’ potentials were successfully monitored with Level 2 sensors. It is clearly visible that, in the cycle performed at low-C Rate (90 h onwards in Figure 10), the achievement of cell voltage limits is mainly associated to the positive electrode, while the negative electrode does not operate in its potential boundaries like in the cycles with higher C-rate. This indicates the overbalancing of the negative electrode.

At higher C-rates, the negative electrode operates in a wider potential window and especially for the highest C-rate cycle (at 73 h in Figure 10) the negative electrode is threatened to meet potentials close to metallic lithium deposition. It will be interesting to monitor the subsequent cycling and to control if the potential window of the negative electrode widens. This would indicate aging effects related to State of Health (SoH), demonstrating the importance of information on the individual electrode potentials next to the cell voltage.

Figure 9: Cell voltage and electrode potential profiles measured for two 1 Ah cells with CMC-based, LFP-based Level 2 sensors at VAR.

Figure 10: Cell voltage and electrode potential profiles measured for a cell incorporating a reference PVDF-based LFP-based level 2.
Figure 10: Time-based voltage and potential changes of 1 Ah cell with PVdF-based, LFP-based Level 2 sensors at VAR.
5 The benefits of introducing reference electrodes in lithium-ion cells

Extended cycling of lithium-ion batteries leads to capacity fading caused by various mechanisms (1). Unfortunately, during operation, only the cell voltage can be monitored and no proper knowledge about the actual potential of the electrodes is observable during cell cycling. Monitoring of anode and cathode potentials, next to the cell voltage, can be achieved by the insertion of a reference electrodes into the original cell.

Potential candidates for reference material are, for example, metallic lithium (see ¡Error! No se encuentra el origen de la referencia.) or lithium titanate (LTO) and the investigated LFP. The latter two materials were investigated within SENSIBAT for the realization of novel reference electrode directly printed onto the cell separator, and the rationale leading to optimal reference electrode configurations has been discussed in the deliverable of work package 2. For the activities related to the present deliverable, LFP-based reference electrodes were selected as suitable reference electrode candidates according to their preliminary electrochemical characterization and electrical modelling reported in D2.3-D2.5.

Due to the demands of high specific capacities as well as high volumetric capacities, industrial lithium-ion cells have space restrictions, and the realization of reference electrodes directly onto cell separator represents an ideal space-saving solution.

After the embedment of reference electrodes, changes in the potential profiles of the electrodes can be assigned to aging behaviour of the electrodes, resulting in changes in the cell balancing between anode and cathode that may lead to overpolarization effects. For example, mobile lithium-ion consumption during the extended cycle life can be observed. An example for such changes of potentials of anode and cathode during prolonged charging/discharging time is obvious within ¡Error! No se encuentra el origen de la referencia. During cycling, the anode potential reach potentials that increases progressively, while the reduction/oxidation reactions at the cathode take place in a potential window that is progressively reduced compared to the first cycles. Within typical cells, the cathode represents the capacity limited electrode, so that the metallic lithium deposition at the anode can be effectively prevented during cell charging. At the beginning of cycling, the anode works in a small potential window, while the cathode works in a potential range from 2.5 V to 3.8 V. This can be attributed to the reason that the anode is not fully intercalated with mobile lithium ions, while the cathode is fully intercalated.
Unfortunately, the aging processes caused by cell cycling suggest the anode progressively become the capacity-limited electrode, increasing its potential window over a cycle. The potential window of the negative electrode progressively increases during cycling, indicating a rise of the electrode’s impedance. This rise of the electrode’s impedance can be associated with continually growing of the SEI passivation layer.

![Graphs showing voltage profiles](image)

**Figure 12: Voltage profiles of a 2.3 Ah A123 cell (C/LiFePO₄) during the first 100 hours of charge/discharge reactions (left) and between 300 and 400 hours of charge/discharge reactions (right)**

The measurements were performed by VAR, outside the SENSIBAT project, but should display the potential of embedding reference electrodes to commercial cells. The authors would like to emphasise that such reference electrodes allow the estimation of the electrode potentials at different state of charges, representing a useful tool for the verification of electrochemical battery model. Further it allows the aging behaviour of cells to be studied during operation, providing valuable information for reliable cell/electrodes design, electrolyte design towards the understanding of cell safety aspects.
6 Discussion & Conclusion

The results presented in this document show that the objective of Task 3.5 was achieved. Accordingly, VAR and ABEE have realized 1 Ah pouch cells with Level 2 sensor, following results developed in the frame of WP2 by BDM and POL for small-area pouch cells. The measurement results are comparable to results obtained in D2.5, which operates the same electrodes in different cell formats.

Further, the results in the frame of this deliverable displayed that the integration of the Level 2 sensors in 1 Ah cells has a minor impact on the cell performance. This conclusion was confirmed by the comparison between results obtained for the Level 2 sensor-integrating cell and baseline cells. The effect of Level 2 sensor integration seems to be negligible compared to those arising by the manual stacking process.

Further, the deliverable also displays a satisfactory inter-comparability of cells with Level 2 sensors. For this purpose, more cells will be constructed in the frame of the SENSIBAT project. According to the planning, this task will be continued in the frame of WP5. The shipping of four 1 Ah cells with Level 2 sensor (after formation, check-up and preconditioning) from VAR to AIT, is scheduled and the cell production is started.

The deliverable is summarised by a description on the importance of the knowledge gain by reference electrode sensors from an industrial, battery producers’ view. By this, the authors would like to underline the importance of such sensors on cell/electrode design, SoH observation and aging processes. This was also stressed in reports and lectures provided within SENSIBAT.
7 Risks

No risks related to D3.5 have been identified.
8 References

(1) Vetter, J., et al. J. of Power Sources. 147, 2005, 269.
9 Acknowledgement

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Project partners

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