Title of the project	Enhanced safety materials for Li-ion batteries
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Duration:	20 months

Deliverable number	**Deliverable**	**Work package code**	**Entity responsible for deliverable**	**Type**	**Access and dissemination**	**Method of verification**	**Delivery (project implementation month)**
D1.4	**Final report on the achievemnts of the project**	WP1	CEMEA	Report	P	Summary of results	M20

Final report on the achievements of the project 01. 2025 to 08. 2026 (M1-M20)

The Final report on the achievements of the project 01. 2025 to 08. 2026 (M1-M20) contains summary of achievements during the project.

Introduction

Overall objective of the project ENSAMAT is to develop materials that enhance safety operation of Li-ion batteries in a passive way. Generation 3 of the Li-ion battery is composed of silicon/graphite anode, layered oxide cathode (NMC, LFP) and separator immersed in a liquid electrolyte. Each of these components can contribute to enhanced safety operation of batteries. During the projects we intend to develop anode and cathode with enhanced performance and flame retardant properties. We expect that surface modification of the anode material (silicon) by coating will increase stability of the solid electrolyte interphase (SEI) layer, thereby enhancing thermal performance and safe operation of the anode. The development of nickel-rich and polyanion cathodes coatings as well as silicon/carbon anodes will push reliability and safety of the Generation 3 Li-ion batteries to a higher level. Furthermore, a new type of separator will be designated to avoid mechanical and thermal abuse during the operation. Finally, electrochemical properties and performance of standard and battery composed of enhanced safety materials will be evaluated at conditions close to thermal runaway.
To achieve the objective of the project following Specific objectives with corresponding performance indicators and targets have been identified:

- Development of novel protected silicon-based anodes
- Flame retardant binders for silicon-based anodes
- Development of ALD coated cathode
- Mechanically robust and thermally stable separators
- Safe Li-ion cell with improved safety performance

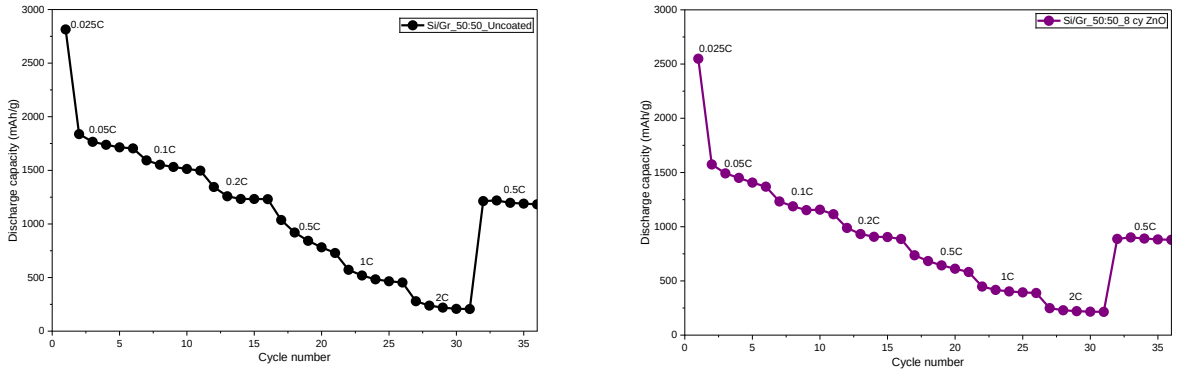
These specific objectives were elaborated in four work packages of the project. Objectives for each work package were defined in the related work packages. Achievements of the project were obtained in related work packages. In this report we will report on achievements obtained within the work packages of the ENSAMAT project.

Work Package 1 (WP1) Anode and Cathode (M1-M20)
The Work Package 1 has following objectives:

- Development of performing and reliable silicon/graphite anode achieving capacity of 1.5 Ah/g.
- Selection of suitable cathode material.
- Demonstration of performance of battery fabricated from enhanced safety materials.

Development of performing and reliable silicon/graphite anode achieving capacity of 1.5 Ah/g.

The silicon/graphite anode prepared using ball milling of a solution of silicon and graphite particles with ethanol. The composition of the anode was 20 wt% silicon / 80 wt% graphite and 50 wt% silicon / 50 wt% graphite. The anodes were coated by atomic layer deposition (ALD) of ZnO either after fabrication of the anode, or silicon powder was coated by ALD before fabrication of the anode. Performance of ALD coated anodes was compared with uncoated electrodes. Figure 1 displays discharge capacity as a function of cycles at C-rates from 0,025 C (forming) up to 2 C. for uncoated and ALD coated Si/Gr anode with 50 wt% Si. In this case the silicon powder was coated using 8



a) b)

Figure 1. Discharge capacity as a function of charging/discharging cycles at different C-rates for a) Si/Gr anode (50 wt% Si) uncoated and b) Si/Gr anode (50 wt% Si) fabricated from Si particles coated by 8 cycles of ZnO by ALD.

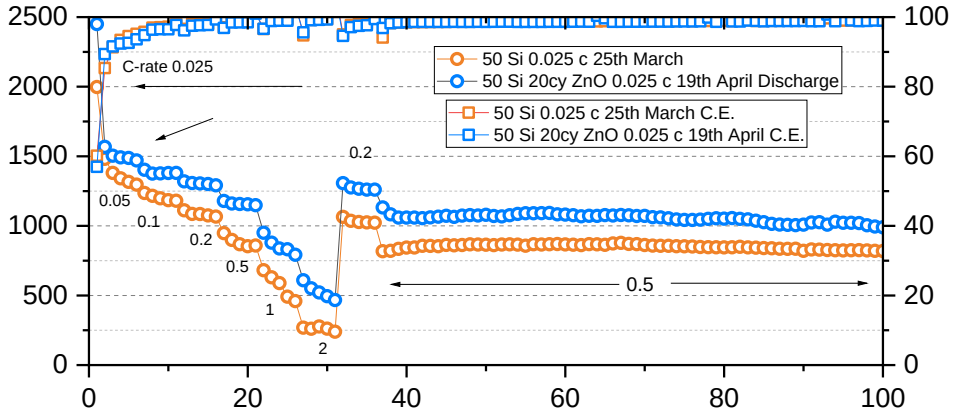


Figure 2. Discharge capacity as a function of charging/discharging cycles for Si/Gr anode (50 wt% Si) uncoated and coated by 20 ZnO ALD cycles after anode fabrication.

ALD cycles of ZnO prior the anode fabrication. Anodes exhibit capacity of 1.5 Ah/g at low C-rates. Figure 2 displays discharge capacity as a function of charging/discharging cycles for uncoated and coated by 20 ZnO ALD cycles anodes. The ALD was applied after the anode fabrication. The thickness of the anode was 5 µm. The ALD coated anode exhibits capacity of 1.5 Ah/g at 0.05 C. Obtained results indicate that the 1st objective of the WP1 (capacity 1.5 Ah/g) was successfully achieved.

Selection of suitable cathode material.

Commercial LFP cathodes from NEI Corp. were selected as a suitable material due to its inherent better stability than LiNiMnCoO (NMC). Discharge capacity of the 5 cycles Al_2O_3 ALD coated cathode in a half-cell and full cell configuration show excellent performance. In addition, long-term cycling in a full-cell configuration complements excellent properties of the LFP cathode coated by Al_2O_3 ALD film. These electrochemical measurements confirm selection of LFP coated by Al_2O_3 tin film by ALD as an enhanced safety material. The 2nd objective of the WP1 "Selection of suitable cathode material" was thus successfully achieved.

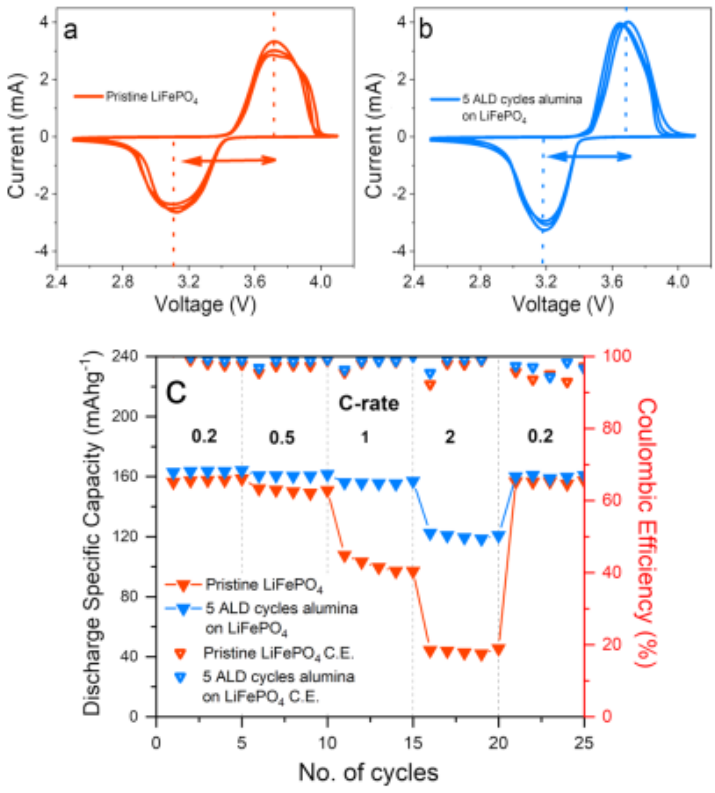


Figure 3. Electrochemical measurements of $LiFePO_4$ cathode uncoated (pristine) and coated with 5 ALD cycles of Al_2O_3 in a configuration with a Li anode (half-cell configuration).

Demonstration of performance of battery fabricated from enhanced safety materials

Goal of this part of the project is a construction and test of performance of full cell laboratory demonstrator composed of enhanced safety materials. To describe properties and performance of the full cell laboratory demonstrator was fabricated on a coin cell level from the developed safety enhanced materials - silicon/graphite anode coated by ZnO nanometer thin film using ALD and flame retardant binder, ALD coated cathode, and ALD and polymers flame retardant coated separator.

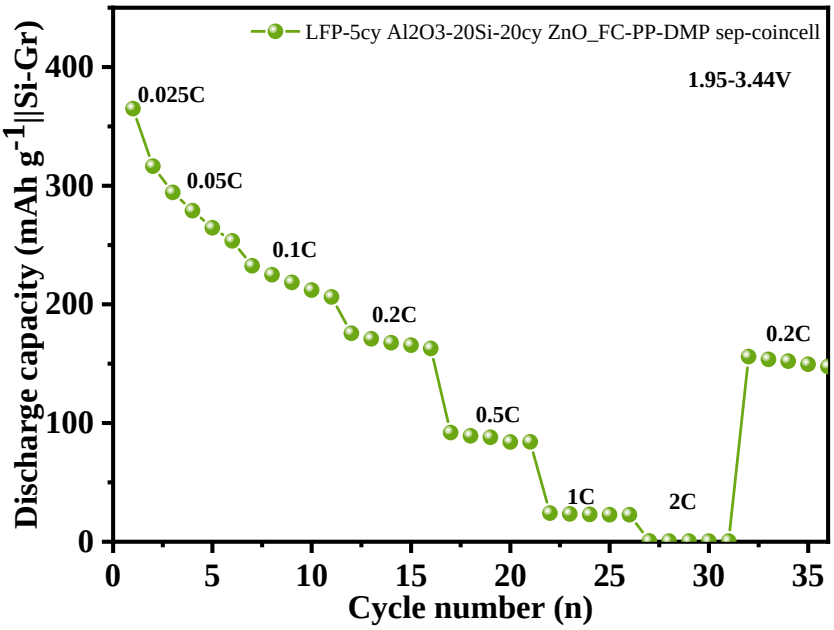


Figure 4. Discharge capacity as a function of charging/discharging cycles at different C rates for a standard full cell composed of Si/Gr anode (20 wt% Si), coated by 20cycles ZnO, LFP cathode, coated by 5 cycles of Al_2O_3 and separator with 50 cycles of Al_2O_3 / DMP polymer coated polypropylene separator.

Goal of this part of the project is a construction and test of performance of full cell laboratory demonstrator composed of enhanced safety materials. Electrochemical properties of standard cells and those fabricated using enhanced safety materials were compared. Based on achieved results we conclude that the goal of the part D1.3 Properties and performance of a full cell laboratory demonstrator composed of enhanced safety materials was successfully achieved.

Work Package 2 (WP2) Polymer materials (M1-M20)
The Work Package 2 has following objectives:

- Development of flame retardant binder.
- Development of flame retardant separator.
- Evaluation of anti-flame properties of polymer coatings.

Development of flame retardant binder

Electrochemical side reactions are caused by local thermal abuse affecting cell binders' thermal stability. Traditional binders, for example PVDF, are linear homopolymers soluble in organic solvents, however, these kinds of binders require organic volatile solvents (e.g., N-methyl pyrrolidone (NMP)) that evaporates at elevated temperature (>165 °C) and produce toxic substances during electrode production. More importantly, common binders undergo side reactions above 160ºC with lithiated graphite or lithium metal and form resistive side-products and cannot stabilize the structure of high energy density electrode materials due to their non-polar nature. Moreover, fluorinated polymers (PVDF) may generate HF during thermal decomposition.

In the frame of the project a modification of biopolymer-based binders (alginate as a model polymer) via different acrylate monomers containing P and N atoms was chosen as procedure to prepare flame retardant binder. Silicone/graphite (Si/Gr)-anode of Li-ion batteries were fabricated using S-Alg binders of different alginate molecular weights (100, 300, and 500 centipoises (cP) in order to study the effect of the molecular weight on the electrochemical measurements. A higher molecular weight (MW) binder generally provides a larger area of coverage and a more effective binding network at lower concentrations compared to lower MW binders. Please note that cP is a metric unit of dynamic viscosity used to measure how thick a liquid and reflects the molecular weight of the alginate.

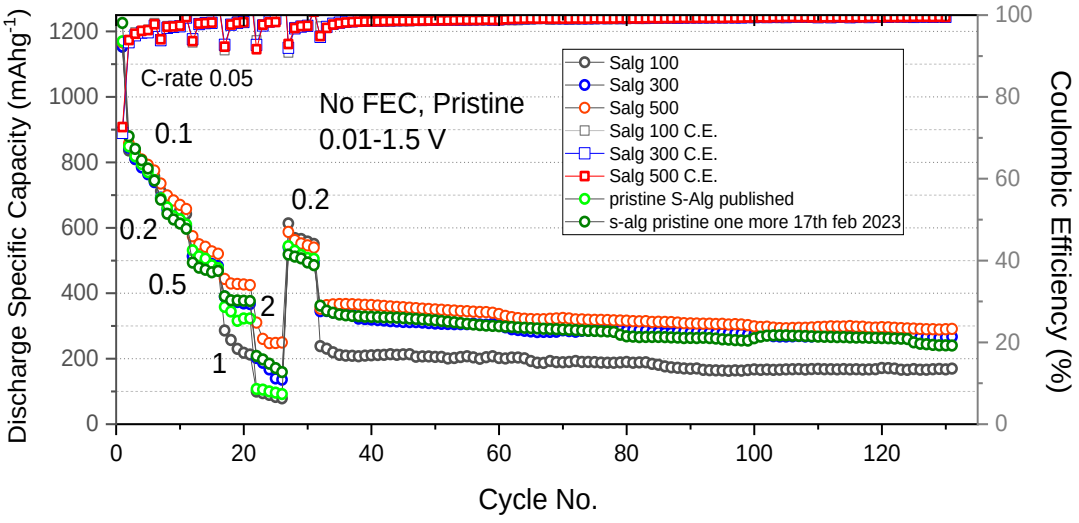


Figure 5. Discharge capacity as a function of the number of charge/discharge cycles for the 20 wt% Si anodes with binders Salg 100, 300 and 500.

Figure 4 displays discharge capacity as a function of the number of charge/discharge cycles of 20 wt% anodes prepared using binders Salg 100,300 and 500. Anodes prepared all Salg binders exhibit similar performance. Due to best properties of Salg 300 during casting, Salg 300 was selected as appropriate binder for Si anode processing. Flame retardant properties of the Salg-based binders are summarized in the Deliverable D2.1. It was stated in the D2.1 that Salg presents effective flame retardant, which not only significantly reduces the flammability of the binder, but also preserves its other key properties necessary for use in Si-G anodes. Therefore, we claim that the objective of the WP2 "Development of flame retardant binder" was successfully achieved.

Development of flame retardant separator

To develop flame retardant battery separator, we have proposed to coat polypropylene-based commercial separator Celgard 2400 by flame retardant polymer. Polymer based separators (pristine or covered by Al_2O_3 within Task 3.3) were grafted by surface-initiated copolymerization of acrylate monomers containing P and N atoms. More details on coating of separator by flame retardant polymer and their properties are presented in the Deliverable D2.2 Coating of separator by polymers. Figure 5 demonstrates electrochemical properties of polymer coated polypropylene separators. Polymer coated separators (PPTES6%, DMP, MPC) have electrochemical properties comparable to uncoated pristine membrane. We can conclude therefore, that the objective of the WP2 "Development of flame retardant separator" was successfully achieved.

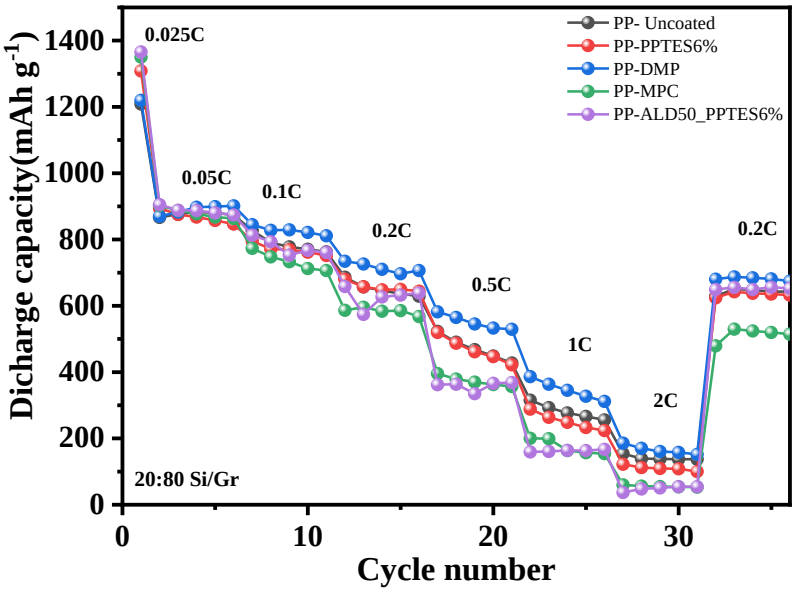


Figure 6. Discharge capacity as a function of charging/discharging cycles at different C-rates for separators coated by various flame retardant polymers

Evaluation of anti-flame properties of polymer coatings

Evaluation of anti-flame properties of polymer coatings was described in the Deliverable D2.2 Coating of separator by polymers. It is shown, that S-alginate provides satisfactory flame-retardant properties, characterized by low heat release and a very high flame temperature. We can conclude that the objective of the WP2 "Evaluation of anti-flame properties of polymer coatings" was successfully achieved.

Work Package 3 (WP3) Protective coatings (M1-M20)
The Work Package 3 has following objectives:

- Coating on silicon particles obtained by ball milling of microelectronic waste.
- Improvement of electrochemical properties of commercial cathodes by ALD coatings.
- Improvement of mechanical properties and wetting of polymer-based separators.

Coating on silicon particles obtained by ball milling of microelectronic waste.

Homogeneous and conformal ZnO coatings were prepared by ALD on silicon particles obtained from microelectronic or photovoltaic industry waste by ball milling. The coatings were free of cracks and defects ensuring good adhesion. ZnO coated silicon particles were used for anode fabrication (WP14, Task 1.1).

Technology of ALD coating on silicon particles was described in the Deliverable D3.1 Silicon powder was coated with ZnO by powder ALD in the Beneq TFS-FBR reactor. Scanning transition electron microscopy STEM revealed conformal thin ZnO layer with a thickness of few nm, Figure 6. Electrochemical properties of optimised silicon/graphite anode (50 wt% of Si) with Si coated by 8 ALD cycles of ZnO exhibits high discharge capacity particularly at low C-rates, achieving 1500 capacity of 1500 mA/h at 0.05 C, WP1, Figure 1b. We can conclude that the WP3 objective "Coating on silicon particles obtained by ball milling of microelectronic waste" was successfully achieved

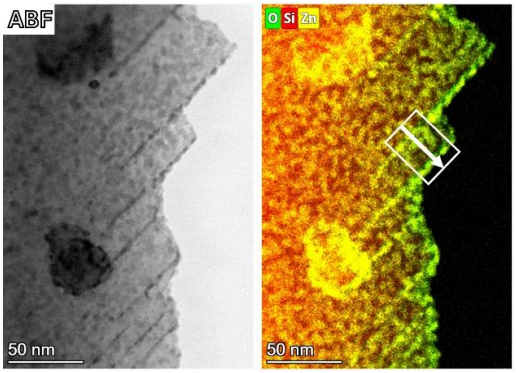


Figure 7. STEM-EDS mapping results with elemental distribution overlay presenting a single silicon grain coated with 8 cycles of ZnO. ZnO layer thickness was estimated to be < 5 nm.

Improvement of electrochemical properties of commercial cathodes by ALD coatings

Al_2O_3 oxide coatings will be deposited by ALD on commercial composite cathodes LFP and NMC (811). Commercial LFP cathodes from NEI Corp. were selected as a suitable material due to its inherent better stability than LiNiMnCoO (NMC). Trimethylaluminum and water vapours were used as precursor and reactant, respectively. Deposition ranged from 50 to 120 °C. Parameters of the ALD process were optimised to achieve conformal coating on porous structure. Thickness of the coating was in the range of a few nm (2-40 ALD cycles). LFP cathodes from NEI Corp. were coated by Al_2O_3 ALD coating using 2, 5 10 and 20 ALD cycles. Electrochemical properties in a full cell configuration with graphite anode are displayed in the Figure 7. It is shown that even 5 ALD cycles resulted in important improvement of the discharge capacity especially at the C-rate 2. Obtained results show that the WP3 objective "Improvement of electrochemical properties of commercial cathodes by ALD coatings" was successfully achieved.

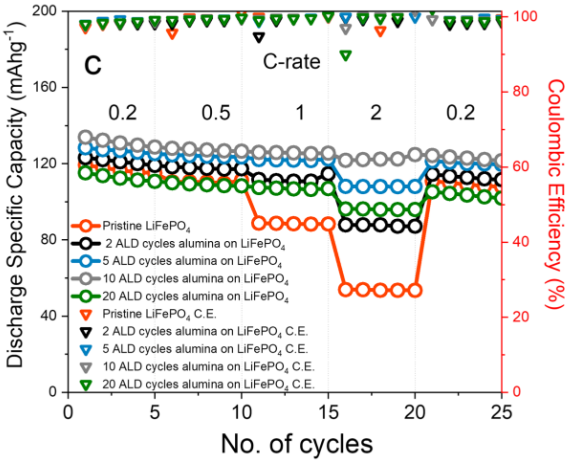


Figure 8. Discharge capacity of LFP cathode in a full cell configuration using graphite as anode as a function of charging/discharging cycles at different C-rates.

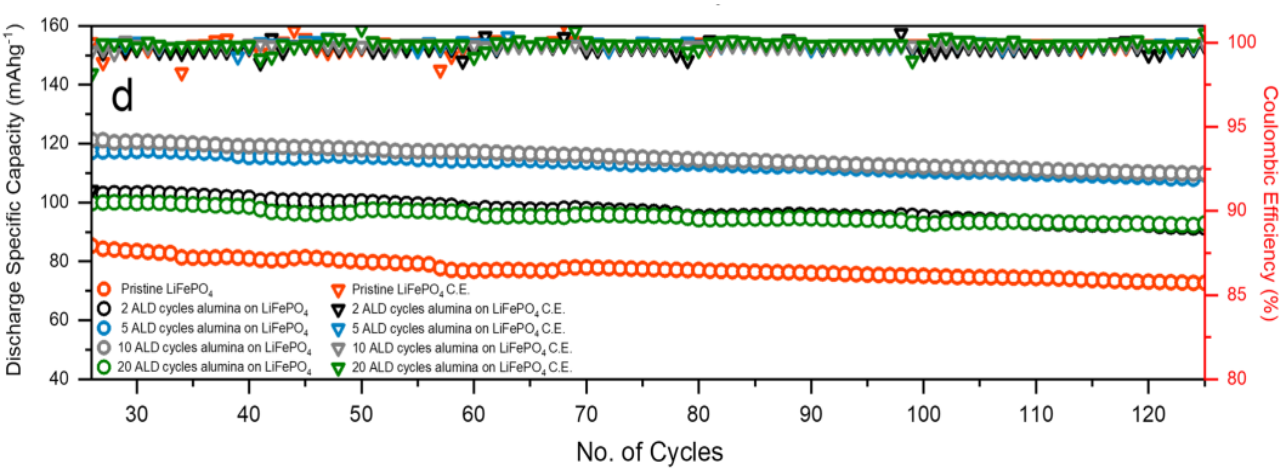


Figure 9. Discharge capacity as a function of the number of charge/discharge cycles for the pristine and alumina-coated $LiFePO_4$ cathodes in a full cell configuration with a graphite anode at a C-rate of 1 for 100 cycles.

Improvement of mechanical properties and wetting of polymer-based separators

To improve separator properties (mechanical, thermal, wettability) standard commercial separators (polypropylene based) were coated by thin Al_2O_3 films using ALD. Expected thickness of the coating is several nm. The properties of ALD coated polypropylene separators (Celgard) were describet in the Deliverable 3.3. Results of nanoindentation revealed an increase in hardness with increasing ALD cycle. It means that ALD coated separators showed increased resistance to being pierced by formed lithium dendrites. Calorimetry measurements revealed that ALD coated separators exhibit reduction of peak release rate and presumably due to the fact that coating prevents oxygen access to the polypropylene. Thermal cycling from room temperature to 130 °C was analysed using Fourier transform infrared spectroscopy (FTIR). The analysis proves, that there is no visible effect on FTIR spectra after thermal cycling. Wettability experiments showed that while ALD coated separators exhibit lowered wettability in the EMC, time to absorption for 50 ALD cycles coated polypropylene is only 2 s. It indicates that such coating doesn't prevent proper operation of the separator. Finally, electrochemical properties of ALD coated polypropylene separator showed that 50 cycles ALD coated separator exhibit the same discharge capacity up to 2 C-rate and has the same long term cycling capacity as uncoated separator up to 500 cycles Figure 9. Presented results confirm that the WP3 objective "Improvement of mechanical properties and wetting of polymer-based separators" was successfully achieved.

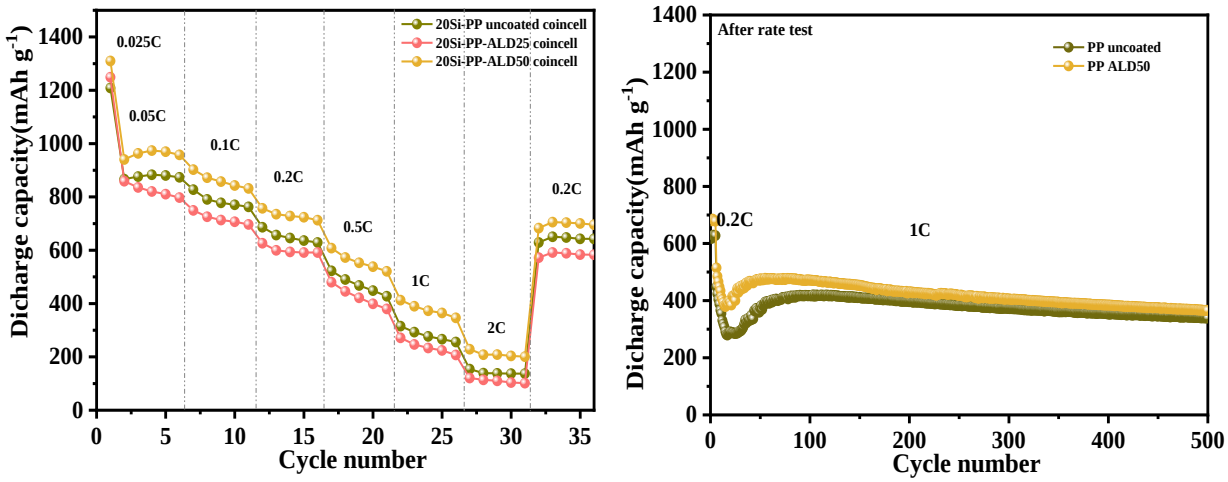


Figure 10. Discharge capacity as a function of the number of charge/discharge cycles for the silicon/graphite anode (20 wt% Si) and ALD coated polypropylene separator with 25 and 50 ALD cycles of Al_2O_3 in a coin cell configuration.

Work Package 4 (WP3) Characterization (M1-M20)
The Work Package 4 has following objectives:

- Determination of standard basic structural and electrochemical properties of modified electrodes.
- Assessment of advanced electrochemical characteristics of modified anodes and cathodes
- Determination of ageing behaviour, monitoring and identification of safety risks.

Determination of standard basic structural and electrochemical properties of modified electrodes

The work presented was focused on the systematic structural, morphological and electrochemical characterization of selected electrodes and batteries with the aim of better understanding the relationship between material properties and cell performance. Structural and morphological analysis was combined with electrochemical methods to assess the electrode-electrolyte interfaces, as well as transport and kinetic processes during cycling. In corresponding tasks 4.1 and 4.2, experiments combining microscopic and spectroscopic techniques with electrochemical methods were performed. Summary below show the most important conclusions of this part.

Si/Gr anodes with ALD ZnO layers demonstrated the protective and stabilizing function of ultrathin ZnO layers. ZnO reduced the resistance of the SEI layer and improved Li-ion transport. The best performance was shown by electrodes with 20 ALD cycles, while the low charge transfer resistance was maintained for at least 100 cycles. $LiFePO_4$ cathodes with ALD Al_2O_3 layers showed improved performance at high C-rates, lower CEI interface resistance and more stable cycling life. Operando XRD and XPS confirmed a more reversible phase transition and better passivation of the investigated surface. Impedance analysis (Figure 10) showed that Al_2O_3-coated samples exhibited lower charge transfer resistance and reduced CEI (parasitic interface at the cathode) resistance compared to the pristine electrodes. This suggests that the ALD Al_2O_3 layers facilitate Li-ion transport across the interface and contribute to more stable electrochemical kinetics.
Summary of the work performed in this part shows that the WP4 objective "Determination of standard basic structural and electrochemical properties of modified electrodes" was fully achieved.

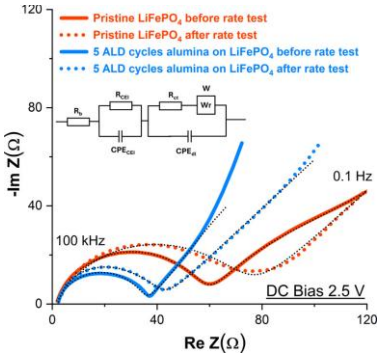


Figure 11. Nyquist plot of the pristine and 5 ALD cycles Al_2O_3 coated $LiFePO_4$ cathode obtained before and after the current load test.

Assessment of advanced electrochemical characteristics of modified anodes and cathodes

Advanced characterization techniques such as impedance characterization EIS, and galvanostatic intermittent titration technique, GITT was used for evaluation of selected half cell and full cell batteries to gain a deep knowledge about electrode/electrolyte interfaces, ion diffusion, and charge transport processes during the cycling.

Operando XRD and XPS confirmed a more reversible phase transition and better passivation of the investigated surface. In-situ EIS measurements allowed to detect corrosion of the aluminum current collector in experimental half-cells with LiFSI electrolyte. At 50 °C and 4.2 V, characteristic induction loops appeared, which were not present in the Nyquist plots after lowering the voltage limit to 3.7 V, confirming the diagnostic potential of EIS for monitoring corrosion degradation of current collectors. Preliminary EIS results on ZnO/SiGr half-cell anodes showed stable ohmic resistance, increase of double layer resistance and charge transfer at low temperatures and low SOC, and suppressed lithium-ion diffusion at 15 °C. The impact of different SOC windows on the degradation of SiOx/graphite anodes and the evolution of OCV curves was analyzed for commercial Molicel M35A cells. A methodology was developed to reconstruct OCV curves based on cycling history, which is important for more accurate SOC estimation in BMS systems. More details an achieved results can be found in the Deliverable D4.1 "Properties of selected electrodes and batteries". Based on achieved results we confirm that the WP4 objective "Assessment of advanced electrochemical characteristics of modified anodes and cathodes" was successfully achieved.

Determination of ageing behaviour, monitoring and identification of safety risks

Focus in this part was on development of methodology for online monitoring and prediction of safety risk based on estimation of internal temperature and possible Li plating. Techniques such as impedance measurements at selected frequency or monitoring of current pulse responses will be used as a nondestructive tool to monitor safety risks with the possible future commercial application in modern BMS systems.

Selected batteries with advanced safety components were characterized by cycling, charging/discharging at different current conditions, temperatures, and cut-off voltages to determine the safety operation limits. Analysis was supported by developed methodology for safety risk identification to validate enhanced safety of prepared batteries. Post-mortem analysis of degraded samples was carried out to further analyze the ageing roots of the batteries.

The methodologies developed within this activity establish a methodological foundation for future work in research and development projects, where they can be applied to advanced battery materials and next-generation cell concepts. Their further integration into multi-sensor diagnostic systems and intelligent Battery Management Systems is expected to contribute to safer, more reliable and longer-lasting lithium-ion batteries for both electric vehicle and stationary energy storage applications.

More details an achieved results can be found in the Deliverable D4.2 "Methodology for monitoring of safety risks" and Deliverable D4.3 "Ageing behaviour and safety risks". Based on achieved results we

confirm that the WP4 objective “Determination of ageing behaviour, monitoring and identification of safety risks” was successfully achieved.

In summary, we can state that the objective of all work packages of the project were successfully achieved. It demonstrates that the Specific objectives defined in the project SO1 “Development of novel protected silicon based anodes, WP1, SO2 “Flame retardant binders for silicon-based anodes, WP2, SO3 “Development of ALD coated cathode, WP3, SO4 “Mechanically robust and thermally stable separators, WP2 and WP3, and SO5 “Safe Li-ion cells with improved safety performance” WP1, were fulfilled and the main objective of the project “Development of materials that enhance safety operation of Li-ion batteries in a passive way” was therefore successfully achieved.

Following papers based on achieved results were published:

1) P. P. Sahoo, B. Hudec, M. Mičušík, M. Mikolášek, M. Precnerová, P. Švec Jr., P. Nadáždy, S. Mičky, M. Zubair, P. Siffalovc, K. Fröhlich, Enahnced Performance of LiFePO4 cathodes with Alumina Nanocoating by Atomic layer Deposition: Insights from Electrochemical, Operando X-ray Diffraction, and X-ray Photoelectron Spectroscopy Analyses, ACS Appl. Energy Mater. 2025, 8, 10594, https://doi.org/10.1021/acsaem.5c01523.

2) P. P. Sahoo, A. Güneren, B. Hudec, M. Mičušík, P. Švec Jr., M. Precnerová, A. Nada, Z. Lenčéš, K. Fröhlich, Silicon/graphite anode performance improvement: a combination of atomic layer-deposited ZnO coatings with a fluoroethylene carbonate additive, ACS Appl. Energy Mater. 2025, 8, 6925, https://doi.org/10.1021/acsaem.4c02912.