IMOTHEP
GETTING HYBRID ELECTRIC

D4.8: SYNTHESIS OF ASS-LA BATTERY TECHNOLOGY EVALUATION

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EXECUTIVE SUMMARY

Hybrid electric propulsion is likely to play a more prominent role for regional aircraft with 40+ passengers in the future air transport system with reduced climatic impact. In IMOTHEP, two hybrid-electric regional (HER) aircraft concepts, a conservative one and a radical one, are developed. Energy dense battery technologies are needed to enable hybrid-electric propulsion of regional aircraft.

This deliverable reports the results from a systematic investigation of all-solid-state lithium-anode (ASS-LA) batteries within the framework of IMOTHEP work package 4 (WP4) Energy generation.

A general strategy on the development of ASS-LA batteries is explored and illustrated. The focus is on the development of key components of ASS-LA batteries including high performance composite cathode, robust hybrid solid electrolyte (HSE) film, and passivated Li metal as anode. In total, more than 260 pieces of 2016-type coin cells have been assembled and tested.

Future focuses on developing high performance ASSB for aeronautic application is outlooked and discussed.

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Glossary

Acronym	Signification
Ah	Ampere hour
ASSB	All-solid-state battery
ASS-LA	All-solid-state Lithium-anode
HSE	Hybrid solid electrolyte
LA	Lithium anode
LATP	Lithium aluminium germanium phosphate
LIB	Lithium-ion battery
LiTFSI	Lithium bis(trifluoromethanesulfonyl)imide
LLZO	Lithium lanthanum zirconium oxide
LNMO	Lithium nickel manganese oxide
LPSCl	Lithium phosphorus sulphur chloride
NMC	Lithium nickel manganese cobalt oxide
NMP	N-Methyl-2-pyrrolidone
OCV	Open circuit voltage
PEO	Polyethylene oxide
PVDF	Polyvinylidene fluoride
SE	Solid electrolyte
SEI	Solid electrolyte interphase
TRL	Technology Readiness Level
WP	Work Package

1 INTRODUCTION

Hybrid electric propulsion is likely to play a more prominent role for regional aircraft with 40+ passengers in the future air transport system with reduced climatic impact. In the H2020 project IMOTHEP [1,2], two hybrid-electric regional (HER) aircraft concepts, a conservative one and a radical one, are developed. Energy dense battery technologies are needed to enable hybrid-electric propulsion of regional aircraft.

As reviewed in the complementary technology survey for aeronautic batteries [3], Gen4b, all-solid-state lithium-anode (ASS-LA) battery technology with an expected gravimetric energy density at cell level of around 500+ Wh/kg is the target technology for air transport applications entering in service in 2035 including hybrid and all-electric propulsion.

Lithium-ion batteries (LIBs) have been well developed for powering road transport including electric vehicles and public transport currently. However, further exploration of LIBs into aeronautic field has not been performed intensively. Therefore, it comes to our strategy to develop next generation of lithium-ion batteries for powering aircraft for a clean sky in the future. The merits of the next generation of lithium-ion batteries include high energy density, high power capability, high safety and long cycling ability and thermal resilience in extreme environmental conditions.

The electrochemical system of the next generation lithium-ion batteries (denoted Gen4b, as per [4]) is all-solid-state batteries with Li-metal anode (ASS-LA), characterized by high Nickel-NMC cathode with high voltage and high capacity, and Li metal as anode (LA), and the most important component of solid electrolyte (films). Figure 1 shows the schematic of an all-solid-state lithium-metal anode battery.
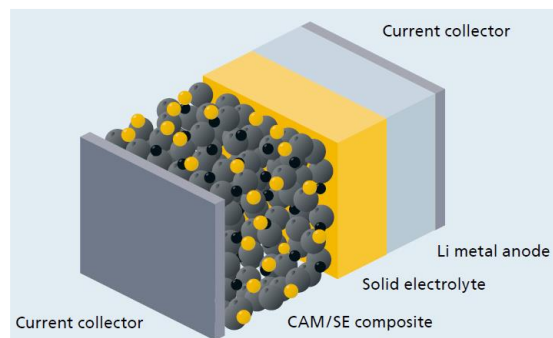
Figure 1: Schematic of all-solid-state lithium-metal anode battery, where composite cathode (CAM/SE composite) [5]

This deliverable reports the results from a systematic investigation at AIT of all-solid-state lithium-anode (ASS-LA) batteries within the framework of the IMOTHEP work package "Energy generation". A general strategy on the development of ASS-LA batteries is explored and illustrated. The focus is on the development of key components of ASS-LA batteries including high performance composite cathode, robust hybrid solid electrolyte (HSE) film, and passivated Li metal as anode. In total, more than 260 pieces of 2016-type coin cells have been assembled and tested.

The experimental exploration on ASS-LA batteries performed in IMOTHEP has two main ambitions:

a) to understand better their potential and limits for airborne applications, as well as to explore strategies to improve performance with respect to aeronautic requirements, i.e. providing high energy density with capability to deliver sufficient power; and

b) to provide parameters from experimental research to the numerical study performed by KIT [6,7].

1.1 ANALYSIS OF KEY FACTORS TO ENERGY DENSITY OF ASS-LA BATTERIES

High energy density is the most important factor attached to ASSB for attracting research in the world. A quantitative evaluation of the energy density of ASSB is performed in [8] for a minimalistic ASS-LA system supported by literature data. Figure 2 shows the gravimetric energy density of typical solid electrolyte systems of polymer electrolyte, sulfide electrolyte or oxide electrolyte in combination with different cathode system (high Nickel- (NMC), high voltage-spinel structure (LNMO), and sulfide (Li_2S) cathode) at different loadings and cathode active material content.
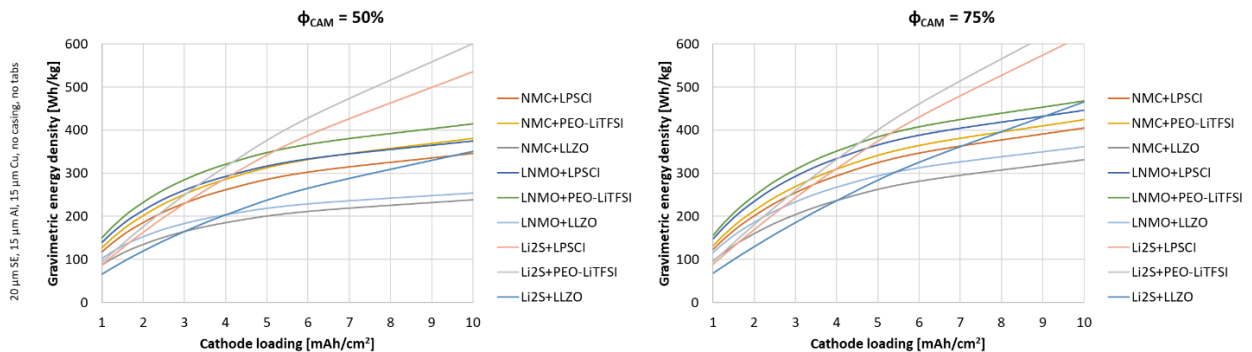
Figure 2: Analysis of energy density of all-solid-state lithium-ion batteries with different electrochemical systems and volume% cathode active material (CAM), calculated with method proposed in [8]

As shown in Figure 2, increasing the active material content in the cathode increases the energy density of all-solid-state lithium-ion batteries, and for cathode loadings up to around 5 mAh/cm^2 (cathode design for high energy density cell) the cases with NMC and LNMO as cathode show higher energy density than that with Li_2S as cathode. Due to the high density of ceramic LLZO, the electrochemical system with ceramic LLZO as solid electrolyte has the lowest energy density comparing to that using polymer electrolyte (PEO-LiTFSI) and sulfide electrolyte (LPSCl). In all those cases, 500Wh/kg is difficult to be reached, only Li_2S with polymer electrolyte could fulfil the requirement, at high cathode loading and only when extremely low internal resistance of the cell could be established. However, sulfide cathode is still at low TRL.

To rationalize the strategy to be adopted in IMOTHEP and based on our previous experience developed in other projects, we performed the following calculation of energy density of all-solid-state lithium-ion batteries based on hybrid solid electrolyte, NMC811 and Li metal anode. The relationship is mainly focused on the areal capacity of the cathode and the thickness of the hybrid solid electrolyte film, since these two process-related variables are easiest to be adjusted during the experiments (within certain limits).

(a)   (b)
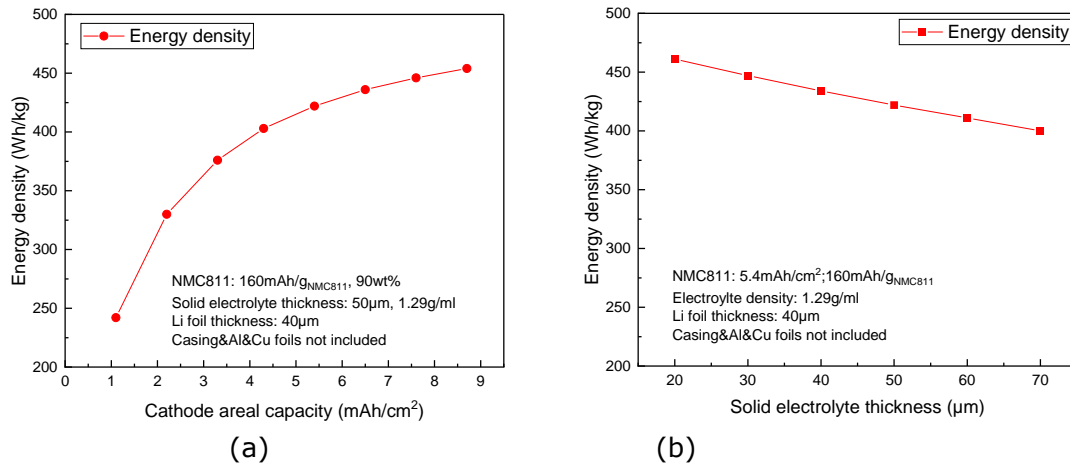
Figure 3: Estimation of energy density of all-solid-state NMC811, hybrid SE, Li-metal batteries using component parameters from AIT lab materials, calculated with method proposed in [8]

In Figure 3, the achievable specific capacity of NMC811 was set to be around 160mAh/g, although this value might be smaller when high areal capacity in terms of a thicker cathode film should be achieved (~50µm cathode film manufactured at AIT with 90wt% of active material loading corresponds to an areal capacity of 1.0mAh/cm^2). The density of PEO based-hybrid solid electrolyte was set to 1.29g/ml.

It can be seen from Figure 3 that the achievable energy density of all-solid-state lithium-ion batteries is very sensitive to the areal capacity of cathode. It increases from 242Wh/kg at 1.1mAh/cm^2 to 454Wh/kg at 8.7mAh/cm^2 (for 50 µm solid electrolyte film). It is less sensitive to the thickness of hybrid solid electrolyte film as it increases from 400Wh/kg at 70µm thick electrolyte film to 461Wh/kg at 20µm thick electrolyte film, although the improved Li$^+$ ionic transport kinetics in thinner solid electrolyte film was not considered here for simplified calculation. This implies that the strategy of IMOTHEP should be focused on developing high performance cathodes in the frame of ASS-LA batteries aiming at high energy density.

2   DEVELOPMENT ON ASS-LA BATTERIES IN IMOTHEP

As discussed above, the target of 500Wh/kg for ASS-LA batteries is challenging to reach. The use of energy-dense active materials needs to be coupled with component optimization and process innovation. The strategy adopted in IMOTHEP for developing high energy density all-solid-state lithium-ion batteries, consists of investigating (a) high-performance cathode, (b) hybrid solid electrolyte with high Li$^+$ ionic conductivity and (c) passivation of Li foil, as shown in Table 1.

For the selection of the solid electrolyte system, Figure 4 compares the advantages and disadvantages of typical solid electrolyte systems [9]. Polymer electrolyte has the best merit of ability for mass production, although it has shortcomings in other aspects including low Li ionic conductivity, stability against Li, narrow electrochemical window and so on, which could be alleviated through adding active fillers and modification of the chain structure of polymer materials. In IMOTHEP, AIT decided to adopt this technical route of adding active fillers to PEO polymer matrix for improving the performance of hybrid solid electrolyte films.
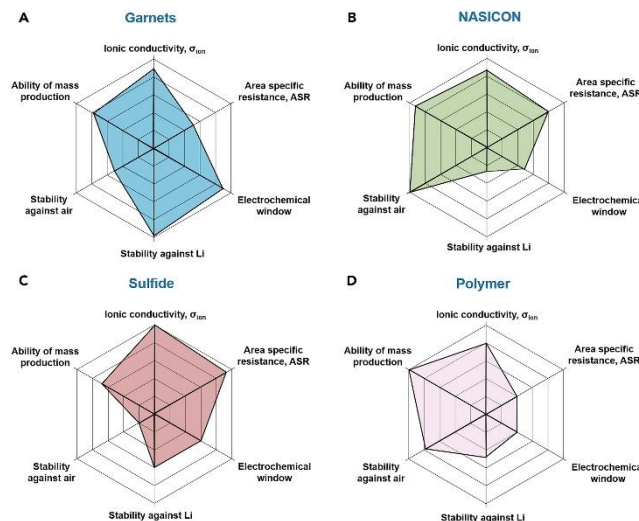
Figure 4: Radar chart of different solid electrolyte systems [9]

Since the key advantage of all-solid-state lithium-ion batteries origins from the application of solid electrolyte that contains no flammable liquid organics and is safe accordingly, the effort was firstly put onto the development of solid electrolyte film, then to the development of high-performance cathode, and finally the passivation treatment of Li foil anode. To facilitate the cyclable performance, other measures including treatment of components, valuable process including testing protocol have been developed, and will be introduced then.

Table 1: Strategy on development of Gen4b lithium-ion batteries in IMOTHEP

Cathode	Anode	Electrolyte	Process
NMC811	**Li anode**	**Hybrid SE**	
Conventional NMC811	Passivation	NASICON (LATP) based	Rolling & lamination
Composite NMC811		Garnet (LLZO) based	

2.1 GENERAL STEPS FOR THE PREPARATION OF HYBRID SOLID ELECTROLYTE AND CATHODE

There are two advantages from incorporating active fillers (LLZO) to PEO based polymer electrolyte. The first one is to improve the mechanical strength of solid electrolyte to resist/suppress the growth of lithium dendrite, and the second one is to suppress the crystallization of polymer matrix (here PEO) to form amorphous structure of PEO and facilitate the transport of Lithium ion, which thus improves the Lithium ionic conductivity in the solid electrolyte.

To obtain a uniform and dense hybrid solid electrolyte, effective dispersion of additive particles in PEO based matrix with high viscosity is a key factor. In the mixing process, strong sonication process was introduced when additive particles were added to acetonitrile solution, and again after the full dissolution of PEO in acetonitrile forming high viscosity PEO solution. Figure 5 shows the procedure snapshots for preparing hybrid solid electrolyte film based on PEO and with LLZO as additives, and key steps for assembling ASS-LA batteries. In total, more than 260 pieces of 2016-type coin cells (20 mm of diameter and 1.6 mm of height) of different compositions have been assembled and tested.

as-prepared slurry → remove air from solution in vacuum before coating → coating of hybrid solid electrolyte with pre-set gap → two hybrid solid electrolyte films after drying → punching electrolyte circles → applying electrolyte film onto cathode (Ø15mm) in dry room → applying lithium anode (Ø 16mm) and drying in vacuum at 60°C for 12 hours → assembled 2016 coin cells of ASSB
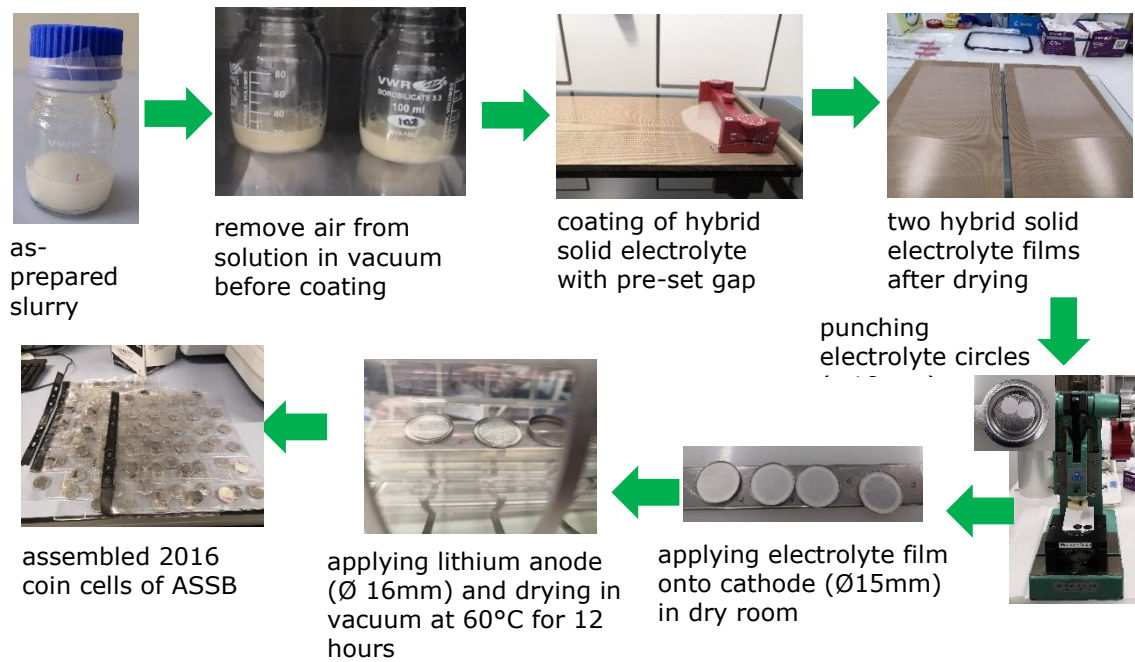
Figure 5: Preparation of hybrid solid electrolyte film and process of assembling all-solid-state coin cells

Figure 6 shows the SEM images of the typical microstructure of the as-prepared hybrid solid electrolyte film in terms of surface and cross-section views.
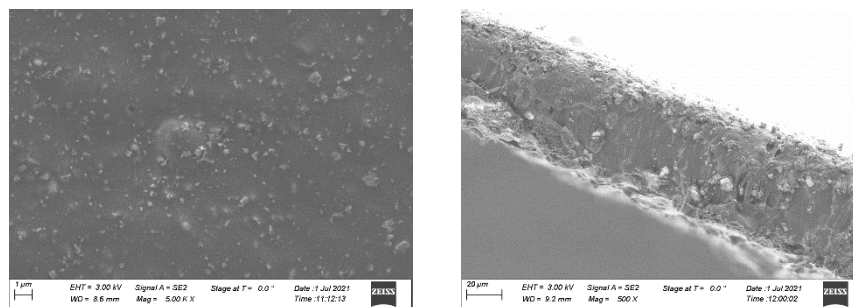
Figure 6: surface microstructure (left) and cross-section view (right) of solid electrolyte film

The preparation of the cathode film is similar to that of the hybrid solid electrolyte, where powder of active material NMC811 (particle size ~20µm, Targray, USA) was firstly dry mixed with electronic additive of carbon black C65 (particle size ~50nm, Imerys, Germany). The mixture was then added to a pre-prepared PVDF solution (8wt%) with NMP as solvent, stirred overnight to obtain a uniformly dispersed cathode slurry. Cathode slurry was then coated on Al foil, dried in vacuum at 150°C for 12 hours, calendared to the target thickness, punched into circle pieces (Ø15mm), and stored in glovebox finally.

Figure 7 shows the typical microstructure of NMC811 cathode tested and Al metal foil tested in IMOTHEP.
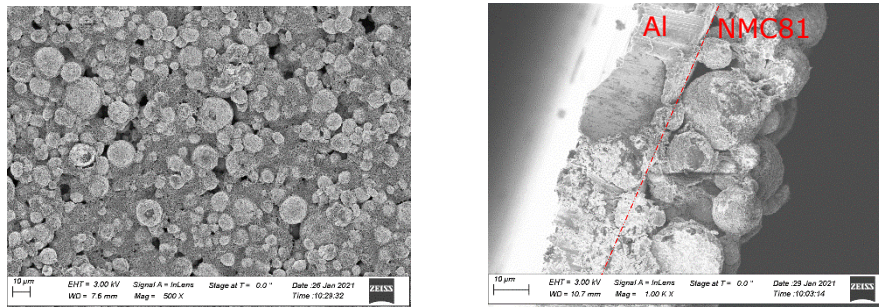
Figure 7: Surface (left) and cross-section view (right) of NMC811 electrodes

To get reasonable results of all-solid-state lithium-ion batteries, the areal capacity of cathode film developed in IMOTHEP was always kept at round 1.0mAh/cm^2 to align the laboratory research to that of industrial level, since areal capacity of at least 1.0mAh/cm^2 or higher is meaningful for evaluating the performance of the whole electrochemical system including cathode, solid electrolyte and lithium metal anode. Specifically, for all-solid-state lithium-ion batteries, the transport of lithium-ions within the bulk of the solid electrolyte and at the interfaces between solid electrolyte and electrodes depends significantly on their pathway length, thus on the thickness of cathode [10].

2.1.1 INFLUENCE OF LLZO CONTENT ON THE ELECTROCHEMICAL PERFORMANCE OF ALL-SOLID-STATE LITHIUM-ION BATTERIES

It is worth noting that all data reported in this section result from coin cells manufactured with a conventional cathode.
Figure 8 shows the voltage-time curves of cells during cycling test as a function of number of solid electrolyte layers (36.0wt% of LICGC in PEO based solid electrolyte) used in the coin cells, where conventional NMC811 cathode and pristine Li foil were used as cathode and anode respectively.
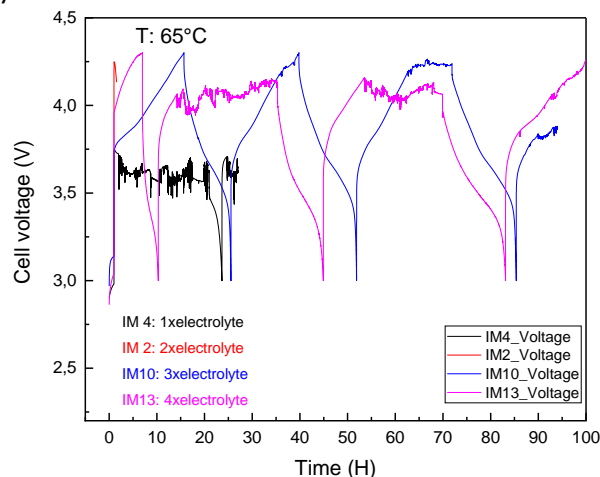
Figure 8: Influence of thickness of solid electrolyte film, from 1 to 4 SE layers

When one or two layers of electrolyte (samples IM4 and IM2) are used, serious lithium dendrite growth occurs, represented by the fluctuating voltage profile that makes the charge process (with upper cut-off OCV to set 4.3V) not able to finish. With the increased thickness of solid electrolyte film via adding more layers of solid electrolyte film, a relatively smooth voltage profile could be obtained during charging process (samples IM10 and IM13), although at higher charging voltage, the growth of lithium dendrite still couldn't be avoided. Therefore, in order to cycle the cells with more stable performance, four layers of solid electrolyte films were used in the following tests.
Figure 9 compares the voltage profiles of coin cells where hybrid solid electrolyte films with different concentration of LLZO were incorporated.
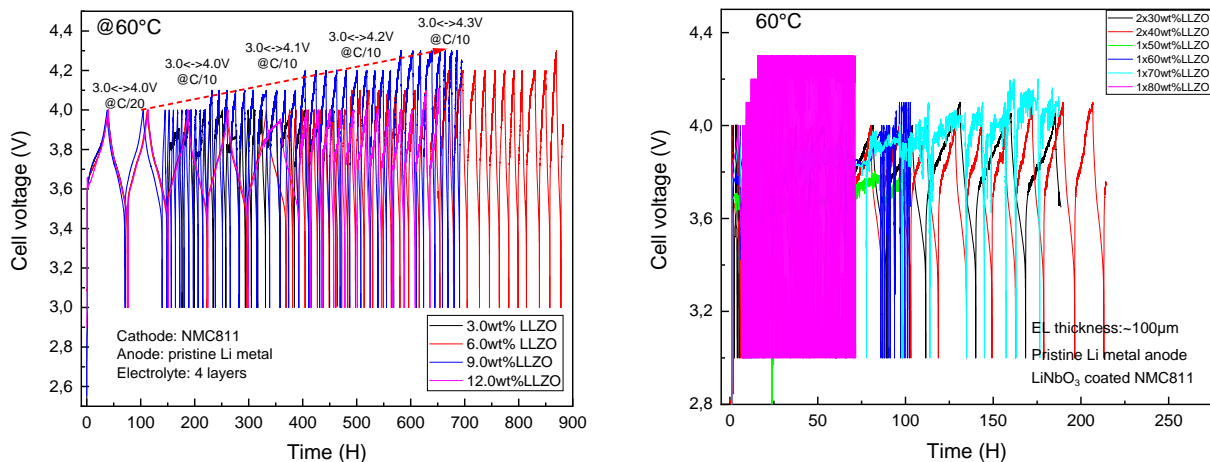
Figure 9: Influence of LLZO concentration of hybrid solid electrolyte on cell performance, increasing the upper cut-off voltage from 4.0 to 4.3 V (left: 3.0% to 12.0wt%, right: 30wt% to 80wt%)

In Figure 9 (left), coin cells with 6.0wt% and 9.0wt% of LLZO in hybrid solid electrolyte show more stable cycle performance when increasing the upper cut-off voltage from 4.0 to 4.3 V. In Figure 9 (right), further increase of LLZO content did not result in better cycling performance, and in case of 80wt% LLZO in hybrid solid electrolyte (pink curve), high polarization seemed to be responsible for the fast cycling at lower achievable capacity. Figure 10 shows that at higher (80wt%) LLZO concentration, porous structure could be observed in hybrid solid electrolyte although vacuum treatment was performed to remove air before coating, which might be responsible for the high polarization.
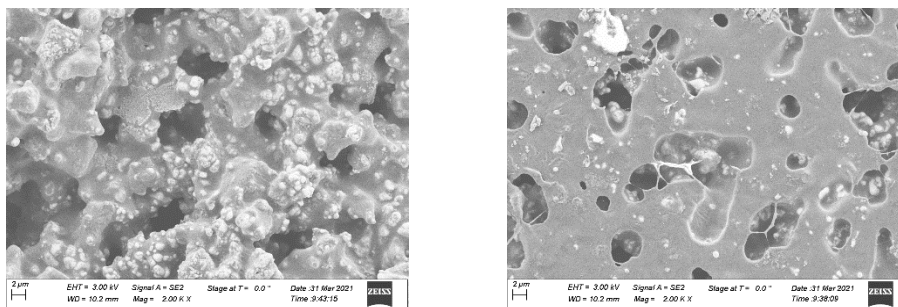
Figure 10: Microstructures of hybrid solid electrolyte with 80wt% LLZO (left: top surface, right: bottom surface)

Although increasing the content of active filler into the solid electrolyte matrix results in increased mechanical strength, the porous structure of hybrid solid electrolyte film results in poor electrochemical performance. In the following research, maximum of 50wt% of active fillers is kept to avoid the generation of porous structure in hybrid solid electrolyte film during drying process.

2.1.2 COMPARISON OF LICGC AND LLZO AS ACTIVE FILLER IN HYBRID SOLID ELECTROLYTE FILMS

It is worth noting that all data reported in this section result from coin cells manufactured with a conventional cathode.
Coin cells with hybrid solid electrolyte film having 6.0wt% and 9.0wt% LLZO show stable cycling performance. This was compared with a benchmark hybrid solid electrolyte with LICGC as active filler. It was expected that the performance of LLZO contained hybrid solid electrolyte should be improved since LLZO is more resistant to Li dendrite growth than that of LICGC. Figure 11 compares the cycle performance of two-coin cells, where cathode was LiNbO$_3$ coated NMC811 (with an areal capacity around 1.2mAh/cm^2), and pristine Li foil as anode. To avoid the uncontrollable growth of lithium dendrite, four layers of solid electrolyte films were applied.
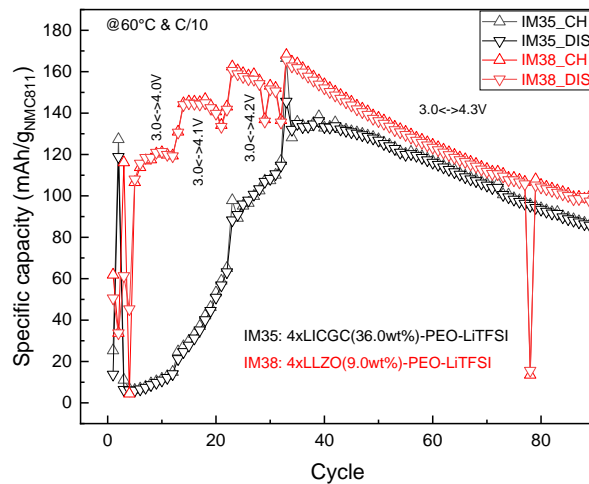
Figure 11: Comparison of cycle performance of cells with different active additives (LLZO vs. LICGC)

As can be seen from Figure 11, the cycle test protocol was set to increase the voltage test window step by step from 3.0<->4.0V to 4.1V, 4.2V each for 10 cycles, and finally to 4.3V for 50 cycles. With the increase of voltage upper limit, the achieved specific capacity increases gradually both in cell with LICGC and LLZO added hybrid solid electrolyte. However, cell with 9.0wt% LLZO shows a quick increase to 120mAh/g_{NMC811} at 4.0V, 145mAh/g_{NMC811} at 4.1V, 160mAh/g_{NMC811} at 4.2V, and 170mAh/g_{NMC811} at 4.3V, which coincides with the value AIT used for energy density calculation at the beginning of this deliverable. Cell with 36.0wt% LICGC also shows increased specific capacity with increased voltage window, which however is much lower than that of cell with LLZO. In the long-term cycle test, both cells show quick capacity fade rate: ~0.72%/cycle for cell IM38 with LLZO added hybrid solid electrolyte, ~0.56%/cycle for cell IM35 with LICGC added hybrid solid electrolyte. Concerning the relatively low content of LLZO (9.0wt%) in relation to that of LICGC (36.0wt%) in PEO based polymer matrix, LLZO is more effective in modulating the Li ionic transport of polymer electrolyte than LICGC, and less LLZO addition favours high energy density of all-solid-state lithium-ion batteries through reduced density of the hybrid solid electrolyte in the cell. Therefore, LLZO as active filler into PEO based solid electrolyte system is mainly focused in IMOTHEP project.

2.1.3 DEVELOPMENT OF COOPERATIVE EFFECT OF DUAL ACTIVE FILLERS IN POLYMER ELECTROLYTE

Although LLZO-added hybrid solid electrolyte film could contribute to stable electrochemical performance of all-solid-state lithium-ion batteries, four layers of hybrid solid electrolyte film must be applied to suppress the uncontrollable growth of lithium dendrite. Using such thick electrolyte film would result in rather low gravimetric energy density and limited power capability of the cell. To decrease the required 4-layer configuration of hybrid solid electrolyte film, a mechanically robust hybrid solid electrolyte film needs to be developed further.

To make use of the high mechanical strength of hybrid solid electrolyte containing high content of active filler LLZO, while avoiding porous structure, a strategy of densified stacking of active fillers through particle size matching has been developed.

In the new strategy, two active fillers of LLZO with particle size of ~2μm and LICGC with particle size of ~0.4μm were used. Ratios between LLZO and LICGC were investigated, thus LLZO (Garnet as G): LICGC (NASICON as N) varied from 6:1, to 3:1 and 1:1 (all in weight), while the total weight percent of active fillers was kept at 50wt% in the hybrid solid electrolyte.
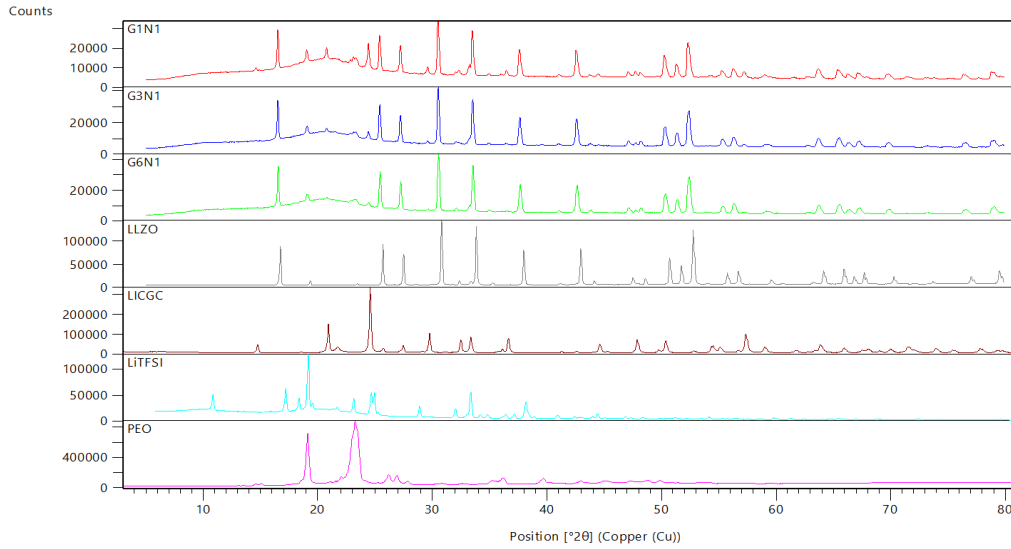
Figure 12: XRD spectra of individual components and the hybrid solid electrolyte films

Figure 12 compares the XRD patterns of hybrid solid electrolyte film with three different combination ratios between Garnet and NASICON particles, the XRD patterns of individual components (PEO, LiTFSI, LICGC and LLZO) are also listed for comparison. It could be seen from Figure 12 that the major diffraction peaks of PEO disappear (~23.5°) in the XRD patterns of hybrid solid electrolyte films G1N1, G3N1 and G6N1, which confirms that the crystalline of PEO at those hybrid solid electrolyte films is weakened through incorporating active additives of LLZO and LICGC particles. This is beneficial for the segmentation movement of PEO chain for lithium-ion transport in hybrid solid electrolytes. The featured diffraction peaks of LiTFSI (~19.0°) salt could be observed in the hybrid solid electrolyte films, implying that it does not decompose in the hybrid solid electrolyte films. With the increase of LLZO content, the characteristic diffraction peaks of LLZO (~31.5°) increase steadily, while that of LICGC (~25°) decrease gradually.
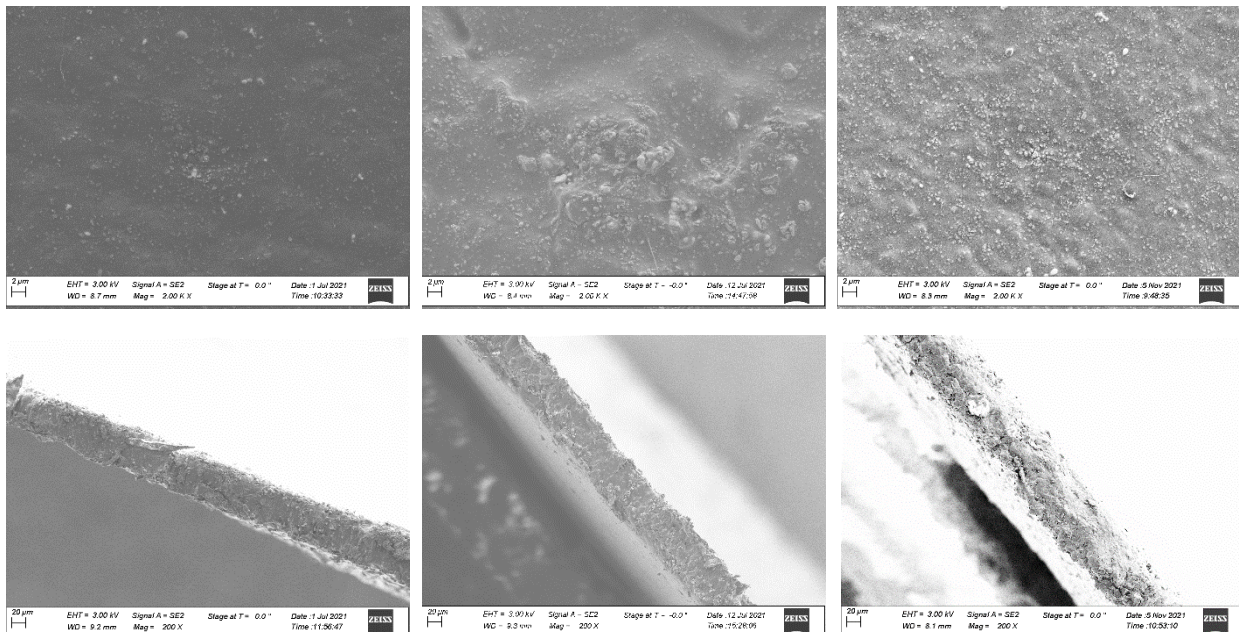
Figure 13: Microstructures of hybrid solid electrolyte films
(left: G6N1; central: G3N1; right: G1N1; top: surface; bottom: cross-section)

Figure 13 shows the microstructures of G6N1, G3N1 and G1N1 electrolyte films via SEM, all three films show dense structure, no porous structure was observed. With the increase of small LICGC particles from left to right, more LICGC particle is more visible, and the film

tends to become wavier. In all three films, dense film could be observed from the cross-section view of the films.

Figure 14 compares the Lithium ionic conductivity of three composite hybrid solid electrolyte and their performance in full cell.
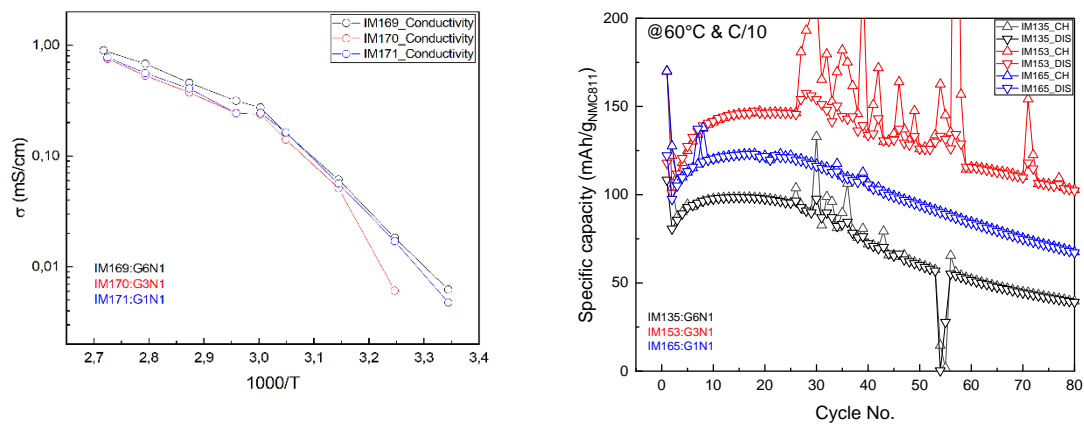
Figure 14: Lithium ionic conductivity of composite hybrid solid electrolytes as function of inverse temperature (left) and their performance in full cells (right)

As shown in Figure 14, the best lithium ionic conductivity is achieved in the composite hybrid solid electrolyte with the ratio between garnet and NASICON of 6:1 in weight. Its lithium-ion conductivity reaches about $2.73 \times 10^{-4}$ S/cm at 60°C, which is comparable to the state-of-the-art results of lithium ionic conductivity in PEO based hybrid solid electrolytes [11] and is 2 to 4 orders of magnitude larger than for pure PEO. However, for the electrochemical performance of all-solid-state lithium-ion batteries in the format of 2016 coin cells, the cell with two layers of G3N1 electrolyte shows the highest specific capacity (150mAh/g) of NMC811, which is ~125mAh/g for cell with G1N1, and ~100mAh/g for cell with G6N1. The cell with G1N1 shows the most stable performance without overcharge effect reflected by extremely high charge capacity during charge process, which is attributed to the uncontrollable growth of lithium dendrite. The better suppression of uncontrollable growth of lithium dendrites during the charging process might be due to the increased density due to the increased LICGC particle content in the G1N1 hybrid solid electrolyte film.

The corresponding energy density of cells with different composition of hybrid solid electrolyte was calculated in consideration of the weight of Al, cathode, electrolyte film and Li foil, while the weight of coin cell stainless-steel housing was not included. Figure 15 shows the cycling performance of cells in terms of cell-level energy density.
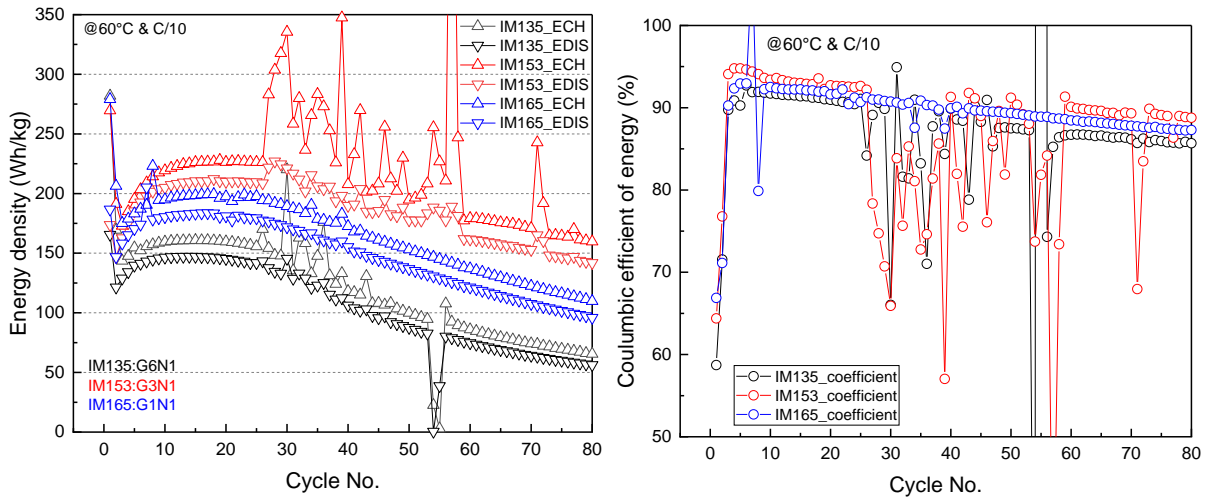
Figure 15: Cell-level energy density (left) and columbic coefficient of energy (right) of all-solid-state lithium-ion battery cells with different hybrid solid electrolyte

On the left of Figure 15, the cell-level energy density during discharge reaches maximum 208Wh/kg in the cell with G3N1 solid electrolyte at the early cycling stage till cycle No.25, to 183Wh/kg in cell with G1N1 solid electrolyte, and ~147Wh/kg in cell with G6N1 solid electrolyte. With the specific material thicknesses, this is in line with the calculated results in Fig.3 in this deliverable, even if it is still a substantial gap towards the ASS-LA battery technology target of 500Wh/kg (TRL9). In Figure 15, right, the columbic efficiency of energy was firstly calculated as a criterion for evaluating the energy performance of ASS-LA batteries cells instead of widely used columbic efficient of capacity. This new parameter helps to evaluate the energy efficiency of lithium-ion batteries mainly focused on the application side, i.e. is more useful for energy management of a complex system such as aeronautic applications.

Since the G3N1 hybrid solid electrolyte shows best performance in current electrochemical system, improving energy density via using less G3N1 electrolyte to reduce the weight of hybrid solid electrolyte was performed. Figure 16 compares the results of cells with one to four layers of G3N1 electrolyte films in the 2016 type coin cells.
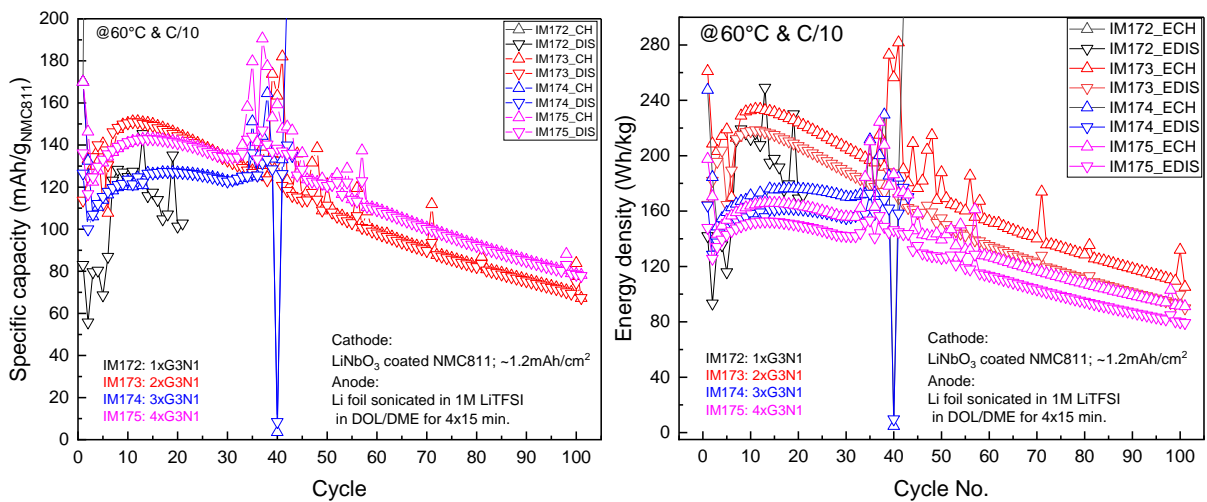
Figure 16: Influence of number of solid electrolyte films in terms of specific capacity of cathode material (left)
and energy density of cells (right)

In Figure 16, left, the cells with one layer (IM172) and three layers (IM174) of G3N1 electrolyte films were both stopped at ~10 cycles and ~30 cycles due to serious lithium dendrite growth during cycling test. For cells IM173 and IM175, the achievable specific capacity of active material NMC811 is comparable to each other, slightly higher for IM175

with 4 layers of G3N1 electrolyte films than for IM173 with 2 layers of G3N1 electrolyte films. However, both cells underwent serious lithium dendrite growth at cycle No. from 40 to 60. However, in Figure 16, right , IM173 shows about 220Wh/kg of discharge energy density at the early stage of cycling test, while in cell IM175 only 150Wh/kg of discharge energy density could be achieved at the early stage of cycling test. Therefore, strategy of two layers or even one layer of solid electrolyte films will be investigated to ensure high achievable energy density in the research.

2.2 DEVELOPMENT OF HIGH-CAPACITY COMPOSITE CATHODE

As the key factor for achieving high capacity and high energy density of all-solid-state lithium-ion batteries, high performance cathode materials and cathode have to be developed and modified in the all-solid-state lithium-ion batteries system.

$LiNbO_3$ coated NMC811 shows high specific capacity and stable performance especially at high charging voltage due to the surface structural stabilization by $LiNbO_3$ layer [12] , thus it is adopted in IMOTHEP for developing high energy density all-solid-state lithium-ion batteries.

Improving the electrochemical kinetic in the cathode is crucial for the improvement of the whole electrochemical performance of all-solid-state lithium-ion batteries since there is a lack of direct contact between electrolyte and active material particle. Especially for thick cathodes, the bulk cathode particle has no chance to contact the solid electrolyte, and even for the cathode particle at the interface between solid electrolyte and cathode there is most likely a 1-D or 2-D interface instead of 3-D contact with liquid electrolyte.

In IMOTHEP, AIT tried to add solid electrolyte particles into the cathode film and to improve the electrochemical kinetics of the cathode through providing more conformal electrochemical interface between cathode particle and solid electrolyte particle within the bulk of cathode film. Typical results are obtained in a composite NMC811 cathode with 10wt% of LICGC particle, where the recipe of composite NMC811 cathode is: NMC811:PVDF:C65:LICGC=80:5:5:10 (all in wt%).
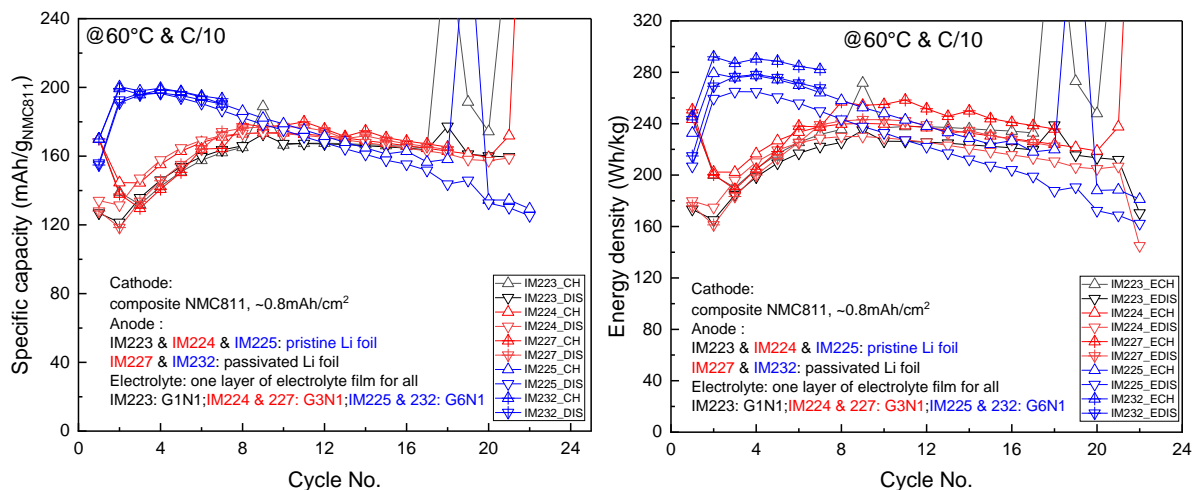
Figure 17: Improvement of electrochemical performance of all-solid-state lithium-ion batteries cells via composite NMC811 in terms of specific capacity (left) and energy density (right)

In Figure 17, a substantial improvement on the electrochemical performance of the composite cathode compared to the conventional one used in section 2.1 was observed. Due to a technical failure and following maintenance of the Maccor testing system in the AIT lab, those cells could not be cycled up to 100 cycles. However, after evaluating the cycling performance of cells with limited cycle numbers, some conclusions could still be drawn as following:

- Firstly, stable cycling performance could be achieved till ~18 cycles when only one layer of solid electrolyte film was adopted instead of four layers of electrolyte film, which is a great improvement.
- Secondly, the achievable specific capacity of NMC811 could reach about 200mAh/g in cells with G6N1 as electrolyte, which was only about 170mAh/g in the case of the conventional NMC811 cathode, indicating about 20% of improvement.
- Reproducibility was improved as can be observed in the overlapping of the cycling curves of the cells IM225 and 232, and that of the cells IM223, IM224 and IM227, which indicates a good potential for upscaling.

These three effects could be attributed to the enhanced lithium-ion transport in the cathode film since lithium-ion diffusion in solid phase is the bottleneck.

On the right side of Figure 17, the improvement in terms of cell energy density is also apparent, where ~280Wh/kg discharge energy density could be achieved for cell IM232, and stable performance of discharge energy density around 220Wh/kg could be obtained in all other cells, although their fading rate is still high. Cells with G3N1 electrolyte show a more stable cycling performance although their initial energy density was not as high as for cells with G6N1 electrolyte. After about 10 cycles, the achieved specific capacity and corresponding energy density of cells with G3N1 electrolyte both exceed that of cells with G6N1 electrolyte.

2.3 PASSIVATION OF LI FOIL AS ANODE FOR ASS-LA BATTERIES

Lithium metal foil has the advantage of high specific capacity of ~3860mAh/g, thus is the ideal anode for lithium-ion batteries to achieve high energy density.

However, due to the high activity of Li metal, the uncontrollable growth of lithium dendrites in lithium metal batteries could lead to penetration of the separator (i.e. the solid electrolyte) and induce internal-short related performance and safety issues, or form dead lithium during long-term cycling which causes capacity fading. Both have hindered the wide application of lithium metal as anode for high energy density lithium-ion batteries including all-solid-state lithium-ion batteries and other type of high energy density batteries (Li-S, and others).

Forming a passive layer on top of the lithium metal has been proposed as an alternative way to make use of the high specific capacity of lithium metal while avoiding the unwanted/uncontrollable side reactions between lithium metal and electrolyte (for both, liquid and solid electrolyte). In IMOTHEP, AIT evaluated the passivation of lithium metal by dry and wet methods.

2.3.1 PHYSICAL PROCESS

It was reported that Li could form alloys with some other metallic elements, including Indium (In), gold (Au), Silver (Ag), and that the formation of Li-metal alloy in terms of a thin buffer layer could help to build a conformal interfacial layer for uniform distribution of the ion current at the interface during lithium depletion (during discharging) and plating (during charging) [13,14].

As a dry method, AIT investigated magnetron sputtering to deposit a thin layer of gold onto the surface of the lithium foil and evaluated the influence of this passivation layer on the cyclic performance during electrochemical test of all-solid-state lithium-ion batteries.

Figure 18 shows the physical passivation process, where Li foil was sputtered with Au in vacuum for 20s, and it turned into gold colour after sputtering. Two 2016-type coin cells of all-solid-state lithium-ion batteries were built and tested, where 4 layers of PEO-LiTFSI-LICGC (~36.0wt%) electrolyte films were used.

Figure 18: Sputtering Au onto Li foil for passivation (left: 2x pristine Li chips; central: in sputtering; right: passivated Li foil)
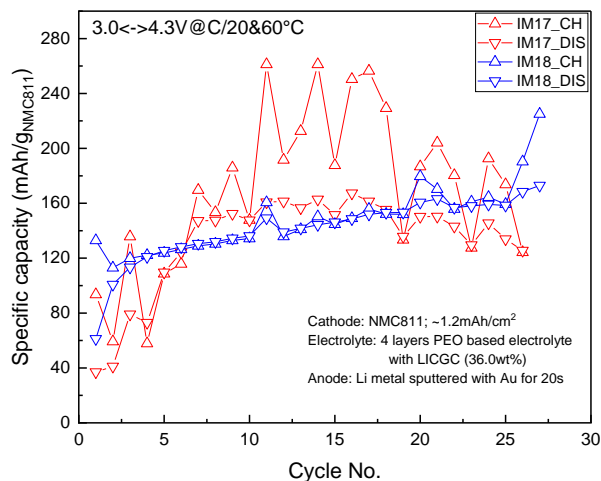

Figure 19: Influence of passivation of Li metal anode with Au sputtering

Figure 19 shows the electrochemical performance of two cells (IM17 and IM18). In cell IM17, serious growth of lithium dendrite was observed as unstable charging process was measured with extra high capacity and low coulombic efficiency. On the contrary, in cell IM18, a steady increase of specific capacity could be observed, indicating a continuous improvement of the electrochemical kinetics at the interface between the passivated Li metal foil and solid electrolyte film till the 25th cycle. After the 25th cycle, it seems that uncontrollable growth of lithium dendrite happened, and stable performance could not be sustained any more.

In Figure 19, the poor reproducibility on the electrochemical performance of cells IM17 and IM18 with passivated Li metal anode via magnetron sputtering method was also observed. This implies that this dry or physical passivation process / method might not be able to form uniform distribution of sputtered Au layer on the surface of Lithium metal oil, which weakens the passivation effect by Au-Li alloy between solid electrolyte and lithium metal anode.

2.3.2 WET CHEMICAL PROCESS

A wet process for passivating Li metal in a solution is likely to provide a uniform passivation layer on the Lithium metal foil surface. Usually, wet chemical passivation of Lithium metal is performed though putting lithium chips into 1M LiTFSI solution in DOL/DME (50:50 in wt%) for a certain time [15]. During passivation, a SEI layer is formed on the surface of highly reactive lithium metal. Because of the self-attenuation property of wet chemical reaction, it is expected that the passivation process slows down with the formation of the initial SEI layer on the lithium metal surface in the passivation solution, which isolates the fresh surface of lithium metal and prevents further contact between lithium metal and passivation solution. With increasing duration of the passivation process, a gradient of certain solvent near the front of fresh passivation layer might form, which also retards further passivation. Here, AIT introduced a sonicating process during the passivation of

lithium metal aiming to form continuously a uniform and dense SEI layer on the top of the lithium metal, which helps to suppress uncontrollable growth of lithium dendrite.

For the determination of optimized passivation parameters including sonication and sonication time, a series of experiments was carried out. To enhance the visibility of passivation effect from naked eyes, scratches were generated on the surfaces of lithium metal foils.

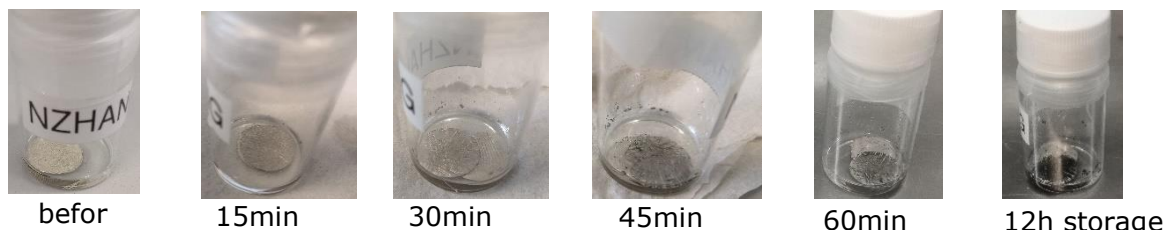| befor | 15min | 30min | 45min | 60min | 12h storage |

Figure 20: Passivation of 2 x Lithium foils in 1M LiTFSI in DOL/DME solution after sonication for different durations

In Figure 20, the colour of lithium foil keeps unchanged after 30 min sonication treatment in passivation solution, becomes slight grey after 45 min, and slight dark after 60 min. Sonication is interrupted every 15 min for checking the integrity of the Li foil. After 12 hours of storage in glove box, the scratches on the lithium foil turned to deep dark. Therefore, AIT determined the passivation strategy as 4 times of 15 min sonication treatment.

Figure 21 shows the passivated Li metal foils and SEM images of lithium metal foils before and after passivation under sonication for 4x15min.
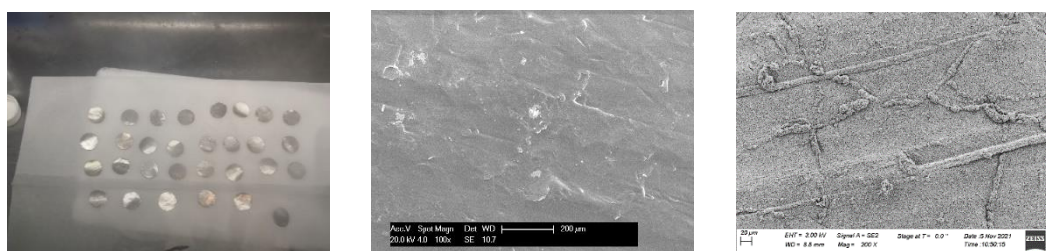
Figure 21: Passivated Li foils (30 pieces, left) and morphologies before (central) and after passivation (right) via SEM

The surface of pristine Li metal is smooth and clean free of small particles. In passivated Li metal, a uniform surficial layer was formed showing a rough structure and the over-growth of the SEI layer is found at positions of cracks or defects, that might have developed due to the fast kinetics of chemical passivation with the fresh lithium metal exposed to the passivation solution.

Figure 22 shows the influence of Li passivation on cell performance, where pristine Li metal was used in Cell IM140, 4 times sonication for 15 minutes of Li foil for passivation was used in cell IM154, and 6 times sonication for 15 minutes of Li foil for passivation was used in cell IM142. The cell configuration for all three cells was the same:

- Cathode: LiNbO$_3$ coated NMC811: ~1.2mAh/cm^2;
- Electrolyte: two layers of G3N1 film;
- Anode: Li metal passivated in 1M LiTFSI in DOL/DME under sonication

Figure 22: Influence of Li passivation on the performance of all-solid-state lithium-ion batteries in terms of specific capacity (left) and voltage profile of cell without Li passivation (right)

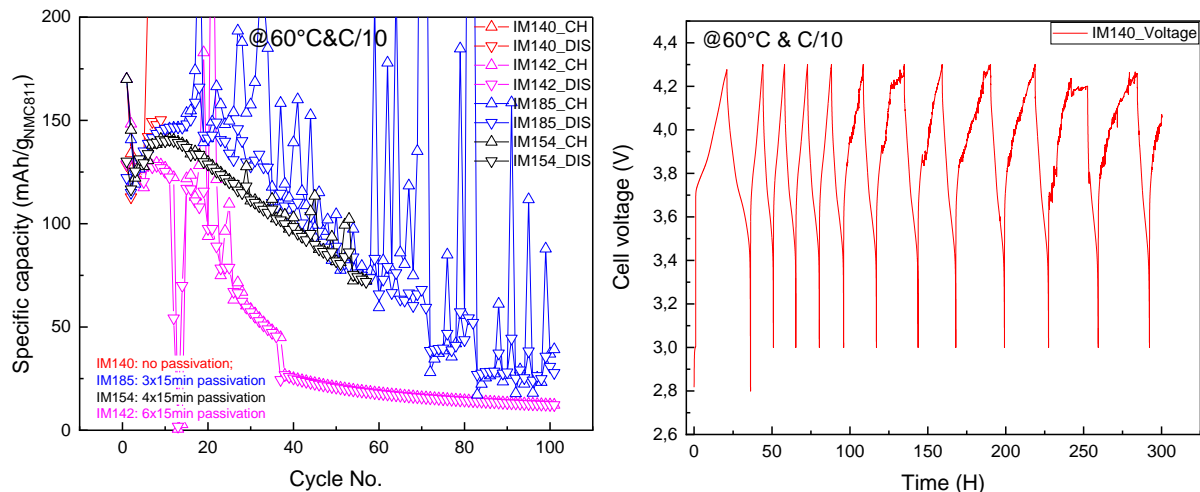In Figure 22, with pristine Li metal as anode in Cell IM140, uncontrollable growth of lithium dendrite happened already after cycle No.5, the corresponding voltage profile is shown in Figure 22 right, where an unstable voltage profile with fluctuating voltage was observed. In cell IM185 with 3x15min. sonication treatment, very disturbed cycle performance was observed, implying also serious lithium dendrite growth. In cell IM154 with lithium metal anode passivated for 4x15min., stable performance could be achieved till Cycle No.57 and the capacity fading is about 1.0%/cycle. Further increasing the time of passivation and sonication did not improve the cycling performance as shown for Cell IM142 with 1 hour 30 min passivation time. After 11 cycles, uncontrollable growth of lithium dendrite happened and faster capacity fading was observed. Therefore, 4x15min of sonication was adopted for the passivation of Lithium metal in 1M LiTFSI solution with DOL/DME (50:50 in wt%) as solvent in the IMOTHEP project. Around 80 coin cells were prepared with passivated Li-metal anode showing high reproducibility of the proposed method. Comparing to other research on passivation of Li foil [16], where passivation was performed over days instead of hours or minutes, the passivation time in this research is extremely short. However, this highly efficient and reproducible passivation of Li foil anode developed within the IMOTHEP project needs to be further investigated for its scalability.

2.4 RATE CAPABILITY TEST

The rate capability of all-solid-state lithium-ion batteries is an important parameter for high power applications such as aeronautics. The rate capability was tested with cells containing (a) the conventional cathode and (b) the composite cathode. Figure 23 shows their electrochemical performance with different hybrid solid electrolyte and cathode composition and under different C-rates, where:

− LiNbO$_3$ coated NMC811 conventional cathode (~1.2mAh/cm^2) and LiNbO$_3$ coated NMC811-LICGC composite cathode (~0.8mAh/cm^2) were used;
− Li foil was passivated in 1M LiTFSI in DOL/DME solution and sonicated for 4x15min;
− two layers of solid electrolyte films (1 layer of SE film for the cells with composite cathode) were applied.
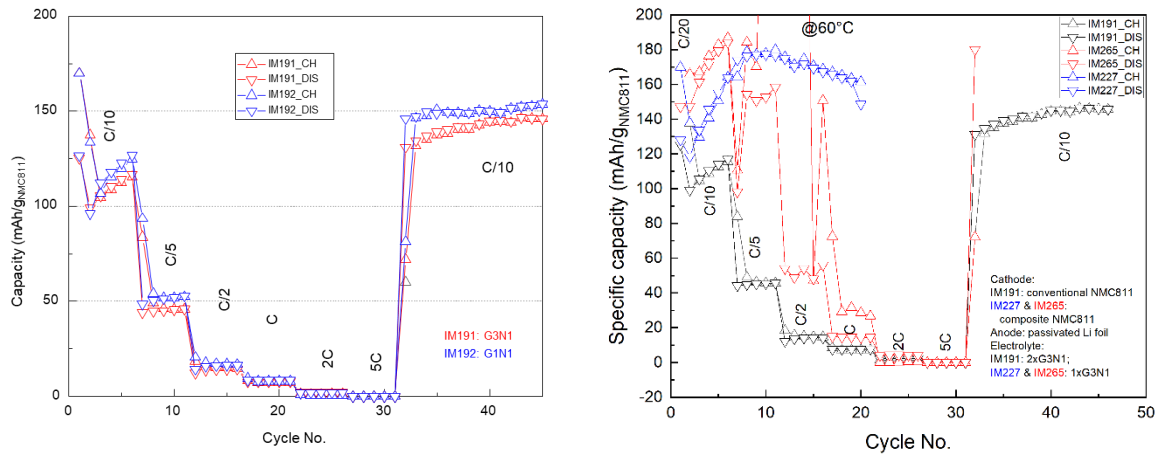
Figure 23: Rate capability of all-solid-state lithium-ion batteries: Left: with conventional cathode (red and blue curves); Right: conventional vs. composite cathode (black vs. red and blue)

As shown in Figure 23 (left), with the increase of testing C-rate, the achievable specific capacity of conventional cathodes (black, red and blue curves) decreases gradually and accordingly, at C/10, around 125mAh/g_{NMC811} (the increasing specific capacity indicates that the cells are still forming the solid-solid interphase) could be achieved in cell IM191 and IM192. This value decreases to ~50mAh/g_{NMC811} at C/5, and ~15mAh/g_{NMC811} at C/2, ~10mAh/g_{NMC811} at 1C, and for higher C-rates almost no capacity could be achieved in all cells. When C-rate was changed back to C/10, around 150mAh/g_{NMC811} could be recovered in cell IM191 and IM192. Even if at high C rates the cells cannot provide sufficient capacity, their mechanical integrity and electrochemical stability is still maintained.

The rate capability for cells (IM227 and IM265) with composite cathode and a single layer solid electrolyte film was also tested. In the first cycles at C/10, a maximum of 180 mAh/g_{NMC811} could be achieved, confirming the high specific capacity (~200mAh/g) found in previous experiments, i.e. around +40% compared to the conventional cathode. For IM265, the rate capability at C/5 is improved substantially, from 50 to 150mAh/g (+200%) and at C/2 it is at least 50mA/g, i.e. +230%. Unfortunately, the two cells failed due to a breakdown of the cell cycler (IM227) and after stopping and restarting the cycler (IM265). Due to time constraints the experiments could not be repeated.

Nevertheless, these first results indicate that the use of composite cathode improves, at the same time, usable capacity and power capability – two parameters essential for aeronautic batteries.

2.5 ASS-LA SAFETY

As the ASS-LA were explored at coin cell level and upscale to larger cells (e.g. pouch cells with capacity in the order of Ahs) was out of scope of IMOTHEP, the resilience performance of all-solid-state lithium-ion batteries under extreme thermal runaway and physical abuse could be evaluated only preliminarly. In particular, investigations on coin cells for external short circuit and overtemperature were conducted. Figure 24 shows the continuous voltage profiles of cell (a) after thermal treatment at 150°C for 6h (in red) and (b) after external short for 10 min (in blue). In both cases, the cells could be cycled with some remaining capacity, although the growth of lithium dendrite could be observed. Either way, there were no issues with gas emission or rapid temperature increase.
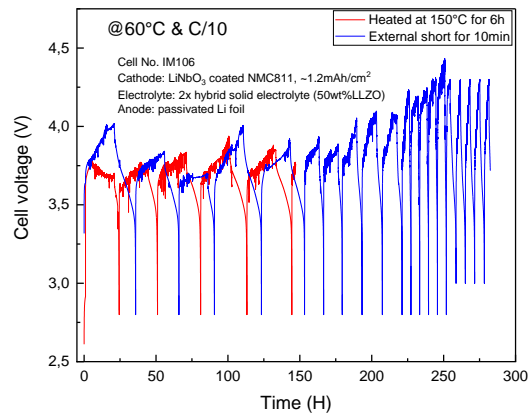
Figure 24: Voltage profiles of ASSB cell after abuse tests of overheating (in red) and external short (in blue)

Although this result could not be treated as a direct confirmation of physical resilience of ASSBs due to the small capacity of coin cell, it is still reasonable to assume that ASSB is safe to certain degree for extreme thermal runaway and under physical abuse, as all components are inflammable and thermally stable up to at least 120°C, when the hybrid solid electrolyte starts melting (at 180°C lithium metal melts and at around 230°C NMC811 decomposes).

3   CONCLUSIONS AND PROSPECTS

Research on the following categories have been carried out in IMOTHEP WP4.2:
- Hybrid solid electrolyte with high ionic conductivity was developed, where a combination of garnet and NASICON structured powder with a weight ratio of 3:1 between garnet and NASICON in PEO based polymer electrolyte film is confirmed to have the best performance.
- High-capacity composite cathode was developed, where 10wt% of NASICON structured LICGC powder was incorporated into $LiNbO_3$ coated NMC811 cathode, and a high specific capacity of NMC811 was achieved to be around 200mAh/g at 60°C and C/10. The rate capability of the cathode needs to be improved.
- A highly efficient (fast) and reproducible passivation process of the Lithium metal anode was realized through 1h sonication in 1M LiTFSI in DOL/DME (50:50 in wt%). Sonication during passivation helps to activate the passivation solution and prevents the formation of a depletion layer at the surface of the Li metal foil during static passivation process, and results in the formation of a dense and uniform protective SEI layer on the top of lithium metal anode.

The key findings of this lab exploration of hybrid polymer-ceramic ASS-LA batteries are:

- Composite cathode has a key role to deliver at the same time high capacity with improved power capability due to enhanced Li ionic transport within cathode. However, further improvements of composite cathode and solid electrolyte are needed to obtain useful capacity at discharge rates of 1C and beyond.
- Li-metal passivation suppressed well Li-dendrites, enabling up to around 100 cycles. Further stabilisation of the cell electrochemistry is needed for increasing further the cell cycle life.
- The prepared ASS-LA coin cells proved to be reasonably safe against abuse by overheating or external short. However, tests on upscaled cells are needed to assess in full their safety.

Increasing energy density towards 500Wh/kg

In Figure 25, Figure 3(a) is replotted with the energy density of around 278Wh/kg achieved in IMOTHEP (solid blue point), applying composite NMC811 cathode, single layer of 50µm G6N1 electrolyte film and 50µm Li foil. Further reducing the thickness of the solid electrolyte film from 50µm to 15µm, of the Li foil from 50µm to 5µm and of the Al foil from 20µm to 5µm would let energy density increase to ~419Wh/kg ("Strategy_1" in pink). Increasing the areal capacity of the composite cathode together with the "anode free" concept could help to increase the energy density to ~500Wh/kg ("Strategy_2" in green). Increasing further the cathode areal capacity was not considered here since this strategy might increase the thickness of the cathode, which reduces the electrochemical kinetic of Li ion transport and which would be difficult to mass-produce.
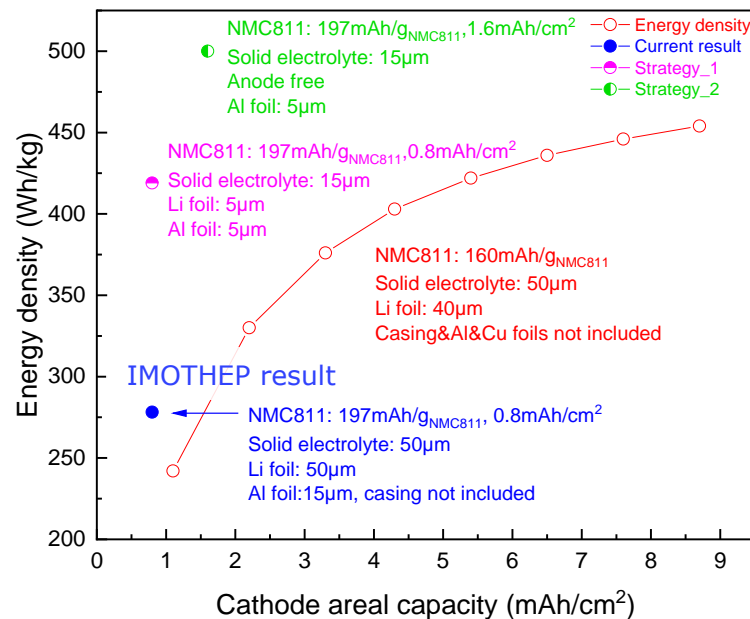

Figure 25: Development route of ASSB: current result and developing strategies towards higher energy density

Cycling performance, rate capability, COSTs

The cycling performance of the ASS-LA coin cells developed in IMOTHEP was not extensive. Developing cells with highly stable cycling performance was out of scope of this technology exploration. The same also applies to the power capability of the current coin cells. The lithium-ion conductivity of the hybrid solid electrolyte and the interfacial electrochemical kinetics in all-solid-state lithium-ion batteries would need to be substantially improved for achieving high power capability.

The cost of all-solid-state lithium-ion batteries cannot be evaluated within this study since scalable and reproducible processes for hybrid solid electrolyte have not been developed yet and are out of scope of this exploratory study.

Prospect

In reviewing the research carried out in IMOTHEP and the challenges faced currently, the future work for developing high performance all-solid-state lithium-ion battery cells for aeronautic applications should cover all the three directions of IMOTHEP:

- high energy and power capable composite cathode,
- thin, mechanically-electrochemically stable, high performance solid-state electrolyte and
- stable thin Li-metal anode.

The upcoming Horizon Europe work programme [17] calls for the development of safe, high power Gen4 cells with an energy density beyond 400 Wh/kg and low environmental impact, while the MOST China [18] aims at pushing the boundaries for energy density

much further to beyond 600 Wh/kg (see Table 2 summarizing the target KPIs for the upcoming ASS-LA battery research and development programmes of EU and China).

Table 2: Target KPIs for Gen4 ASS-LA battery development in EU and China till 2025

	Cathode	Electrolyte	Lithium metal anode	Programme
Component level	high voltage cathode (>4V)	Li$^+$ conductivity: >0.5mS/cm;	• Stability during handling, processing and operation • Thickness below 20µm, contributing towards energy density levels of 400-500 Wh/kg. • Reduced energy/carbon footprint • Process compatible with recycling targets	EU Horizon Europe - Work Programme 2023-2024 [17]
Cell level	• Capacity: > 1Ah (at TRL5) • Energy density: > 400Wh/kg and 1000Wh/l • Cycling: > 500 cycles • C-rate: up to 10C for aviation applications • Safety: EUCAR level 2 at module/pack level for aviation applications			
Component level	>400mAh/g for active material	• RT Li+ conductivity: 1mS/cm • Li+ transfer number: >0.8 • Film thickness: <15µm	Sp. capacity: >1500mAh/g	MOST China [18]
Cell level	Capacity: > 10Ah; Energy density: > 600Wh/kg; Cycle life: > 500			

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