ASTRABAT

NEW EFFICIENT LITHIUM BATTERIES FOR ELECTRIC VEHICLES

Funded by
the European Union

Table of Contents

Introduction

The transport sector is responsible for around one quarter of Europe's greenhouse gas (GHG) emissions. The EU-funded project, ASTRABAT (All-Solid-sTate Reliable Battery for 2025), is part of a broader drive by the European Union to make electric mobility become the next transport mode and contribute to the EU overall goal to reduce GHG emissions by 80-95% by 2050. E-mobility is expected to represent 88% of the total rechargeable Li-ion battery cell market value in 2026 and 70% of the EU electricity should be produced by renewable energy. Hence, the electric battery storage is vital in this transition to clean mobility and clean energy systems.

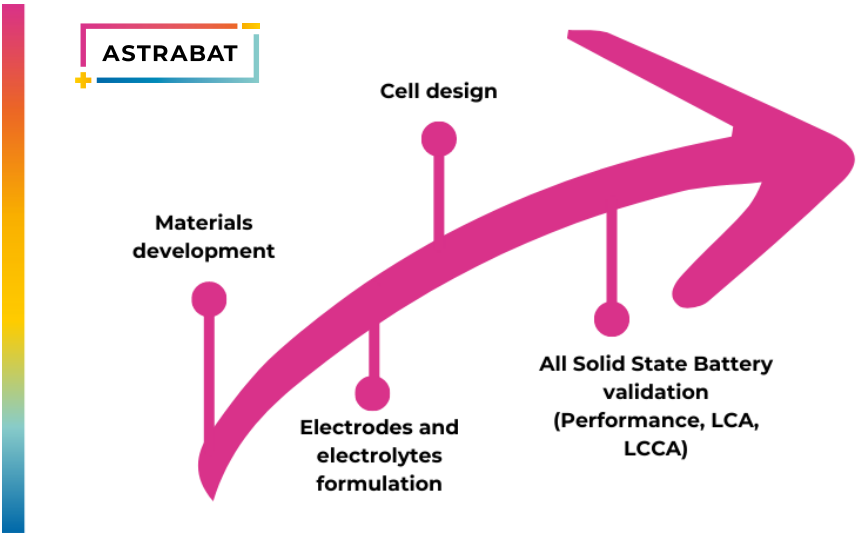
The goal is to fulfil Europe's need for a safe, high-energy, sustainable and marketable battery for green mobility that could be mass-produced in Europe. A new battery that not only outperforms current batteries but is also easier to recycle. The new ASTRABAT cells enable:

Higher energy density and power

Increased safety and longer life cycle

Larger operating temperature range

Lower electric vehicle costs



During these 4 years (January 2020 - December 2023), ASTRABAT investigated and developed a new all-solid-state Li-ion cell architecture suitable for the use of high-energy electrode materials. The ASTRABAT hybrid electrolyte is based on polymers (ORMOCER® and fluorocarbon polymers) and an inorganic filler and membrane (LLZO). These materials tackle the generation 4a of cells using high voltage cathode materials, based on Nickel Manganese Cobalt Oxide (NMC) such as NMC622 and NMC811, and Si-based anode. The project aimed to assess compatible processes for mass production and to generate a new value chain of all-solid-state batteries, including eco-design, end-of-life and recycling.

1. New materials for efficient solid-state batteries

1.1 Electrode materials and upscaling: Ni-rich NMC and Silicon nanoparticles

Positive electrode

During the last five years, the $LiNi_xMn_yCo_zO_2$ research has heavily shifted towards higher energy density. One means to achieve such high density is to increase the Ni content and to target so-called "Ni-rich" compositions starting at 622 (60% of Ni, 20% of Mn and Co) providing a specific capacity of 180 mAh/g and going even higher towards 811 compositions, which provides materials with 210 mAh/g. Reducing cobalt content allows to the energy density and voltage to be increased, and reduces battery costs and sustainability.
ASTRABAT addressed the development of NMC622 stable at high voltage (>4.45 V vs Li/Li+) and high nickel NMC (NMC811). NMC grades were specifically designed for the fluoropolymer electrolyte developed in the project and the core architecture of the cell considering the process of ink jet printing required for 3D manufactured cells.

Stabilizing strategies used for liquid electrolytes are most likely not transposable for polymer electrolytes, as the interface and the mechanical constraints are changed. The following points were addressed:

- a very clean NMC surface to prevent polymer contamination from any impurities,
- the wettability of the NMC with the polymer and ceramic composite were investigated,
- a better control of the microstructure and the bulk evolution to prevent huge volume
- expansion and cracks upon cycling.

While those materials with high Ni-content were being developed, another challenge emerged: the need for longer-lasting batteries. This increased density would require lower particles cracking (creating new surfaces) and in general materials with a lower specific surface (lower interfaces providing with lower CEI formations (standing for Cathode Electrolyte Interphase).
The Umicore proprietary materials supplied for ASTRABAT combine cutting-edge approaches with both a high nickel content and a monolithical design. These materials combine the benefits of a 1) high specific capacity 2) high Ni-content and 3) are expected to be the most relevant materials for solid-electrolyte based batteries (due to their lower specific sur-

face than normal, polycrystalline materials).

Negative electrode

In conventional Li-ion batteries, the active anode material is mainly made of graphite, with good capacities (compared to cathode materials), high stability during cycling, moderate costs and limited availability issues. However, other materials exhibit better properties. The storage capacity of silicon is 10 times greater than graphite, (3576 mAh/g for silicon against 350-372 mAh/g for graphite). But, the use of silicon is limited by two big constraints: its fracturation during the insertion of Li ions and its oxidation during the cycling. Nanomakers silicon nanopowders make it possible to bypass these constraints. Indeed, Nanomakers has developed and patented the carbon-coated silicon (SiΩC) in order to allow the use of silicon inside Li-ion batteries and then to optimise their performances. Nanomakers technology makes it possible to produce and coat nanoparticles in a single step. Thus, the coating is made on particles that have not been brought into contact with air, the interface between the particle and the coating is therefore free of oxygen.

Silicon offers a huge advantage for energy storage, due to its ability to form alloys with lithium. This property has been widely studied and the main alloys at room temperature are $Li_{13}Si_4$; Li_7Si_3; $Li_{12}Si_7$ LiSi and $L_{22}Si_4$ as found in the Li-Si binary

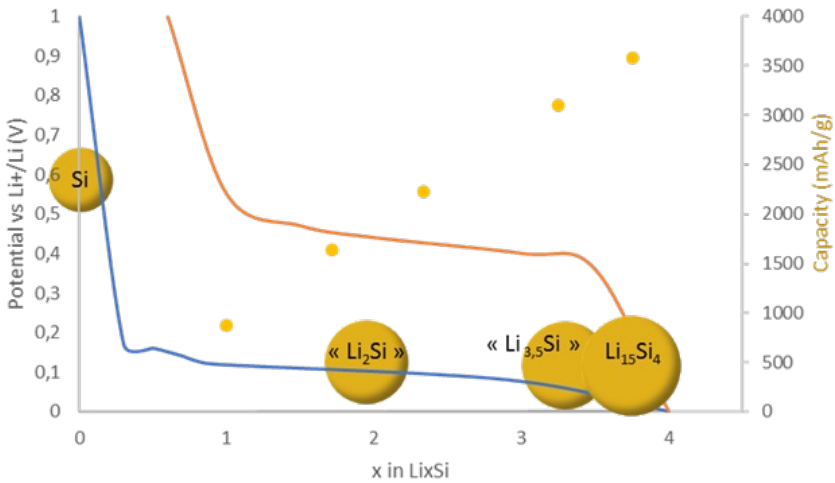


Figure 1: Silicon particle size evolution and LixSi alloy stoichiometry during lithiation (corresponding electrochemical capacities in yellow dots).

phase diagram. The $Li_{22}Si_5$ alloy is the richest in lithium and has a theoretical capacity of 4200 mAh/g but its formation is not observed under normal electrochemical conditions. Their electrochemical domain is illustrated in Figure 1 along with the corresponding volume changes and particle size increases.
At the end of discharge below 50 mV, the crystallized $L_{15}Si_4$ phase is observed. For this alloy, the volumetric expansion is 270% which, for spherical particles, means a particle diameter increase of 55%.

The TEM picture in Figure 2 indicates that the reduction is progressive from the separator side. After delithiation, silicon is amorphous. The lithiation occurs at the surface of the silicon particles and uncompleted lithiation can leave a crystalline core surrounded by a lithiated surface.
For ASTRABAT, Nanomakers supplied different sizes and types of particles to select the best one which appeared to be the smallest ones at 40 nm sizes. Moreover, with ASTRABAT solid-state cells, it seems that the carbon coating has a large effect, and formulation differences can lead to the selection of the products with or without the carbon coating. Within the project, silicon use has been demonstrated up to 2000 mAh/g, as a preliminary step. Its compatibility with the solid electrolyte is good and also with other binder formulation tested.

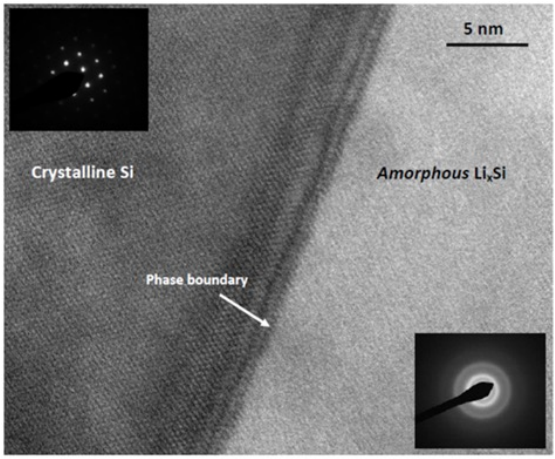


Figure 2: TEM image of silicon electrode after partial lithiation.

1.2 Polymer electrolytes designed for ASTRABAT cells

The ASTRABAT cell is based on a hybrid electrolyte (ORMOCER® and fluorocarbon polymers) and an inorganic filler and membrane (LLZO). The two polymers were tailored to the specific materials electrodes, ORMOCER® as anolyte and fluoropolymer as catholyte.

Anolyte: ORMOCER®, a hybrid polymer electrolyte with higher ionic conductivity

Polymer electrolytes offer higher thermal stability and more safety compared to standard liquid electrolytes. Compared to ceramic solid electrolytes, which usually have high ionic conductivity and mechanical strength, polymer electrolytes offer higher flexibility, which is important to maintain contact between the electrolyte and the electrodes to ensure long cell life.
The ASTRABAT approach is based on inorganic-organic hybrid polymers as anolyte, developed by Fraunhofer ISC. This class of polymers is an ion-conducting material composed of inorganic and organic nanodomains formed by a sol-gel reaction of functionalized alkoxysilanes. The majority of the silane side chains consist of polyethylene oxide (PEO) chains, which facilitates the ionic conductivity within the polymer electrolyte, while a smaller portion of the silanes are functionalized with terminal organic groups to provide additional crosslinking of the prepolymer after the siloxane backbone is built. The solid electrolyte is obtained by mixing the polymer precursor with a suitable lithium salt, a small amount of ionic liquid, and crosslinking via the polymerizable moieties (i.e., epoxide group). The resulting structure consists of crosslinked oligosiloxane networks with attached polyether chains. The high degree of mixing between inorganic and organic domains prevents reorganization of the polyether domains (which leads to. crystallization) and results in a very flexible polymer electrolyte.

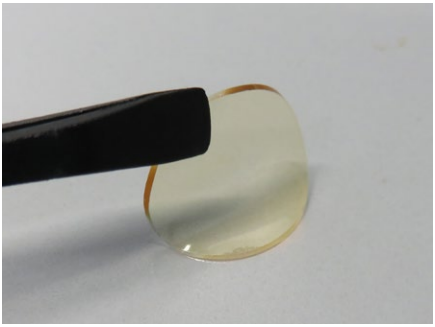


Figure 3: Flexible polymer membrane based on ORMOCER polymer.

Catholyte: tailor-made high voltage stable fluoropolymer electrolytes for high safety batteries

Daikin's mission in ASTRABAT is the development of a catholyte polymer electrolyte that enables the use of next generation active materials. Generally, the replacement of cobalt from the active material leads to a higher reactivity of the materials towards electrolyte systems. Consequently, the development work for the electrolyte system, particularly with the challenges of solid-state batteries, needs to keep up with the highest standards. Fluoropolymers are well known for their high voltage stability but need to be engineered smartly to meet the requirements of battery applications.

Daikin developed a hybrid electrolyte approach, which uses a high voltage stable, plasticized fluoropolymer electrolyte material as a matrix. The fluoropolymer ionic conductivity was greatly increased by tailoring the salt-to-plasticizer-to-matrix ratio and in particular through ceramic additives, which enable a substantial increase in conductivity even when used in small fractions. The developed electrolytes were used as free-standing membranes and they were also cast from various non-toxic solvents. The result is an easy-to-process, easy to-adapt, and fully tailorable set of materials, which can be used in many different concepts and in combination with many materials. The newly developed fluoropolymer electrolytes do not only increase the safety of the battery, contributing to their inherent non-flammability, but also offer best-in-class high-voltage stability, enabling even highest Nickel contents in the project's active material cathode particles. They thus way provide a unique platform fulfilling core-necessities for a successful development implementation of the base material in all other parts of the project.

The next section will present the ceramic additives used in combination with the fluoropolymers from Daikin.

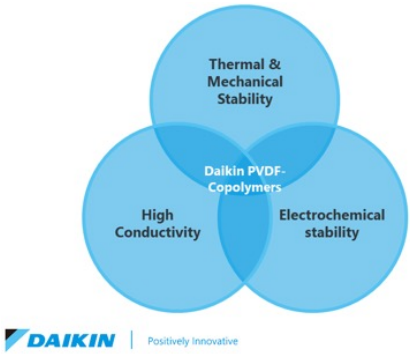


Figure 4: DAIKIN PVDF-copolymers properties.

Ceramic $Li_7La_3Zr_2O_{12}$ (LLZO) as highly ion-conductive ceramic additive for hybrid solid separators

In the large class of solid electrolytes, lithium lanthanum zirconate (LLZO) of the formula $Li_7La_3Zr_2O_{12}$ is one of the most widely studied oxide materials. With doping, conductivities of 10^{-4} to 10^{-3} S/cm are obtained, and it shows a wide electrochemical stability range in contact with metallic lithium of up to 6 V. To use its attractive properties, many scientific groups and companies study LLZO as a free-standing, ceramic electrolyte. Additionally, it has been shown to be beneficial as a conductive additive in hybrid ceramic–polymer solid separators. This is also the use-case in ASTRABAT, where Fraunhofer IKTS deployed a synthesis process that allows half a kilogram of high-quality LLZO powder per batch to be obtained under ambient conditions. This LLZO powder was made available to the project partners to facilitate the joint research and cell development.

LLZO is humidity-sensitive and quickly reacts with water traces to lose ionic conductivity. This makes innovative post-processing necessary in order to use LLZO powder prepared under air to enhance polymer solid electrolytes. Nonetheless, this processing route is advantageous as it is much easier and cheaper to deploy, and the scale-up is also less complicated. One important aspect here is the particle size of the LLZO powder that could be reduced in ASTRABAT after synthesis with high-energy milling. In general, sub-micron particles allow for a more homogeneous distribution in the hybrid electrolyte, and it also allows for printable dispersions.

The development of such printable dispersions was also part of the project, and both inks as well as screen-printing pastes with LLZO were prepared (Figure 5 middle). With optimization, the right solvents, and additional organic additives, LLZO and the fluoropolymer electrolyte from Daikin could be dispersed in the inks together such that the hybrid electrolyte could be printed directly. Alternatively, LLZO inks and pastes without polymer can be used to infiltrate existing polymer membranes.

Figure 5: from left to right, LLZO powder as fabricated at Fraunhofer IKTS, hybrid separator ink, screen-printing paste, and sedimentation test of the former over three days.

1.3 Fluorine-free anions for lithium salts and ionic liquid plasticizers

Lithium salt

Lithium salt is a necessary component of each liquid or hybrid solid polymer electrolyte. It provides lithium cations transporting the charge from anode to cathode and back, making charge and discharge of the battery possible. Commercially available lithium salts are often Achilles heel of the lithium-ion battery. They limit operation temperature of the battery by being thermally unstable (in case of $LiPF_6$ above 70°C), as well as causing chemical instability. All commercially used lithium salts so far contain fluorine which potentially makes recycling harder.

That is why in ASTRABAT, the Warsaw University of Technology team proposed the use of university's proprietary LiPCP salt as a hybrid solid polymer component (alternative proposed salt - LiHCAP). Over the course of the project, synthesis of the new salt has been improved and upscaled. LiPCP conducts on par with the best salts on the market, achieving conductivity ca. 10 mS/cm in liquid electrolytes. It has superior thermal stability (up to 300°C) to commonly used $LiPF_6$, so it would not limit the operation temperature of the ASTRABAT cell. In addition, LiPCP would allow the use of thermal processing methods for hybrid polymer electrolyte, which otherwise would be impossible. As LiPCP is fully stable in the presence of water, it is also possible to work with it outside pure argon atmosphere. As such, it could make future hybrid polymer electrolyte/cell production lines easier and cheaper to build and operate. Furthermore, LiPCP is a fluorine-free salt, which makes it a better choice in a long run, when the absence of fluorine should increase the recycling yield of metals from the battery waste in the future.

Figure 6: Pure LiPCP (lithium 1,1,2,3,3-pentacyanopropenide) and LiHCAP (1,1,2,4,5,5-hexacyano-3-azapenta-1,4-diene) salts.

Ionic liquid plasticizers

Plasticization of the polymer for hybrid polymer electrolytes is necessary to achieve high ionic conductivity and flexibility – required in lithium-ion batteries. Traditionally, it is made using organic solvents. However, solvents are volatile, and as such they are emitted during use in the production line, polluting the air or requiring special filters to limit the emission. Their thermal stability is also limited – even the most stable ones quickly increase their vapour pressure with the rise of temperature. Additionally, organic solvents do not conduct on their own at all.

That is where the ionic liquids come in – they plasticise the hybrid polymer electrolyte just like solvents. However, they conduct better than solid electrolyte itself, thus, even large share of plasticizer is not an issue for the overall conductivity. Furthermore, ionic liquids are not volatile, and as such, not flammable, so adding them commits to the overall safety of the hybrid polymer electrolyte and the cell. So far, all commonly used ionic liquids in the battery industry contain fluorine, usually the one easily detached in the case of decomposition. Thus, use of ionic liquids based on WUT's proprietary anions PCP or HCAP is also supporting an effort towards decreasing critical raw materials share in lithium-ion batteries. Just like fluorine-free salts use, it should help the future battery recycling.

In the course of the project, the new ionic liquids based on PCP and HCAP anions were designed, synthesized and tested. Subsequently, hybrid polymer electrolytes containing those new ionic liquids as plasticizers were manufactured and tested, showing successful plasticization and an increase in functional parameters.

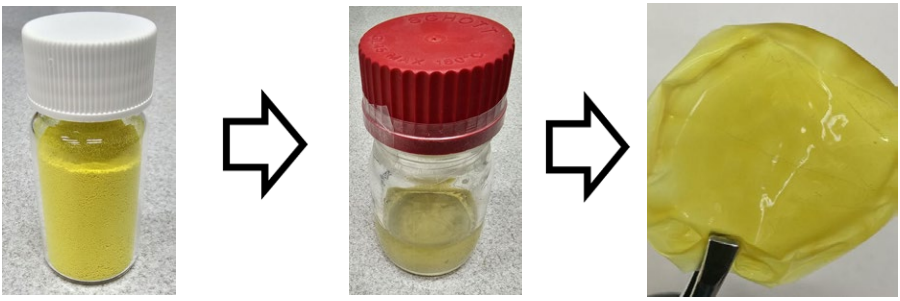


Figure 7: Lithium salt (LiPCP) is used for synthesis of the ionic liquid which is used for hybrid solid polymer electrolyte manufacturing.

2. Challenges to fabricate new electrode architectures and innovative cells for all-solid-state batteries

2.1 Status of the ASTRABAT cell and challenges for manufacturing solid-state cells

This section provides a status update on the manufacturability of the ASTRABAT cell which emerged as a first pouch cell prototype in 2022. The production chain of the ASTRABAT cell, designed with high-energy electrode materials, was also compared to the manufacturing of current state-of-the-art Li-ion cells.

Promises offered by All-Solid-State Batteries

Solid-state cells containing solid electrolytes could offer higher thermal stability and improved safety compared to conventional lithium-ion cells which contain a liquid electrolyte. Solid-state batteries would require less complex thermal management systems and could thus offer higher volumetric energy density at the pack level.

Manufacturability of the ASTRABAT cells vs. conventional Li-On cells

Three process steps can be identified in the production chain of a lithium-ion cell, whether it contains a solid or a liquid electrolyte: the electrode production, the cell assembly, and the final cell packaging and cell testing (See Figure 1). How to upscale the solid electrolytes and electrodes developed in the ASTRABAT project for large volume production is still under investigation. It is clear that those materials require dry rooms to be processed. Planetary mixing or extrusion-based methods followed by slot die coating processes could potentially present a viable option when considering a roll-to-roll process. In the ideal case, some of the production processes for solid-state cells would be carried out on equipment already existing for the production of conventional lithium-ion cells. For cell assembly, packaging and testing, the current infrastructure used for the production of conventional lithium-ion cells could likely be adapted to the requirements for the production of solid-state cells. It is expected that the formation cycle will be shorter and no degassing of the cells would be required, which could then also reduce the production cost.

Figure 1: Process chain for producing lithium-ion cells.

Competitivity of European Li-On cell manufacturers in EV Market

The cost per kWh, the cell performance and the most environmentally-friendly production process are important parameters to be competitive in the EV market. Producing Li-ion cells at a GWh scale at low cost in Europe is a real challenge given that Asian manufacturers are years ahead. Therefore, developing the know-how to produce next-generation cells such as solid-state cells in Europe is a vital step for the European automotive sector. Scaling-up comes with financial risks. Going from a successful research solid-state cell prototype to large-scale production requires planning the production processes and costs which will determine the competitiveness of the product on the market. To de-risk financially the upscaling of a cell manufacturing chain, the right machine manufacturers need to be chosen as the capital investments are huge to meet the growing cell demand in Europe.

Time for market for the ASTRABAT cell

We believe 2030 could be a realistic goal to see large scale production of all-solid-state batteries. Currently, fundamental research is still needed to solve interfacial issues and mechanical stability of these solid-state cells before addressing the series production. We will most likely first see the ASTRABAT type of cells in niche markets before they are mass produced for the EV markets where low cost is a crucial factor. The power performance is also a very important aspect for the final customer.

Outlook

The ASTRABAT solid-state cell offers promising cell properties. Nevertheless, to mass produce such ASTRABAT cells, the appropriate commercial tools need to be carefully selected. Most of the production processes are not yet upscaled as the solid-state cell technology is still in a rather early stage of development. Moreover, the upscaling of the solid electrolyte syntheses needs to be established. Producing solid-state batteries in series and optimizing its technical, economic and environmental aspects is a well-known challenge. Innovative recycling methods also need to be investigated to ensure the long-term sustainability of the developed technology (see Section 3.2).

2.2 Theoretical insights of ASTRABAT cell and 3D architecture

Calculation of the 10 Ah and 50 Ah cells' theoretical energy density

A geometrical model of the Si/solid electrolyte/NMC cell was proposed in the beginning of ASTRABAT to evaluate the energy density and the influence of the different parameters (material properties, geometrical design) on the latter. It was further used to provide guidelines for the optimization of the cell. The theoretical energy density of 10 Ah and 50 Ah cell prototypes were assessed. The calculation was based on basic properties of the materials (density, content), on electrochemical features of the active materials (specific capacity, mean reaction voltage, irreversible capacity at the first cycle), then on design assumptions (electrode loading, electrode balancing, relative proportion of each part or component). The energy density also depends on the type of packaging and the geometrical aspect ratio of the cell.

For the Leclanché cell design, characterized by a flat geometry and the use of a soft packaging, the theoretical energy density of the 50 Ah ASTRABAT cell is expected to be approximately 290 $Wh.kg^{-1}$ and 1050 $Wh.l^{-1}$. In the case of the 10 Ah ASTRABAT cell, since the contribution of the packaging to the weight and the volume of the cell would be too high, an alternative with a reduced footprint 60 x 120 mm^2 was proposed. Then, the energy density of the cell is expected to be close to 242 $Wh.kg^{-1}$ and 958 $Wh.l^{-1}$. The number of stacked electrodes in both prototypes is around 20. This would lead to cells that are ~5mm thick. For automotive design purposes, this aspect needs to be optimized.

Given the proposed parameter values and cell design, the main influential parameters on the energy density of the active materials are most likely the irreversible capacity of the negative electrode, the electrode loading and balancing, and the LLZO content in the hybrid electrolyte.

3D architecture of ASTRABAT cell

Lithium-ion batteries currently available in the market are composed of planar electrode structures, whose fabrication method is already well-elaborated and easily implemented for large-scale production. How-

ever, these layered electrodes face a trade-off between energy density and power density. In simple terms, energy density indicates how much energy can be packed in a given battery, while power density refers to the rate at which a battery can deliver energy. Therefore, in planar cell architecture, the energy density can be enhanced by increasing the loading of active material (building thicker electrodes), but this limits the lithium-ion transport leading to poor power density. On the other hand, three-dimensional (3D) battery architectures offer a favourable balance between energy density and power density by effectively exploiting the electrode's volume. Unlike planar structures, 3D electrodes provide a higher surface area, which promotes efficient ion transport and reduces diffusion distances within the electrode. This enables faster charging and discharging rates, leading to improved power density. At the same time, the 3D architecture allows for increased active material loading, enhancing energy density.

The model developed in ASTRABAT aims to predict the electrode behaviour and electrochemical performances depending on the microstructure design, considering solid-state electrolyte properties, in order to inform the electrode design. To reach this goal, the numerical simulations are performed on virtual microstructures.

Numerical simulations based on an innovative cell design Gen#3DC (see Figure 2) led to an optimization of this design according to electrochemical performances. For this design the NMC 811 vs SiC targeted chemistry of the project is considered. The starting design took into account manufacturing constraints. Then, numerical results showed that considering the same amount of active material and loading, reducing the distance between electrodes from 50µm to 10µm lead to improve by 36% the cell chargeability at 4C. In addition, reducing the base of electrodes from 50µm to 10µm and to have interdigital electrodes improve by a factor 2 the cell chargeability at 4C.

Thanks to the model, it has also been demonstrated that there is a lithium plating risk starting from 1C regime on the cell design Gen#3DC. This lithium plating risk can be reduced by using the optimal configuration of Figure 2 (c) where the interdigitating of the electrodes has been increased.

The hybrid electrolyte properties, for different microstructures, have also been studied. The hybrid electrolyte is made of

a blend of polymer and ceramic. The numerical simulations can quantify the improvement of the effective conductivity when adding ceramic in the electrolyte for both Gen#2D and Gen#3DS designs. For example the effective conductivity is improved by 35% by adding 40%wt spherical LLZO particles of Gen#2D design whereas only 12%wt LLZO sticks parallel to the lithium-ion flux is necessary for the Gen#3DS design to reach this gain. Nevertheless, the gain always remains limited (below a factor 3) even if the conductivity of the LLZO is very high compared to the polymer one.

These theoretical results were tested in ASTRABAT cells by using 3D additive manufacturing. These techniques will be further described in the next part.

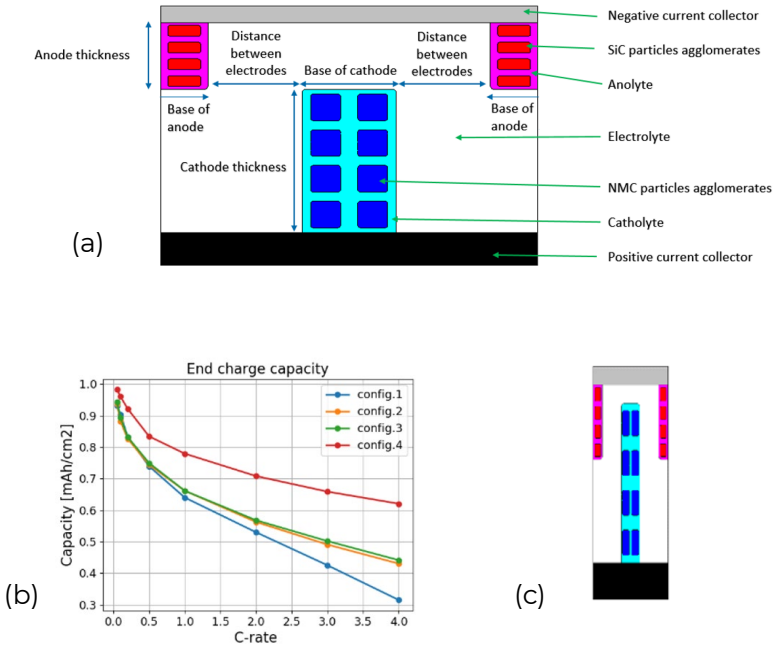


Figure 2 : (a) Cross section of innovative cell design considering that electrodes are extended in depth and where manufacturing constraints are taking into account. (b) Comparison of cell performances at end of charge step between four configurations in function of the C-rate. (c) Illustration of the cross section associated the optimal configuration, i.e. config.4 in plot (b).

2.3 Exploring printing techniques for advanced 3D manufacturing of solid-state batteries

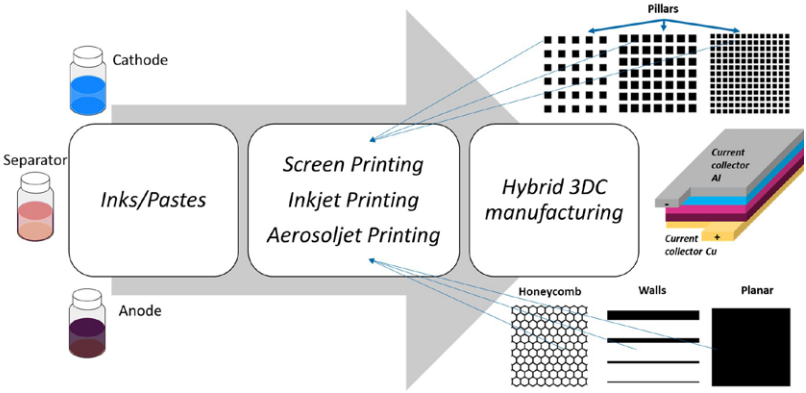


Figure 3 : Manufacturing value chain of 3D concept realization.

The emergence of 3D printed lithium-ion batteries presents a unique opportunity for energy storage, offering exceptional potential for diverse microscale dimensions and geometric variations in future battery production. Fraunhofer IKTS is at the forefront of identifying manufacturing technologies for solid-state 3D lithium-ion batteries. By employing screen, inkjet, and aerosol jetting-based printing processes, they provide alternative methods for battery production (Figure 3).

Screen printing

Screen printing is a cost-effective technique for the small-scale production of battery electrodes. This method allows for the utilization of various electrode pastes, such as cathode, separator and anode pastes. In ASTRABAT, different pastes were developed for screen printing with a 10 x 10 mm area, enabling the creation of various structural designs such as honeycomb or pillars, or multilayer printing. The subsequent scaling for larger printing areas such as 50 x 50 mm can however produce issues such as delamination, which can be adressed by modified substrates.

Inkjet and aerosol jetting

Inkjet and aerosol jetting technologies are able to create high-resolution micro-patterns and its fast printing speed makes them highly suitable for industrial applications. But they

are additionally more stringent regarding ink compositions. Aerosol printing offers superior print resolution, typically achieving resolutions 2-4 times higher than inkjet printing (aerosol: 10 µm, inkjet: 20-25 µm). Additionally, aerosol jetting allows for a wider range of materials to be tested due to its less stringent ink viscosity requirements. As part of ASTRABAT, cathode ink compositions were tested for both inkjet and aerosol jetting, to produce structured cathodes.

Inkjet Printing, a promising fabrication method for advanced 3D electrodes

In the project, the possibilities to fabricate 3D lithium-ion batteries electrodes using inkjet printing technology were explored.
In our studies, electrodes inks specifically designed for inkjet printing were developed. UNILIM fine-tuned the printing parameters and showcased the potential for constructing three-dimensional electrode structures. Cathode micro-pillars were successfully deposited onto the aluminium foil (Figure 4). However, before a full battery cell can be built using this technique, further advancements are necessary, particularly in terms of technological modifications.

A major challenge in the development of these techniques lies in the improvement of the printed electrodes' electrochemical performance, as the requirements for electrochemical and printing properties can greatly differ. For example, increasing the polymer content may enhance printability but could also reduce electrochemical performance. Resolving such issues required in-depth research into the parameters involved.

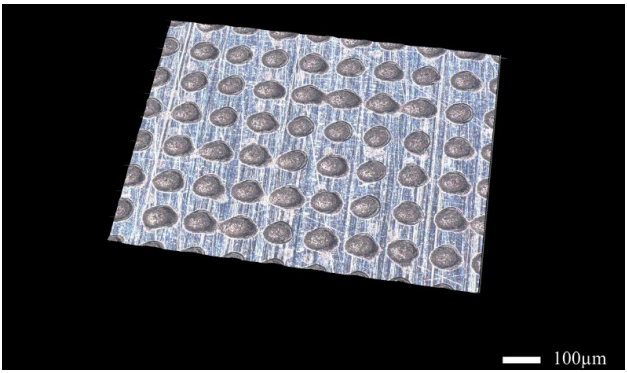


Figure 4: Cathode micro-pillars fabricated by ink-jet printing.

3. How to ensure ASTRABAT cell sustainability?

3.1 Eco-design recommendations

Ensuring the environmental and economic sustainability of the novel cell developed by ASTRABAT is an objective of the project and also a necessary market requirement for novel batteries, outlined by the recently adopted Regulation on Batteries and waste batteries. The partner LOMARTOV has provided Eco-design recommendations to support the decision-making process on the compounds and processes that can be used in ASTRABAT battery to enhance its environmental profile, before evaluating the final results through an environmental and economic Life Cycle Assessment (LCA).

The methodology

Eco-design aims at integrating environmental aspects during product design to improve its environmental performance throughout all the stages of its life cycle (European Commission, 2009). Applied to ASTRABAT, it entails the need of incorporating environmental and sustainability criteria into the basic requirements of lithium-ion battery design, such as costs, functionality, quality, reliability, and safety, among others (Figure 1).
The integration could lead to a reconsideration of some of the parameters (e.g., minimization of all resources consumptions to as well as reduction of ASTRABAT's emissions and pollutants, not only during the manufacturing process, but up to the end of the useful life of the product).

Figure 1: Eco-design approach is not just about the environment.

The eco-design approach directly targets environmental performance, but it can also affect economic and social considerations in parallel. Indeed, economic and social benefits are often consequences of environmental performance improvement, such as the issue of critical raw materials, which is

also considered by eco-design.

Many companies, and also the European Commission through different regulatory frameworks, have recognised the potential of eco-design for their long-term success. Hence, the approach is playing a fundamental role in meeting customer expectations and empowering them to choose greener products. It will also help inform future environmental regulatory requirements that will accelerate the European green transition.

Eco-design has been adapted and applied to guide the materials development of ASTRABAT's cell based on 3 steps:

1. Definition of the specifications of the product.
2. Environmental assessment of conceptual development, combining a functional analysis and a streamlined-LCA, which allowed to screen and identify the main environmental hotspots.
3. Preliminary cradle-to-gate LCA of the ASTRABAT cell.

The main hotspots

This study successfully guided the battery developers towards more environmentally-friendly components and manufacturing processes to design ASTRABAT GEN #2D cell.

After the selection of the best components for the ASTRABAT cell, a "cradle-to-gate" lab-scale LCA study was carried out to determine the main hotspots of the design, which can be potentially transferred to the full-scale deployment and that mainly rely on the following elements:

- The anode and cathode drying processes as the most energy consuming steps, which should be optimized when upscaling.
- The copper used as current collector and the use of NMC are among the main components causing a significant impact on mineral resource consumption.
- The anolyte curing process should be addressed during the scale-up and industrialization phase (e.g. by studying alternative curing processes which are less energy-demanding).
- LLZO is one of the main drivers of mineral resource use, which is an addition in the new generation of all-solid-state batteries.
- ORMOCER® (an innovative element used in ASTRABAT) has a strong potential for ozone depletion, and this should be carefully managed during in-

dustrialization and recycling of the ASTRABAT battery to avoid the release reactants or derivatives to the atmosphere.

The conclusions

The main hotspots identified in the ASTRABAT design are the same that contribute the most to the conventional liquid lithium-ion battery.

Compared to other existing industrialized batteries, the ASTRABAT design still needs further improvement when scaling-up to be competitive in the market. Positively, when compared to other lab scale developments, either conventional lithium-ion battery or SSB battery developments, the impacts of ASTRABAT are in the same range. Therefore, it is likely that the optimization, once the new manufacturing methods are more developed and scaled up, will lead to more competitive all-solid-state batteries in environmental terms as well.

3.2 Two approaches for ASTRABAT's cell recycling

The development of battery dismantling and recycling technologies with high efficiencies is essential to ensure the long-term sustainability of the battery economy. Accordingly, most ambitious targets on minimum levels of materials recovered from waste batteries were included in the new EU proposal for a Regulation on Batteries and Waste Batteries (COM/2020/798 final): lithium – 50% by 2027 and 80% by 2031; cobalt, copper, lead and nickel – 90% by 2027 and 95% by 2031.

Nowadays, two different approaches for batteries recycling and valorisation are used at industrial scale. The first is the extraction or regeneration of valuable elements, which can be addressed by simple methods (mostly pyrometallurgy treatment), to produce lower-value products or raw materials, less sensitive to economic fluctuations. The second approach is to use hydrometallurgical schemes to generate high-quality precursors for the synthesis of fresh active material for batteries manufacturing. Regarding the latter, the products obtained meet the battery manufacturing specifications in a circular fashion.

ASTRABAT aims to validate the efficiency of these industrial-scale recycling methods towards the recovery of high-residual-value materials once the cells reach end of life. To do so, the project partners LOMARTOV and CEA will engage in a set of experiments dedicated to designing a recycling strategy for ASTRABAT cells, as depicted in Figure 2.

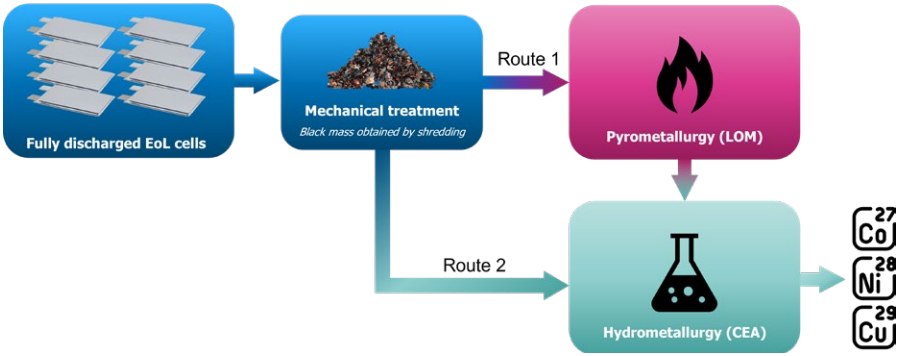


Figure 2: The two routes for ASTRABAT's cell recycling.

The hydrometallurgical recycling of lithium-ion batteries involves several steps. The Black Mass (containing cathode materials, metallic impurities and graphite) is leached. This allows metals to be dissolved and graphite to be removed. Then, the impurities such as Al or Cu are removed. Lastly, the cathode metals (Li, Co, Ni, Mn) are separated. The classical route to do this is liquid/liquid extraction. It allows high recovery rates but involves expensive organic solvents. Alternative routes are therefore being investigated, such as selective precipitation or selective adsorption.
In the project's case, selective adsorption on ion exchange resin was used. It has the advantage of being more selective than L/L extraction in multi-metal system.

A black mass leachate is simulated in the laboratory according to the ASTRABAT cell composition. The copper, nickel and cobalt contained in the leachate are separated by continuous chromatography. The process uses an ion exchange resin to separate first the copper, then the nickel and finally the cobalt.

The state of the art has allowed the identification of the type of resin adapted to the selective separation of these ions. Bispicolylamine resin such as DOWEX-M4195 allows the recovery of Cu^{2+} at lower pH, then Ni^{2+}, and then Co^{2+}.
The treatment conditions were studied in order to reach optimum sorption selectivity for copper, nickel and cobalt. Then, desorption tests on a simple column determined the concentration of the desorbent (H_2SO_4) adapted to eliminate the impregnant and the impurities. Finally, a carousel test on a pilot equipment of three 70mL columns was performed.
The resin capacity for each element was calculated: 38 g/L for Copper, 13 g/L for Nickel and 10 g/L for Cobalt. Extracts have good purities: 98% for $CuSO_4$ and more than 99% for $NiSO_4$ and $CoSO_4$. The process has

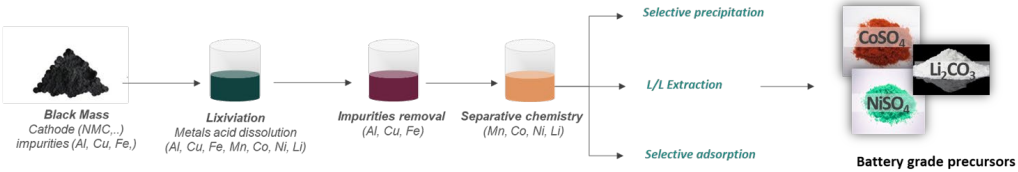


Figure 3: Hydrometallurgical steps of Li-ion battery recycling.

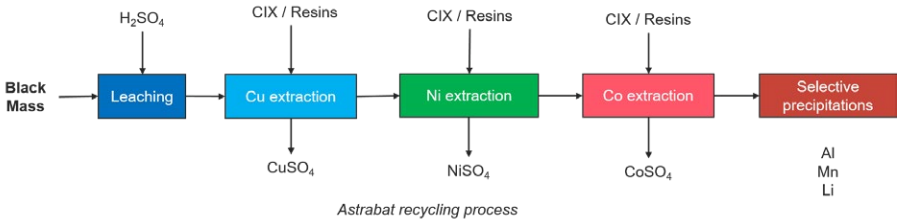


Figure 4: Astrabat hydrometallurgical recycling process.

good selectivity.
Yields of recuperation in the extracts are good for copper (99%). Nevertheless, the process is undersized for Ni and Co. Indeed, these metals have less affinity with resin and are more concentrated in the leachate so bigger columns need to be used to recover all of it in the extract.

Conclusions

Within these four years, the ASTRABAT project has been a significant endeavour in the pursuit of electric mobility as the main transport mode in the near future. Throughout the project lifecycle, extensive research, collaboration and innovation have been employed to address the challenges associated with conventional lithium-ion batteries and pave the way for the widespread adoption of all-solid-state battery technology.

ASTRABAT has made substantial progress in various critical areas. Extensive efforts have been dedicated to improving solid-state electrolytes in term of ionic conductivity, electrochemical stability and thermal/mechanical stability. By carefully selecting the electrode materials, the overall performance of ASTRABAT's cells could be improved. The materials synthesis processes were upscaled to reach 1 kg-batch production. The cell design and scale-up have been also addressed through conventional manufacturing techniques. The ASTRABAT solid-state cell offers promising properties but it is still in a rather early stage of development before industrialization. Additive manufacturing such as ink-jet and screen-printing has been also studied in order to create 3D microscale patterns. The main challenge is to find a balance between the printability of an ink and its electrochemical performances. The last months of the project have been dedicated to safety tests, recycling and LCA study.

Furthermore, the project within a consortium of 14 partners has fostered strong partnerships and collaborations among academia, industry and research institutions across Europe. The exchange of knowledge, expertise and resources has accelerated the development process in ASTRABAT. Through joint efforts, the project has contributed to strengthening Europe's position as a global leader in sustainable energy technologies.

The all-solid-state battery technology, as developed in ASTRABAT, has the potential to revolutionize various industries, including electric vehicles, portable electronics and renewable energy systems. However, the scaling-up is still challenging and further research and development are still required in the coming years, to achieve the commercialization of all-solid-state Batteries, ultimately driving the transition to a greener and more sustainable future.

ASTRABAT

astrabat.eu @astrabat astrabat-project coordinator@astrabat.eu

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