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AM4BAT PROJECT

Deliverable 2.2

Roadmap for material and manufacturing integration in conventional Li-ion manufacturing line

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WP	2	Specifications

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[1] Dissemination level: **PU** = Public, **PP** = Restricted to other programme participants (including the JU), **RE** = Restricted to a group specified by the consortium (including the JU), **CO** = Confidential, only for members of the consortium (including the JU) **SEN**= Sensitive, limited under the conditions of the Grant Agreement.

[2] Nature of the deliverable: **R** = Report, **P** = Prototype, **D** = Demonstrator, **O** = Other

[3] Creation, modification, final version for evaluation, revised version following evaluation, final

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LIST OF ABBREVIATIONS

AM: Additive Manufacturing

CAPEX: Capital Expenditures

HSE: Hybrid Solid Electrolyte

LCD: Liquid Crystal Display

LLZO: Li7La3Zr2O12

LMNO: LiMn1.5Ni0.5O4

NMC: Nickel Manganese Cobalt. 622, 811, 955 refer to content of nickel, manganese and cobalt ratios in the end powder

NMP: n-methylpryrrolidone

UV: Ultraviolet-visible

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1. Executive Summary

The principal objectives of this deliverable are directly linked to WP2 and more precisely, to task T2.2:

- To define the production processes specifications

All objectives were achieved in content and time as shown in the next sections. The general synthesis processes used for LLZO, NMC, and LMNO for the use within the AM4BAt project have been set out combined with the roadmap for generation and deployment of 3D printed materials within the battery sector.

2. Introduction

This document is to be used as a general roadmapping solution for the outcomes of materials and processes design within the AM4BAt project. It outlines the materials synthesis, generation route using additive manufacturing (AM) including the process description itself, and potential routes to market dependant on success criteria.

3. Roadmap - Direct Roadmap

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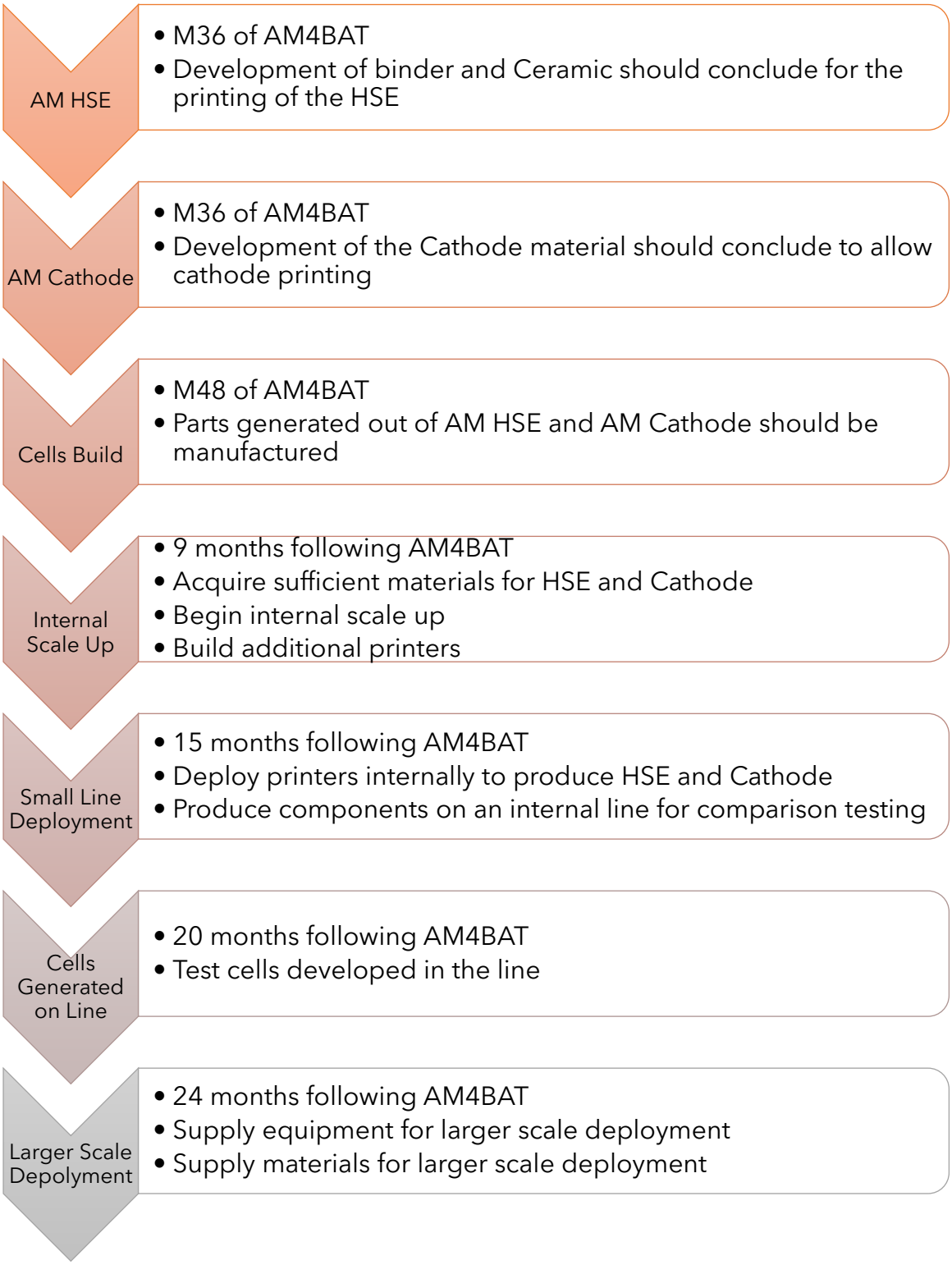

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3.2. Printing Process

3.2.1. Material Roadmap

3.2.1.1. Hybrid solid electrolyte processing

The Hybrid Solid electrolyte (HSE) comprises a mixture of ceramic material, photopolymer, and lithium salts.

From M1 to M24 LLZO powders will be synthesized by TOR adjusting the grains size for proper mixing with the binder.

LLZO (Li7La3Zr2O12 Lithium Lanthanum Zirconium oxide) will be the selected composition for the HSE development in AM4BAT project. LLZO will be synthetized both by solid state and coprecipitation reaction routes.

- Solid state synthesis route:

The solid-state synthesis consists of a chemical reaction between solid particles. For solid state synthesis, the reaction precursors will be based on oxides of the principal compounds. The general procedure can be summarized in the following steps:

1. Milling of the raw materials (oxides of Li, La, and Zr) to generate a homogeneous mix.
2. First sintering step
3. Milling and homogenization of the reaction product from the first sintering step
4. Second sintering step
5. Milling, homogenization and sieving to adjust the solid to the desired particle size distribution

Coprecipitation route:

The coprecipitation route is based on the reaction of the dissolved precursors in a liquid media. In this case, the raw materials will be based on nitrates, hydroxides, sulphates, or other inorganic salts that have proper solubility in water. The general procedure could be summarized in the following steps:

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1. Addition and mixing in water of the precursors until the complete dissolution
2. Precipitation of the solved materials through the addition of precipitating agent
3. Drying and milling of the precipitate
4. First sintering step
5. Milling and homogenization of the reaction product
6. Second sintering step
7. Milling, homogenization and sieving to adjust the solid to the desired particle size distribution

The LLZO materials synthetized by TOR will be characterized regarding electrochemical properties by LEITAT and CEA. After the comparison between the different trials, best options will be selected and used by PHO to use in the HSE manufacturing.

3.2.1.2. Cathode powder processing

AM4BAT provides ceramic cathodes NMC811 and LMNO from commercial sources. TOR will synthetize NMC811 through solid state synthesis route. As the same situation that is described for LLZO, precursors for solid state synthesis will be base in oxides of the main elements of this compound (Lithium, Nickel, Manganese and Cobalt). The process can be described accordingly by the following steps:

1. Milling the compounds of Nickel, Manganese and Cobalt to generate a homogeneous solid mix
2. First sintering step
3. Addition of the Lithium and homogenization through milling process
4. Second sintering step
5. Milling, homogenization and sieving to adjust the solid electrolyte to the desired particle size distribution. NMC811 materials synthetized by TOR will be characterized by LEITAT and AIT regarding electrochemical properties.

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3.2.2. LCD Printing Process

Below can be found a schematic for an LCD based 3D printer (Figure 1). Light at λmax = 450 nm is generated by the LED's (A). Due to LCD screens being designed around human usage, they are designed to allow visible light (400 – 700 nm) through and block potentially hazardous wavelengths in the UV region (< 400 nm). In the photocurable realm, most initiators are in the UV region (350 – 385 nm), however these can't be used due to the screen blocking. A compromise of both wavelength that initiators are active at and the transmittance of light through the LCD screen (B) is therefore made to increase the processes efficiency. Pixels on the LCD screen are either switched to the on position (transmissive) or off (opaque). This forms the design to be cured within the photoreactive resin (C). The resin is tuned to cure with the correct wavelength (450 nm) in the shortest time frame (< 1 min) without causing stability issues. These issues could be any combination of settling of particles, uncontrolled curing of resin, or a loss of definition. The photoreactive resin is comprised of monomers, oligomers, active material, and photoinitiator. Monomer and oligomers are required to undergo free radical polymerisation to form a crosslinked species so that a 3D object can be formed via curing multiple layers. The active material (LLZO, NMC, LiTFSI etc) is required to ensure the parts are capable of either ionic transfer (LLZO and LiTFSI), reduction/oxidation (NMC), or electronic conduction (carbon black/C65). The initiator is chosen to undergo homolytic fission upon irradiation with 450 nm light, creating free radicals to cure the resin into the desired shape (D), dictated by open pixels. The resin is cured onto the build plate (E) which is lifted in and out of the resin to allow for replenishment underneath the object for the next layer to cure. This whole process is controlled by a computing unit (F).

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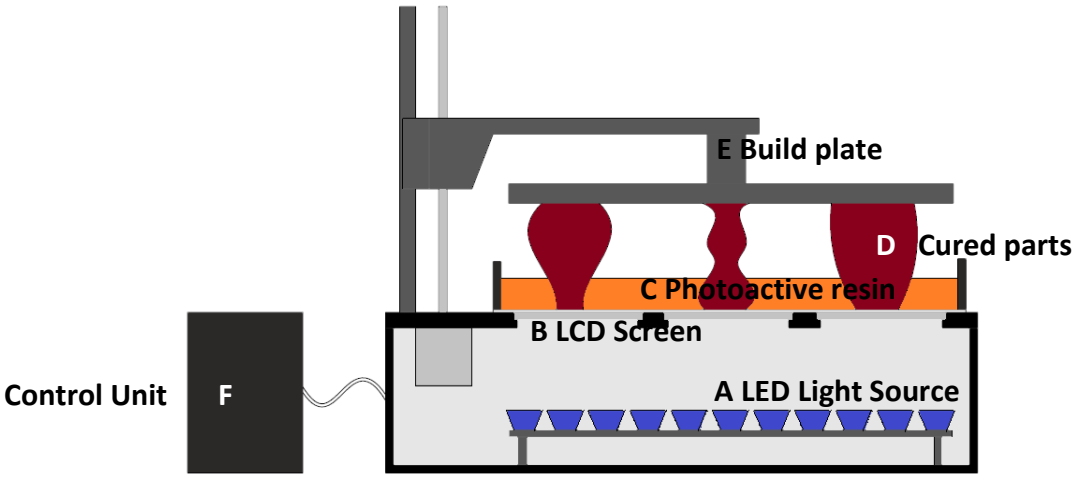

Figure 1. General Schematic of 3D printer

3.2.3. Post Processing

Following the printing process, several steps are still required to ensure that all parts are fit for purpose. The separator or cathode need initial cleaning to remove excess residue. Allowing these to remain will lead to a loss in the overall print accuracy and geometry and could skew the results of any testing. Traditional cleaning approaches use materials such as isopropanol to clean off resin, however due to the potential for large quantities of water being dissolved within the solvent, this could cause reactions with LLZO within the system. Anhydrous solvents can be employed to clean parts as well as centrifugal cleaning methods to reduce the need for additional solvents. Once the parts are clean, they require post curing to lead to high levels of conversion. This also ensures that the chemical and physical properties will not change during use due to changes in degree of cure. Post curing is employed within a UV light box with a radiant power of 60 mW/cm2. Depending on part size, time of up to 2 hours may need to be employed to fully cure the parts. However, due to the thinness of parts required within the battery market for film thicknesses, low curing time (<10 minutes) can be employed to cure the parts for use in minimal time. Unlike traditional electrode manufacture, no drying time is required as no solvent is used in the system.

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3.2.4. Benefits of Printing Over Traditional Route

Lithium lanthanum zirconium oxide (LLZO) has long been known to react with H2O in the air to form side products of both LiOH and Li2CO3. Both materials are then ionically insulating/inert in comparison to LLZO. The transformation can lead to bulk conductivity dropping from 6.45 x 10-4 to 3.61 x 10-4 S·cm-1 as seen in studies (J Am Ceram Soc. 2017;100:2832–2839). Due to this change in conductivity, it is vital that all environments that the LLZO is employed in are dry air based. In a traditional route, this would require a whole room to be a dry room. In traditional coating lines for lithium-ion batteries, the coating line including the drying step can be up to 100 meters long. A surface of 5000m2 could easily be attributed to the electrode coating step. If in such a line LLZO which is moisture sensitive is employed, it would require the processing to be carried out in a dried atmosphere with a dew point not lower than -40°C. This comes with additional infrastructure cost as well as running cost and human protections and restrictions. With the employment of a 3D printer to generate electrodes and HSE, this can be reduced. Each printer can have either an internal dry air environment built into the machine, or a drastically reduced dry room volume by reducing the height of the room required to have a dry environment. Current printer sizes have an internal height of 35 cm, in comparison to a 240 cm height room. In the assumption that the same floor space will be used in the generation of traditional electrodes, there is a reduction of 85% of air volume with the implementation of dry air environment just within the printer system, leading to a reduction in running costs. This is due to the intended automation within the 3D printing process that will reduce the need for human intervention.

Advancements in LCD screens have led to advancements in print speeds and areas within the AM industry. Screens have become more efficient in the transmittance of light, resulting in high radiant power within the printer. Each resin requires a minimal energy dosage to cure at specified wavelengths. With the increase in radiant power within the printer, a reduction in the time required for curing a single layer can be greatly reduced. Coupling this with large surface of LCD screens, fast turnaround times for printed parts are capable on 3D printers, with a reduction in idle time due to driving off of solvent and calendaring requirements. As mentioned earlier, due to the thinness of the layers, low post curing times (<10 minutes) can be employed, resulting in faster production time of parts. This also removes the requirement of NMP or

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acetone (which are still widely used to produce cathodes) solvent capture to stop leaching into the environment, resulting in lower running cost and initial CAPEX requirements. For the fabrication of the graphite-based anodes, most cell manufacturers have already adopted a more environmentally benign process using water as a solvent and thus do not require recovery lines for this process.

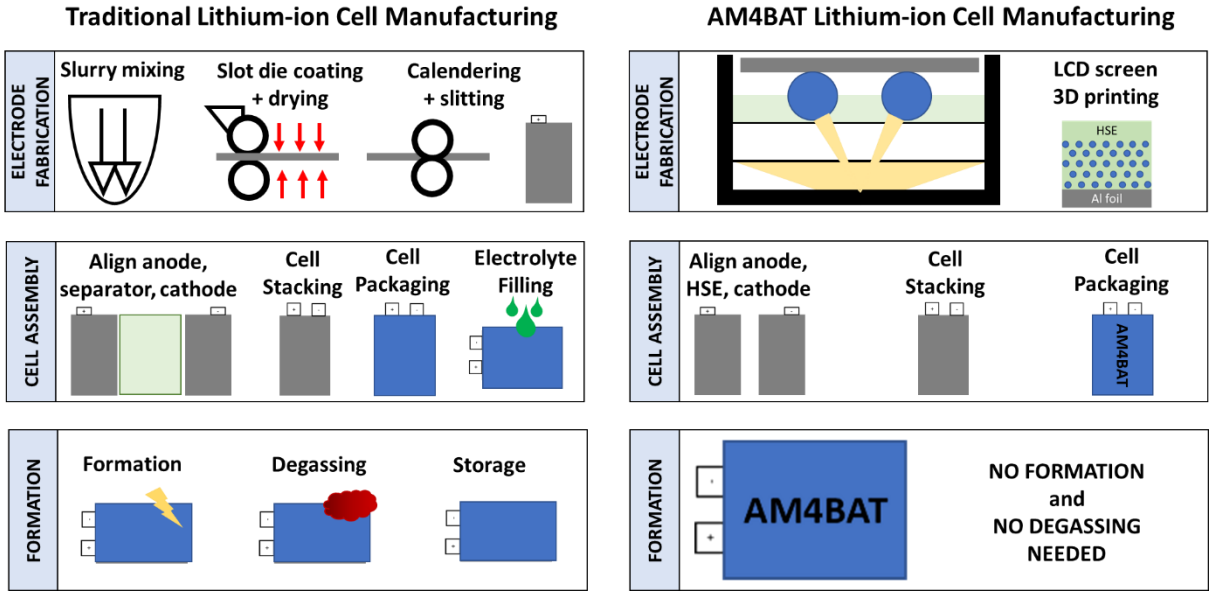

Figure 2: Comparison between the traditional and AM4BAT Li-ion fabrication process

Another major benefit of the 3D printed Li-ion cells containing solid electrolytes is that No formation cycle nor degassing step would in theory be required, which represents another advantage in terms of capital expenditure. A summary of the comparison between the traditional and AM4BAT Li-ion fabrication process can be found in Figure 2.

Customization possible with AM has already been exploited widely within the dental industry. They have shown versatility in both customization and scale of 3D printing. The customization aspect can be leant on for the battery industry for not only the cell micro-morphology but also the macro cell geometry. A battery line made using 3D printers will allow the line to generate cells of different form factors without the need to change the equipment being used. This would allow for cell manufacturers to easily generate bespoke cells to customers on demand, rather than restricting end users' applicability.

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3.3. Potential Routes to Market

3.3.1. In the event HSE printing possible and cathode printing not possible

During the AM4BAT project, work on 3D printing both the solid-state electrolyte and cathode material will be undertaken. In the case where the HSE can be taken forward into production and the same is not possible for the cathode, the HSE can still be employed into a traditional solid state electrolyte system. The HSE will be printed on top of the prepared cathode (by composite and ink coating traditional methods) or as a free-standing film. Possible issues regarding conductivity or contact could be solved by improving either the composition of the HSE or the stack pressure.

3.3.2.In the event Cathode printing possible and HSE not possible

Work on additive manufacturing of cathodes will introduce functional 3D structured electrodes. In the scenario that printing of cathode material is successful whilst the HSE is unsuccessful, there is a route to utilize within current technology approaches. These can be readily deployed in a traditional “wet” cell approach, replacing the current flat cathode system, and utilizing traditional separator and anode materials along with traditional liquid electrolytes. 3D structures in traditional “wet” cells have been proven to bring additional benefits such as access to increased internal surface area and reduction in tortuosity. These changes can allow up to 2 x accessible capacity, reduction of up to 50% in charge time, and increased safety due to more uniform thermal management. Similar changes in geometry to add in 3D structure into electrodes has already been commercialized by Addionics into wet cells with added benefits (https://www.addionics.com/technology access 21/12/22).

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3.3.3.In the event neither Cathode or HSE are possible

During AM4Bat, work will be undertaken to develop high capacity NMC and LMNO electrodes. Both materials can be used in traditional “wet” electrolyte coating systems as a replacement for current cathode materials, resulting in higher capacity traditional cells. NMC-811 exhibits an increase in specific discharge capacity to 200 mA·h·g-1 from 180 mA·h·g-1 of NMC–622. Further increases to nickel content (NMC-955) results in an increase in capacity in the range of 230 mA·h·g-1.

4. Conclusions

To conclude, D2.2 covers the initial strategies to ensure project success on the route map to the fabrication of electrodes and HSE. This includes not only the definition of the key parameters and steps to consider on the fabrication process but also a possible backup plan in case the processability is not working nor providing the required specifications.

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