THE MUSIC PROJECT

Materials for sUstainable Sodium-Ion Capacitors

Deliverable D3.5 Scale-up of Materials

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Publishable summary

The MUSIC project is dedicated to the scaling up of sustainable materials for Sodium-Ion Capacitors (SICs) and the establishment of a European value chain through collaborations between industry and research institutions. A pivotal milestone in this endeavour is Deliverable D3.5 by M42, serving this version as an intermediary step for upscaling materials, involving material selection and testing through partnerships.

As part of D3.5, BYD focused on the scale up of the positive active material, an activated carbon synthesized from Norwegian sawdust biowaste. Simultaneously, JVI and CNRS-IMN is focussing on Carbon Fibres recycled form the aeronautic industry.

Another facet of D3.5 involves CICE's efforts in the development, testing, and scaling up of a novel sacrificial sodium salt for pre-sodiation, having scaled up the synthesis to produce 1 kg of sacrificial salt.

Further, ELY has scale-up GEN0 electrolyte formulation, reaching a production of 2 litres, and delivered to all MUSIC partners.

In summary, the MUSIC project's primary goal is the acceleration of sustainable material development for SICs, and Deliverable D3.5 plays a crucial role in addressing material synthesis, pre-sodiation strategies, and electrolyte development, while navigating challenges in scaling up proprietary materials.

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Abbreviations

SYMBOL	SHORTNAME
SIC	Sodium-Ion Capacitor
HC	Hard Carbon
SAC	Super-Active Carbon
AC	Activated Carbon
LICs	Lithium-Ion Capacitors
CFs	Carbon Fibers
XRD	X-Ray Diffraction

1 Introduction

A core focus of the MUSIC project is the scaling up of sustainable materials for Sodium-Ion Capacitors (SICs) and building the European value chain. To achieve this, the MUSIC project has organized collaborations between industry and research institutions to accelerate this development.

Deliverable D3.5 exists as an intermediary milestone for the upscaling of these materials in which material selection is performed and small-scale samples are delivered between partners for testing and verification.

D3.5 is divided into separate tasks, as detailed below.

1.1 Synthesis of advanced Active Materials

As part of the MUSIC project, novel active materials are a focus. CICE will develop advanced cathode materials in conjunction with BYD as well as advanced anode materials. CICE has produced and tested Hard Carbons from four different synthesis procedures.

Simultaneously, JVI CNRS-IMN and UPS are developing Carbon Fibres and MXenes as novel anode materials.

1.2 Development of sacrificial components and pre-sodiation strategies

CICE will develop, test and scale-up sacrificial sodium salt for pre-sodiation. The pre-sodiation is a critical step in increasing the energy density of SICs, and CICE's sacrificial salt is novel and based on previously developed Lithium analogues. As part of D3.5 CICE has successfully synthesised disodium squarate in 10 g batches and begun the scaling up of this material to 1 kg.

CNRS-IMN has successfully investigated sodium malate and trisodium citrate as additives to the cathode and found that these are capable of providing sodium to the cell. However, the breakdown products form insulating layers on the cathode. Nevertheless, this is a promising method for pre-sodiation.

1.3 Development of innovative electrolytes

Together with FSU, ELY will develop innovative electrolytes suitable for the characterization of high performance SICs operating at more than 4V. Important electrolyte properties such as high conductivity, high electrochemical stability, high thermal stability, high safety, low flammability and good solubility of the sacrificial salts/sodium compounds in the electrolyte are required to ensure the performance of the SICs. ELY has delivered a number of electrolyte formulations to FSU for testing. The electrolytes have been subjected to storage tests and rate tests.

ELY will scale up a 1st generation of sodium electrolytes for the activities in WP5 and WP6. ELY can upscale up to 2L (bottle) or up to 20 kg.

1.4 Scale-up of Super-Active Carbon

Super-Active Carbon (SAC) is Beyonder's (BYD) proprietary active carbon (AC) product designed specifically for use in Lithium-Ion Capacitors (LICs). Deliverable D3.5 entails bringing the production of SAC from 500 g batches up to 5-10 kg batches. However, due to a lack of market demand, this level of upscaling means that production of large quantities of SAC had to be paused. In order to satisfy the requirements of the MUSIC project, several commercially available AC materials have been assessed, and a suitable substitute has been identified. This ensures that other deliverables will not be affected, and no delays will be encountered as a result of this change.

2 Methods and Results

2.1 Synthesis of advanced Active Materials

Carbon Fibres

CFs from several sources have been evaluated by JVI CNRS-IMN. Small scale samples have been ground, and an assessment of the cost of materials has been carried out. Scale-up analysis will come when the screening of fibers is completed.

MXenes

Mxenes are novel materials whose viability is not demonstrated yet, and their low maturity (TRL1-2) discourages their incorporation onto prototypes. However, a proof of concept in a 10F prototype is expected by the end of the project.

2.2 Development of sacrificial components and pre-sodiation strategies

The scale-up of disodium squarate was externalized to a technology center located in Spain named AIMPLAS. The synthesis procedure is as follows: Disodium squarate ($Na_2C_4O_4$) is synthesized using 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid) and Na_2CO_3 as starting materials. They have been purchased from Apollo and Sigma respectively. The sodium carbonate is ACS reagent anhydrous with ≥99.5% purity (Ref. 222321, CAS: 497-19-8, https://www.sigmaaldrich.com/ES/es/product/sigald/222321) and the squaric acid by HPCL ≥99.7% (Ref. 54-OR28821, CAS: 2892-51-5, https://cymitquimica.com/es/productos/54-OR28821/2892-51-5/34-dihydroxycyclobut-3-ene-12-dione/).

Within a 1:1 molar stoichiometric relation, each precursor is dissolved in the required deionized water. Once both are well-dissolved, Na_2CO_3 solution is added slowly into the one of the squaric acid and stirred overnight (at least 16 hours). Then, the deionized water is removed by using a Rotavapor at 50ºC and the obtained sodium salt is dried under vacuum at 60ºC for 12 hours. Before using it, the salt is dried at higher temperature (120ºC) overnight and under vacuum just to remove any solvent that may remain.

The synthesis procedure carried out at CICe is done in 10 g batches. The synthesis procedure in AIMPLAS consisted in two batches of 500g each which were combined afterwards to reach 1kg. Quality control was carried out by XRD shown in Figure A.

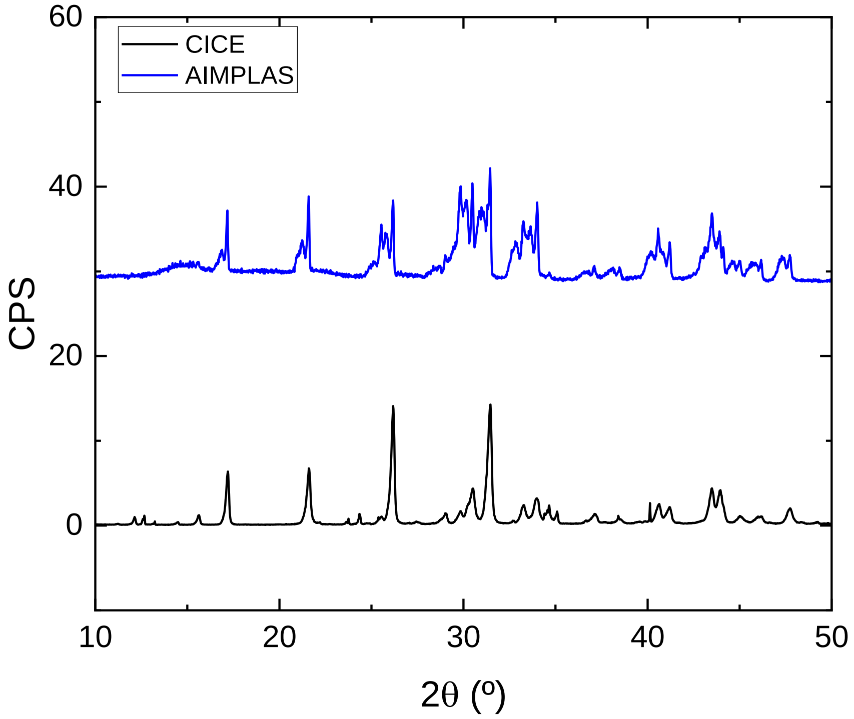

Figure 1: XRD pattern of Na2C4O4 synthesized in CICE and in AIMPLAS

As can be observed from the XRD pattern, the peaks corresponding to the $Na_2C_4O_4$ are present in the scale-up sample. However, there are other peaks appearing in the salt, that might correspond to the original unreacted reagents, what means that the reaction was not complete, and a mixture of the sacrificial salt coexists with the initial reagents. However, this is a hypothesis that needs to be confirmed by in-depth analysis of the XRD pattern.

2.3 Development of innovative electrolytes

A first electrolyte generation (1M $NaPF_6$ in EC: PC (1:1 by weight) was defined with the project partners in common agreement to characterize the different components developed in WP3.

For the upscaling of the GEN1 (1M $NaPF_6$ in EC:PC 1:1 (by weight)), battery grade components were purchased and used. The major challenges was the identification of sodium salt suppliers, that can provide the material in highest quality (>99 %) and high quantities for large scale production. All components were redried before use to minimize the water content in the formulation (< 20ppm). The electrolyte formulation was carried out in a Glove box (H_2O and 0_2 < 0.1 ppm) to guarantee the production of a high quality

electrolyte. A 2-liter batch was produced to cover the electrolyte demand of the project partners. EC and PC were mixed in a weight ratio of 1:1 and the sodium salt was added to this solution and dissolved. To control quality of the components and the final electrolyte, H2O and HF values were measured (< 12 ppm). After the formulation, the electrolyte was filled into small bottles and delivered to the project partners.

For further scale-up of the electrolyte, the E-Lyte pilot line can be used, to produce barrils up to 20 kg.

New electrolytes formulations has been developed together with FSU, trying to use innovative salts, solvents and additives, that not only improve the performance of the system, but also reduced the toxicity and cost production of the electrolytes.

The use of reduced fluorine content salts (NaTFSI, NaFSI), high thermal stable solvents (glyoxals) and SEI/CEI additives (FEC, VC, NaDFOB) should help to improve the performance of sodium-ion capacitors.

Following electrolytes has been formulated so far:

- 1M $NaPF_6$ in EC:PC 1:1 (by weight), GEN 1
- 1M NaTFSI EC:PC (1:1) (by weight)
- 1M NaFSI EC:PC (1:1) (by weight)
- 1M NaTFSI EC:PC (1:1) (by weight) + 2wt.% FEC
- 1M NaTFSI EC:PC (1:1) (by weight) + 2 wt.% NaDFOB
- 1M $NaPF_6$ in TEG:PC (3:7) (by weight) + 2wt.% FEC
- 1M NaTFSI in TEG:PC (3:7) (by weight)
- 1M NaTFSIin TEG:PC (3:7) (by weight) + 2wt.% FEC

Electrolyte samples supplied by ELY were tested by FSU using cathodic and anodic half cells, and pre-sodiated full cells.

The characterization of the electrolytes so far has shown that the use of NaTFSI as electrolyte salt as well as of the different additives helped to improve the performance of lab-scale SICs.

The most promising electrolyte formulation will be scaled up for the development of prototypes and cells.

2.4 Scale-up of Super-Active Carbon

Beyonder has developed a series of patented approaches towards producing high-performance activated carbons, initially on the gram scale. These have predominantly been conducted using chemical activation, where a chemical activating agent is mixed with the precursor (Sawdust) and, heat treated with selected oxygen scavengers under a controlled atmosphere to optimise the porosity generation. This activated method led to the production of activated carbons with a surface area beyond 3000 m^2/g and Volumetric capacitance above 90 F/ cm^3.

Upscaling this process proved challenging due to the corrosive nature of the chemical reagents, flow problems compounded by the plasticisation of the chemical agent/precursor mix and, in summary, incompatibility of the activation method with the rotary kiln. Beyonder, therefore, diversified into developing an alternative activation method, this time using a milder two-step activation process involving the use of a chemical reagent and a second physical activation step to optimise the porosity. This alternative activation method was indeed compatible with the rotary kiln, and the AC production capacity was increased from a few g's to above 500 g per processing batch. The properties of the activated carbon produced using this method were comparable to commercial alternatives, with a specific surface area of around 2000 m^2/g and specific capacitance above 100 F/g. More effort was required to improve the purity after extensive analysis of the structure revealed remnant chemical reagents trapped in the micropores and high metal content inherited from the precursor. More investments were therefore needed in the washing step, along with the purchase of equipment suitable for larger-scale activation processes. In summary, the technology for the upscaling has been demonstrated and is available but activation process equipment capable of producing 10's of Kg of the activated carbon is needed to effectively upscale the process.

3 Discussion and Conclusions

In general, task 3.5 in WP3 is progressing well. D3.5 is linked to Key Project Result of the project, KPR9, where the scale up of i) carbon fibers ii) super activated carbon (10kg) iii) pre-sodiation agent (10kg) iv) electrolyte (1L).

i) Carbon fibers

Research in carbon fibers is ongoing but is not yet on the scale-up phase. Several fibers have been evaluated from the processing point of view. Once their performance is evaluated the best candidate will be selected and a scale-up feasibility assessment will be carried out.

ii) Super activated carbon (SAC)

The main issue encountered in this WP is with the scale-up of SAC. The scale-up feasibility has been demonstrated up to 500 grams, but larger scale up to the range of kilograms requires to adapt the scale-up process to the equipment. Obtention of SAC requires first the obtention of HC, which is the active material of the negative electrode. Research will focus first on the obtention of HC as a previous step before moving to SAC obtention.

iii) Sacrificial salt

The scale up the production of the sodium sacrificial salt necessary for WP6.2. in a 1 kg batch has been successfully achieved.

iv) Electrolyte

The production of a 1 L electrolyte batch was achieved.

4 Recommendation

BYD has shifted its carbon development to focus on the development of HC for sodium and lithium-ion batteries. It is therefore recommended that the goal of scaling up SAC be changed to instead focus on HC. The MUSIC project will incorporate a new partner focused on the up-scaling of HC, with the support of the MUSIC-HOP-ON project (proposal no. 101159544), submitted as part of the HORIZON-WIDERA-2023-ACCESS-06-01 topic and selected for funding by the European Commission. However, BYD has expertise on the development and up-scaling of carbon materials specifically for sodium storage purposes, which makes it a valuable partner for the upscaling of HC. It is therefore recommended that BYD act as a go-between for CICE (who are developing HC on lab scale) and the new incorporated member, providing expertise and input to aid the scale-up process. This will reduce the risk of potential delays in up-scaling. Meanwhile, BYD will purchase the AC necessary to complete this project without incurring delays.

5 Risk register

Risk No.	What is the risk	Probability of risk occurrence[1]	Effect of risk[2]	Solutions to overcome the risk
3.5.1	Activated carbon upscaling to 10kg is not feasible within project timeframes	1	3	The project can be run with commercially available ACs
3.5.2	Sacrificial salt may cause issues on scale			Try first with lithium analogue. AND/OR Test with sodium salt in NMP

Table 1: Risk Register

[1] Probability risk will occur: 1 = high, 2 = medium, 3 = low
[2] Effect when risk occurs: 1 = high, 2 = medium, 3 = low

6 Acknowledgement

The author(s) would like to thank the partners in the project for their valuable comments on previous drafts and for performing the review.

Project partners

#	PARTICIPANT SHORT NAME	PARTNER ORGANISATION NAME	COUNTRY
1	CICE	CENTRO DE INVESTIGACION COOPERATIVA DE ENERGIAS ALTERNATIVAS FUNDACION, CIC ENERGIGUNE FUNDAZIOA	Spain
2	EUR	CLANCY HAUSSLER RITA	Austria
3	KIT	KARLSRUHER INSTITUT FUER TECHNOLOGIE	Germany
4	CNRS	CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE CNRS	France
4.1	IMN	NANTES UNIVERSITE (Affiliated)	France
5	UPS	UNIVERSITE PAUL SABATIER TOULOUSE III	France
6	FSU	FRIEDRICH-SCHILLER-UNIVERSITAT JENA	Germany
7	IRT-JV	INSTITUT DE RECHERCHE TECHNOLOGIQUE JULES VERNE	France
8	ELY	E-LYTE INNOVATIONS GMBH	Germany
9	BYD	BEYONDER AS	Norway
10	BCARE	BATTERYCARE S. L.	Spain
12	TALGO	PATENTES TALGO SL	Spain

Table 2: Project Partners

7 Appendix A – Quality Assurance

The following questions should be answered by all reviewers (WP Leader, peer reviewer 1, peer reviewer 2 and the technical coordinator) as part of the Quality Assurance Procedure. Questions answered with NO should be motivated. The author will then make an updated version of the Deliverable. When all reviewers have answered all questions with YES, only then the Deliverable can be submitted to the EC.

Question	**WP Leader**	**Peer reviewer 1**	**Peer reviewer 2**	**Technical Coordinator**
	Andrea Balducci	Frederik Huld	Juan Pablo Badillo	Jon Ajuria
1. Do you accept this deliverable as it is?	Yes	Yes	Yes	Yes
2. Is the deliverable completely ready (or are any changes required)?	Yes	Yes	Yes	Yes
3. Does this deliverable correspond to the DoW?	Yes	Yes	Yes	Yes
4. Is the Deliverable in line with the MUSIC objectives?	Yes	Yes	Yes	Yes
a. WP Objectives?	Yes	Yes	Yes	Yes
b. Task Objectives?	Yes	Yes	Yes	Yes
5. Is the technical quality sufficient?	Yes	Yes	Yes	Yes

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