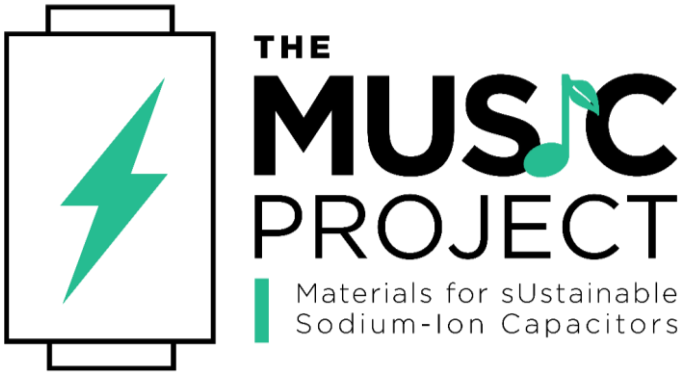

Deliverable D6.2 Production of SIC electrodes (positive and negative)

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PUBLISHABLE SUMMMARY

The effect of human activities such as deforestation, burning of fossil fuels and industrial processes results in significant changes in global climate patterns.These activities increase the concentration of green house gases in the atmosphere, leading to global warming and a host of related events, including more frequent and severe weather changes, rising sea levels, and disruptions to ecosystems and biodiversity.

Addresssing the climate challenges of our time requires a multifaceted approach, including reducing GHG emissions, transitioning to renewable energy sources and improving energy storage techologies. [1] [2]

Whenever we talk about improving energy storage, the first thing that comes to mind is batteries. Unfortunately, batteries aren't the complete solution package as they depend on the availability of critical metals such as lithium and cobalt, which are largely mined in a handful of places in the world, posing a supply risk. [3]

Capacitors on the other hand, are made primarily from carbon and it's compounds, which are not only easily available, but also are more biodegradable and easier to get rid of, compared to battery materials.

Sodium-ion capacitors are emerging as promising candidates to conventional batteries as a result of their cost advantages, environmental benefits, reduced supply chain risks and ease of scalability. [4] [5]

The MUSIC project aims to accelerate the development of sustainable materials for Sodium ion capacitors, and WP6 facilitates this by focusing on the large scale production, assembly and safety testing of prototype SIC cells (30-50 cells). Deliverable 6.2 as part of the work package 6 structure, marks the completion of production of SIC electrodes. Further optimization of cell preconditioning will be carried out in Task 6.4 Assembly and preconditioning of SIC cells in the following 9 months. Moreover, assembled cells will go through abuse test in Task 6.5. Finally, 50 SIC cells will be given to BCARE in M34 for testing in WP7, Task 7.6, and module assembly and validation in M42.

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Abbreviations

SYMBOL	SHORTNAME
SIC	Sodium-Ion Capacitor
HC	Hard Carbon
SBR	Styrene-butadiene rubber
AC	Activated Carbon
LICs	Lithium-Ion Capacitors
Na2C4O4:C65	Sodium squarate salt, coated with carbon
CMC	Carboxymethyl cellulose

1 INTRODUCTION

The MUSIC (Materials for Sustainable Sodium Ion Capacitors) project attempts to solve the challenge of developing new material concepts to be used in supercapacitors, which will reduce the dependence or totally eradicate the necessity to utilize CRMs in energy storage solutions.

Deliverable 6.2 is an important step in this process, as it marks the completion of production of SIC positive electrodes, comprising sacrificial salt, used for presodiation. The development of an appropriate pre-sodiation strategy will be key to the success of the MUSIC project, as it will determine the successful fabrication of competitive SIC cells that will meet the requirements in Work Package 2 (led by BCARE, which creates technical requirements and specifications [6]. The tasks leading up to the achievement of this deliverable are explained in the following sections.

2 MATERIALS

2.1 Reception of scale-up 1kg Na2C4O4:C65

The Sodium squarate salt was received from CICE at the end of the third quarter of 2024. CICE has developed a patent protected technology, consisting of mixing a sacrificial salt together with the active carbon at the positive electrode CICE is responsible for developing, testing and scaling up this pre-sodiation salt. The introduction of the pre-sodiation salt enhances the performance of the Sodium ion capacitor. Material was black/grey in appearance, had a pH of around 5 and particle size of approximately 10 µm. The salt was identified as hazardous, with a likelihood of causing eye and skin irritation, so strict use of personal protective equipment was recommended while conducting experiments.

2.2 Activated carbon

The commercial AC, YP50F, was purchased from Kuraray Japan to guarantee sufficient material availability in the production runs. YP50F was chosen because it represented the base industry standard for commercial AC, possessing a moderately high surface area of 1649 m^2/g, a specific capacitance of 100 F/g [7], and being less complex to handle in production process lines. The latter point is a common issue encountered with very high surface area microporous carbons, which require significant effort to eliminate residual moisture and solvents after electrode fabrication. Additionally, YP50F is also widely used by the consortium partners in the development activities of the project. Hence, it is possible to compare results and upscale developmental progress directly among the partners.

2.3 Sodium squarate

Sodium squarate salt coated with carbon black by a simple ball milling in a 6:1 ratio was received from CICE. The mixture was dried in the vacuum oven at 120 °C before use.

2.4 NMP and PVDF

NMP and PVDF were obtained from Beyonder's internal inventory in the cathode mixing room and used without any modifications. A 6wt% PVDF/NMP solution was prepared overnight by adding the appropriate amount of PVDF and the equivalent of NMP in a Pyrex bottle. After that, a magnetic stirrer was placed inside the bottle, and the mixture was left overnight under stirring at 600 rpm and a temperature of 40 °C. The following day, the mixture was inspected to ensure complete dissolution of the PVDF particles and a clear PVDF/NMP suspension prior to using the solution.

2.5 Electrolyte

1M $NaPF_6$ in EC/PC is considered the Gen 0 electrolyte in the MUSIC project and is used by the partners in the related developmental activities. The commercial partner in the MUSIC consortium, ELYTE, is supplying this electrolyte under request. Moreover, input from Beyonder is required to assist optimization efforts, especially regarding performance in realistic commercial environments.

3 SMALL SCALE VALIDATION

The electrodes were first fabricated on a small scale in the laboratory to validate the materials and the process. This step is crucial as it provides instructions for the large-scale electrode manufacturing process. The materials used in the construction of the coin cells are listed below. After assembling the coin cells in an argon-filled glovebox, they are tested electrochemically to ascertain their performance, highlighting the integrity of the materials employed therein.

3.1 Positive electrode fabrication 

The positive electrode recipe consisted of AC/$Na_2C_4O_4$/C65/PVDF in the ratio 60/30/5/5 wt% using NMP as a solvent. This ratio was received from CICE as the recommended recipe based on their previous experiments and optimised conditions. These conditions were developed under Work Package 5, task 5.2 positive electrode processing. The coating was performed using the doctor blade and mini coater and a double-side carbon-coated Al foil current collector. Different electrode loadings were obtained, ranging from 6.5 – 9 mg/cm^2. The obtained electrodes were calendared to 15% thickness reduction and achieved press densities ranging from 0.7 - 0.9 g/cm^3.

3.2 Negative electrode fabrication 

The negative electrode recipe consisted of HC/C65/CMC/SBR in similar ratios as used in the production line. The coating was conducted in the laboratory using the doctor blade and mini coater and a bare Al current collector foil Electrode loading ranging from 2.9 – 4.5 mg/cm^2 and press densities around 0.9 g/cm^3 were achieved during the coating and calendaring process, respectively.

All the prepared electrodes were transferred to the glovebox and dried overnight before cell assembly.

3.3 Full Coin cell assembly (for material validation) 

Full coin cells consisting of an AC/sodium squarate cathode and an HC anode were assembled using the prepared electrodes and allowed to rest for 24 hours prior to testing. The initial assembly procedure utilized a Polyolefin (PE) separator and 75 µl of ELYTE electrolyte. The electrolyte was eventually replaced with SOBEY-01. Charge and discharge cycles at 0.1 C (C=calculated combined capacity of AC + Sodium squarate) were conducted in potential window 2.2- 4.2V for the formation cycles as suggested by CICE to realize full de-sodiation of the sodium squarate salt.

4. ROLL-TO-ROLL ELECTRODE FABRICATION

The results from the material validation in section 3 were used as a guide in designing the final process instructions for the first electrode production trial phase. Three potential challenges were identified prior to the kick-off meeting, and approaches to resolve them were proposed. The challenges are listed below.

1. Dissolution of $Na_2C_4O_4$ in water-based slurries
2. Gelation arising from too high $Na_2C_4O_4$ content (30wt%) in the electrode slurry
3. Gas generation and swelling following the de-sodiation of $Na_2C_4O_4$ during the formation step

Beginning from the first, according to the proposal, slurry production processes were to be performed using water-based slurries. However, it was observed that the carbon coating on the sodium squarate dissolved completely during mixing and coating. Subsequently, after drying, the squarate salt separates and migrates to the edges of the coated electrodes, with clearly visible white particles. As a result of this occurrence, mitigation plan was agreed to proceed with PVDF-NMP coatings as the binder/dispersion media, pending the discovery of a suitable alternative that alleviates the squarate salt dissolution.

The positive electrode slurry consisted of AC/$Na_2C_4O_4$/C65/PVDF in the ratio 60/30/5/5 wt% using NMP as a solvent. A 10L mixer was used in the cathode coating line, the mixing location of which no external humidity control measures were adopted but was influenced by the outside weather conditions. The weight of the final slurry was around 5 kg with pH of 5.41 and the measured solid content was about 33.5%. The final slurry viscosity was 9431 mPa.S

The negative electrode (anode) coating was conducted with an etched Aluminum foil previously purchased for LIC development. Isolated bubbles were observed when trying to coat with the initial foil, with probable surface tension-related effects from likely impurities on the surface of the foil. This was resolved by switching to etched Aluminum foil, which was coincidentally the only alternative bare Aluminum foil in stock. Poor adhesion and low electrode quality were observed in these trial runs. Hence, a water-compatible primer coating on the Aluminum foil is mandatory to guarantee the successful coating of water-based anode slurries. In summary, 110 m of double-sided coated negative electrodes were produced during the run.

Table 1. Cathode mixing process specification

S/N	Component	Ratio (%)
1	AC (YP50F)	60
2	PVDF	5
3	Na2C4O4	30
4	C65	5
5	Total	100
Target solid content (SC%) = 34%		

Figure 1. Process data from the cathode 10L mixing batch: (a) tank and blades during dry mixing (b) Mixing tank frontal view (c) Hegmans gauge for checking slurry solid content (d) Die-cutting start (e) Die-cut electrodes

4 DISCUSSIONS AND CONCLUSIONS

Electrodes to fabricate sodium-ion capacitors have been successfully assembled in Beyonder's prototype line facilities using a commercial AC YP50F, scale-up $Na_2C_4O_4$ and HC SHC-2D. In order to validate them, first pouch cells were assembled using SOBEY-01 electrolyte. Though beyond this deliverable, pre-sodiation of the cells was achieved during the formation step by the de-sodiation of the incorporated sodium squarate sacrificial salt. An improvised in-house set-up to handle gas generation was developed and implemented successfully during the formation step, which mitigated the anticipated risks of uncontrollable swelling due to the gaseous by-products from the sodium squarate salt and validated performance of electrodes.

Next, large production of electrodes will be carried out for the fabrication of 50 SIC cells that will be given to BCARE in M34 for testing in WP7, Task 7.6, and module assembly and validation in M42. Prior to this, some extra cells will be tested in the following 9 months in Task 6.4 Assembly and preconditioning of SIC cells for further optimization of cell preconditioning. Moreover, assembled cells will go through abuse test in Task 6.5.

5 RECOMMENDATION

Several valuable lessons have been obtained from this trial, and the following recommendations and aspects for improvement will be considered in the upcoming tasks:

- Improved carbon coating on the sodium squarate salt. (T3.5)
- Detailed study and optimisation of the formation process to shorten the duration and achieve 100% CE in a fast and efficient manner. (T6.4)
- Revision of the pouch cell fixtures for handling the evolved gas. Alternatively, highly chemical-resistant parts are needed to guarantee gas evacuation for prolonged periods. (T6.4)
- Electrolyte optimisation is needed to improve stability at high voltages and maintain the performance characteristics of capacitors (High power density and cycle life). (T3.3)
- Electrolyte volume revision is needed to compensate for decomposition, electrode void spaces, and leakage during gas evacuation. (T5.5, T6.4)

6 RISK REGISTER

Based on the results obtained in this WP, additional risks were identified and registered in the risk register of the project, that can be observed in the following table.

Table 2. Risk Register

Risk No.	What is the risk	Probability of risk occurence	Effect of risk	Solutions to overcome the risk
6.2.1	Sacrificial salt may generate gas at certain voltages	1	2	Develop gas handling systems to control gas evolution
6.2.2	Electrolyte stability at high voltages	1	2	Electrolyte optimization is necessary to improve stability at high voltages.

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

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

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Table 3. 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
13	UPC	UP CATALYST	Estonia

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