

# THE MUSIC PROJECT

Materials for sUstainable  
Sodium-Ion Capacitors

## Deliverable 4.2 Electrode-electrolyte interaction analysis

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## Publishable summary

WP4 aims to deepen understanding of interfacial phenomena in sodium-ion capacitors (SICs) to deliver targeted feedback for materials engineering and to optimise the sacrificial compounds used during the pre-sodiation stage. The primary outcome of this work package is to provide essential insights into the safety, durability, and efficiency of the selected active and inactive materials and the electrolytes used to develop high-performance SICs.

One focus is assessing compatibility among the various materials, including positive and negative active materials, binders, and electrolyte formulations, with particular attention paid to the two sacrificial salt candidates selected for the pre-sodiation of the negative electrode: disodium squarate ( $\text{Na}_2\text{C}_4\text{O}_4$ ) and disodium croconate ( $\text{Na}_2\text{C}_5\text{O}_5$ ).

Thus, a panel of characterisation tools have been applied to shed light on the pre-sodiation mechanism and SEI formation, which is the goal of this deliverable. In more detail, this work provides an integrated assessment of the electrochemical, interfacial, and gas-evolution phenomena governing charge storage and pre-sodiation in sodium-ion capacitors, by combining *operando*-sensitive techniques (*operando* optical microscopy, *operando* Raman spectroscopy, electrochemical dilatometry, and differential electrochemical mass spectrometry) with complementary spectroscopic analyses (FTIR and UV-visible spectroscopy, DFT simulations), gas-sorption porosimetry (BET), and X-ray photoelectron spectroscopy (XPS). Particular attention was given to the influence of the sacrificial salt on the oxidation mechanism, gas evolution, porosity, and SEI formation on the negative hard carbon electrode.

*Operando* optical microscopy and *operando* Raman spectroscopy confirmed the distinct oxidation pathways of the two oxocarbon salts during the first charge. The croconate framework remains stable up to about 3.6 V vs  $\text{Na}^+/\text{Na}$  before oxidising at higher potential into a neutral cyclopentanepentone ( $\text{C}_5\text{O}_5$ ) species that dissolves in the carbonate electrolyte without significant gas generation. The salt crystals were tracked as they were progressively consumed upon their oxidation. In contrast, disodium squarate decomposes rapidly at high potentials, accompanied by pronounced  $\text{CO}_2$  evolution, as evidenced by bubble formation and a pronounced baseline distortion of the Raman signal. DFT calculations were used to simulate the UV-visible signatures of  $\text{Na}_2\text{C}_5\text{O}_5$ ,  $\text{C}_5\text{O}_5^{2-}$ , and neutral  $\text{C}_5\text{O}_5$  in different solvent environments, providing a reliable theoretical reference ahead of the *operando* UV-visible measurements currently being implemented to validate the croconate oxidation mechanism.

BET measurements showed that incorporating sacrificial salts limits access to the activated carbon surface area in its pristine state, while preserving the microporous character of the electrode. After the first oxidation, the electrode containing disodium croconate retained the highest adsorbed quantity, indicating that the croconate oxidises preferentially to the electrolyte and protects the positive electrode against pore blocking, whereas disodium squarate partially blocks the porosity, consistent with carbon deposition and electrolyte decomposition.

Electrochemical dilatometry was used as an innovative means to simultaneously track volume change and gas emission, revealing that the pristine activated carbon electrode exhibits only  $\text{PF}_6^-$ -electrosorption-related volume variations, as expected. The croconate-containing electrode displays redox peaks that correlate with a negative volume change and no gas release during the first cycle, consistent with the dissolution of the oxidation product. The squarate-containing electrode could not be measured reliably because excessive gas release saturated the sensor. These observations were corroborated by differential electrochemical mass spectrometry (DEMS), which detected significant  $\text{CO}_2$  evolution during the first cycles of disodium squarate. In contrast, no  $\text{CO}_2$  was observed for croconate, thereby preventing the buildup of internal pressure and the associated risk of electrode breakage.

XPS of the hard carbon negative electrode demonstrated that the pre-sodiation route governs the SEI chemistry. Compared with *ex situ* electrochemical pre-sodiation, *in situ* oxidation of the sacrificial salt yields an SEI with a markedly higher inorganic ( $\text{NaF}$ ) content (around twice as much), together with a more developed organic fraction, pointing to a more robust and ordered interfacial layer that is likely responsible for the superior capacity retention observed for this pre-sodiation strategy.

All these results support the beneficial role of the sacrificial salt in SEI formation on a hard carbon-based negative electrode, and allow the two sacrificial salt candidates to be clearly discriminated. Disodium squarate generates significant gas ( $\text{CO}_2$ ) upon oxidation, leading to swelling of the pouch cells and to a partial blocking of the electrode porosity. Overcoming these drawbacks at the cell level would require additional steps in the industrial process. In contrast, disodium croconate is believed to release no gases, forming a soluble and non-shuttling oxidation product (neutral cyclopentanepentone,  $\text{C}_5\text{O}_5$ ), and promotes a more robust, inorganic-rich SEI associated with superior capacity retention, requiring no additional fabrication step for scale-up, besides its higher cost relative to disodium squarate.

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No entries for the list of equations found.

## Abbreviations

| SYMBOL | SHORTNAME                                      |
|--------|------------------------------------------------|
| eQCM   | Electrochemical Quartz Crystal Microbalance    |
| SIC    | Sodium-ion Capacitor                           |
| HC     | Hard Carbon                                    |
| AC     | Activated Carbon                               |
| PVDF   | Polyvinylidene Fluoride                        |
| PTFE   | Polytetrafluoroethylene                        |
| CMC    | Carboxymethyl Cellulose                        |
| SBR    | Styrene-Butadiene Rubber                       |
| NMP    | N-Methyl-2-pyrrolidone                         |
| EC     | Ethylene Carbonate                             |
| PC     | Propylene Carbonate                            |
| DMC    | Dimethyl Carbonate                             |
| ICE    | Initial Coulombic Efficiency                   |
| YP     | YP-50F (Reference Activated Carbon)            |
| PZC    | Point of Zero Charge                           |
| FTIR   | Fourier Transform Infrared Spectroscopy        |
| SEM    | Scanning Electron Microscopy                   |
| EDS    | Energy Dispersive X-Ray Spectroscopy           |
| TEM    | Transmission Electron Microscopy               |
| BET    | Brunauer–Emmett–Teller surface area analysis   |
| EIS    | Electrochemical Impedance Spectroscopy         |
| XPS    | X-ray Photoelectron Spectroscopy               |
| BE     | Binding Energy                                 |
| SEI    | Solid Electrolyte Interphase                   |
| DEMS   | Differential Electrochemical Mass Spectrometry |
| DFT    | Density Functional Theory                      |
| OCV    | Open Circuit Voltage                           |
| CV     | Cyclic Voltammetry                             |

# 1. Introduction

## 1.1 Objectives

WP4 aims to deepen understanding of interfacial phenomena in sodium-ion capacitors (SICs) to provide targeted feedback for materials engineering and to optimise the sacrificial compounds used during the pre-sodiation stage. These investigations are often updated due to the optimisation of electrolyte formulation concerning cell performances, safety and the use of greener compounds.

The primary outcome of this work package is to provide essential insights into the interactions between the electrodes and the electrolyte using standard and advanced characterisation techniques. The positive electrode is made of activated carbon, and the improvement in double-layer capacitance is a main concern, which is strongly dependent on pore size distribution and electrolyte formulation. Moreover, the absence of side reactions involving gas evolution at high potentials, the possible carbon oxidation during oxidative scans, or the presence of redox shuttles arising from sacrificial salt decomposition is highly desirable. Indeed, due to the pre-sodiation step thanks to sacrificial salt strategies (see Deliverables 3.2 and 4.1), the positive electrode is a composite one, namely a mixture of activated carbon and sacrificial salt, and to a lesser extent, carbon conductive additives and binder.

Similar problems were raised at the negative electrode with the SEI formation on hard carbon electrode or on alternative materials such as recycled carbon fibres. This SEI, in turn, directly influences the reactivity of sodium cations with the electrode and, more precisely, the different components of this insertion mechanism, including surface adsorption, intercalation of  $\text{Na}^+$  in 2D-confined interlayers, and  $\text{Na}^+$  filling in 3D-confined nanopores.

As a consequence, the electrodes cannot be considered model components interacting with the electrolyte. They are rather complex systems that can only be approached using a panel of analytical techniques: operando sensing techniques (microscopy, Raman analysis, differential Electrochemical Mass Spectrometry, and dilatometry), and complementary in-situ analyses (spectroscopic tools, and structural/microstructural investigations), most of which are coupled with electrochemical tests to track, in situ or *operando*, the evolution of the electrolyte-electrode interaction upon cycling. This is the main goal of this deliverable.

A special focus has been made on the sacrificial salt, which has a strong influence on cell performance (capacity, ageing, etc.), and a specific focus has been dedicated to this peculiar component of MUSIC SIC design. Such focus helps to unveil some issues raised in deliverables 4.1 and 3.2, especially about the different oxidation mechanisms of the two selected sacrificial salts: di-sodium squarate and di-sodium croconate.

# 2. Technical section

## 2.1 Electrode and cell preparation

Three positive electrode formulations were investigated in this work. A pristine activated carbon electrode containing 90 wt.% activated carbon, 5 wt.% C45 conductive carbon, and 5 wt.% CMC binder was used as a reference and is hereafter denoted as AC pristine. Two sacrificial additive-containing electrodes were also prepared by replacing a fraction of the activated carbon with 30 wt.% of either disodium squarate or disodium croconate, resulting in compositions of 60 wt.% activated carbon, 30 wt.% sacrificial salt, 5 wt.% C45, and 5 wt.% CMC. These electrodes are referred to as AC+Sq and AC+C, respectively. All components were mixed together and manually ground until a homogeneous slurry was obtained. The resulting slurry was cast onto aluminium foil using a doctor blade and subsequently dried to remove residual water. After drying, the electrodes were punched into disks of the desired diameter and used for electrochemical measurements. Self-standing electrodes (for BET measurements) used the same slurry formulation, but with PTFE as a binder.

Electrochemical cells were assembled in a three-electrode Swagelok configuration. Sodium metal was used as both the counter electrode and the reference electrode. The prepared composite electrode

served as the working electrode. Cell assembly was performed in a glove box under Ar atmosphere ( $O_2$  and  $H_2O$  under 1ppm).

## 2.2 Reaction mechanism during the first charge for disodium squarate and disodium croconate

The first charge of SICs containing disodium squarate ( $Na_2C_4O_4$ ) or disodium croconate ( $Na_2C_5O_5$ ) is associated with the irreversible oxidation of the oxocarbon salts, which act as sacrificial sodium sources for the presodiation of the negative electrode. During this process, sodium ions are released from the sacrificial additive and transferred through the electrolyte toward the negative electrode, while the corresponding electrons flow through the external circuit. This mechanism compensates for the sodium consumption associated with SEI formation and improves the sodium balance of the full device.

For disodium squarate, the oxidation of the squarate dianion destabilises the highly conjugated four-membered ring. Following the extraction of sodium ions and electron removal, the oxidised species become unstable and undergo irreversible decomposition. A plausible reaction pathway involves ring opening and subsequent decarboxylation reactions, ultimately leading to the formation of carbon dioxide. As a consequence, the pristine squarate phase is progressively consumed during the first charge. The generation of gaseous products is potentially detrimental for SIC applications, as gas evolution may increase the internal pressure of the cell and negatively affect its long-term stability.

In contrast, the oxidation of disodium croconate is proposed to proceed through the formation of a neutral  $C_5O_5$  species after the release of sodium ions and electrons. Owing to the greater electronic delocalisation within the five-membered ring, the oxidised intermediate is expected to exhibit higher stability than the corresponding squarate species. Rather than decomposing into gaseous products, the neutral  $C_5O_5$  species is expected to dissolve into the electrolyte, resulting in the gradual disappearance of the initial croconate particles from the electrode. This pathway enables sodium release while minimizing gas evolution, thereby preserving long-term cell stability and reliable electrochemical performance.

Although both compounds operate through an irreversible oxidation mechanism and serve as sodium reservoirs for presodiation, the nature of their oxidation products differs markedly. Disodium squarate is proposed to generate carbon dioxide upon oxidation, whereas disodium croconate forms a neutral soluble species. These distinct reaction pathways may have important consequences for the practical implementation of sacrificial additives in SICs, since gas evolution can induce pressure build-up and electrode degradation, while dissolution of the oxidation product is expected to have a lower mechanical impact on the cell. The proposed mechanisms are consistent with the electrochemical behaviour observed during the first charge and are further supported by the structural and morphological changes discussed in the following sections.

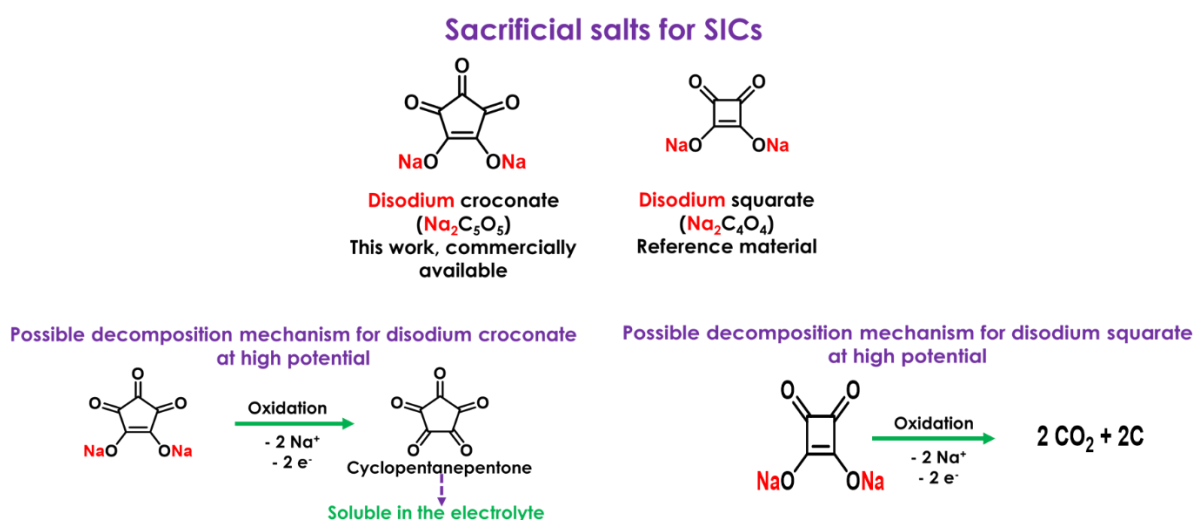


Figure 1: Schematic illustration of the irreversible oxidation and decomposition pathways of disodium croconate and disodium squarate at high potential.

## 2.3 Investigations of electrode-electrolyte interaction using optical microscopy

### 2.3.1 Operando optical microscopy

The operando optical microscopy sequence shows the evolution of the electrode surface during electrochemical cycling of the AC+C electrode versus sodium metal. The corresponding electrochemical potentials at each stage are simultaneously monitored by operando CV and indicated on each image.

At the beginning of the experiment, elongated needle-like crystals attributed to sodium croconate are clearly visible on the electrode surface. During cycling, these crystals progressively decrease in size and eventually disappear, indicating the gradual electrochemical consumption of sodium croconate. The disappearance of these needle-like structures correlates with the electrochemical processes observed along the CV profile, confirming the active participation of sodium croconate during cycling. In contrast, the surrounding electrode morphology remains relatively stable throughout the experiment.

Importantly, sodium croconate was intentionally not ground prior to electrode preparation in order to preserve its large crystalline needle morphology, enabling direct visualisation and tracking by operando optical microscopy. Mechanical grinding would have reduced the crystal size below the optical detection limit, preventing reliable observation of their evolution during cycling.

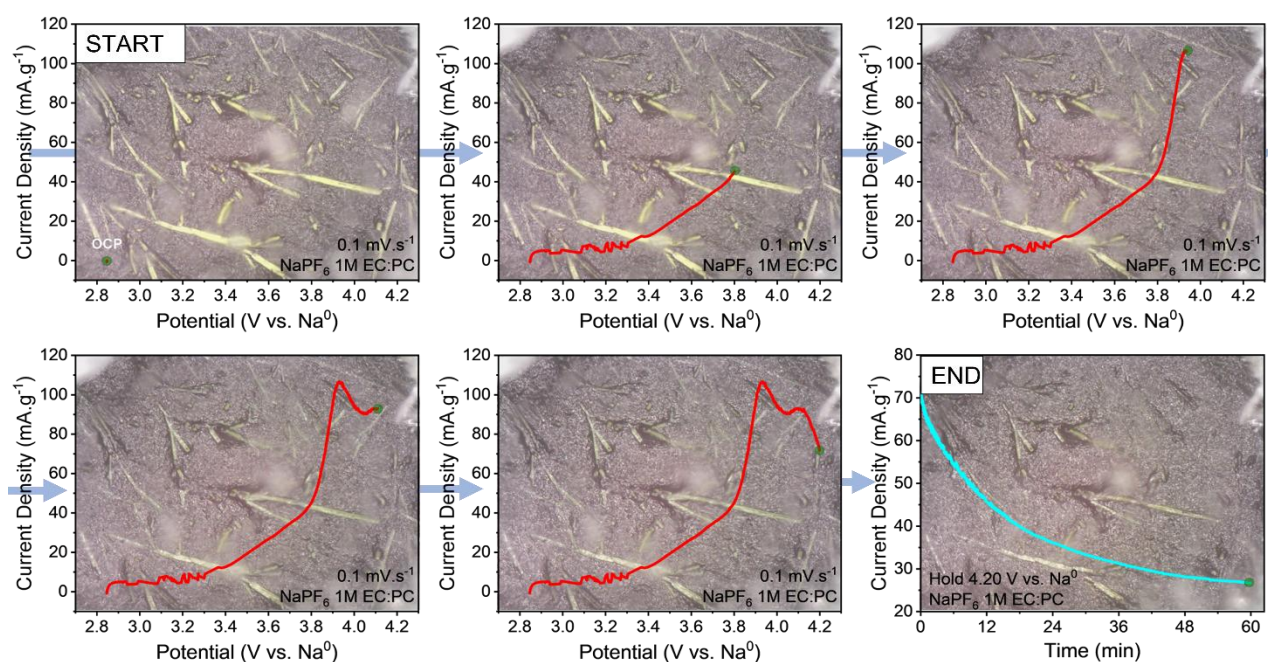


Figure 2: Operando optical microscopy of AC + sodium croconate vs. Na.

For comparison, operando videos of AC + sodium squarate vs Na are available through the link provided below. In contrast to sodium croconate, sodium squarate particles could not be clearly detected by optical microscopy, even without prior grinding, due to their significantly higher solubility in the electrolyte, as shown in Figure 6. More generally, the oxidation of squarate species is associated with CO<sub>2</sub> evolution. Here, operando optical microscopy further confirms the dissolution of Na<sub>2</sub>C<sub>4</sub>O<sub>4</sub> and evidences CO<sub>2</sub> bubble formation during cycling. Under operando conditions, Raman spectra show a progressive loss of Na<sub>2</sub>C<sub>4</sub>O<sub>4</sub> signal, with signals rapidly decreasing and becoming dominated by NaPF<sub>6</sub> EC:PC electrolyte and carbon contributions, consistent with dissolution of crystalline Na<sub>2</sub>C<sub>4</sub>O<sub>4</sub>. At 3.77 V, Raman signals almost completely vanish, with strong baseline distortion attributed to CO<sub>2</sub> evolution and interfacial changes, as confirmed by optical microscopy below.

Access the comparison videos here: <https://uncloud.univ-nantes.fr/index.php/s/Gs44JaXEAAb2oRgZ>

## 2.4 Investigations of electrode-electrolyte interaction using Raman and UV-visible spectroscopies

### 2.4.1 Raman and FTIR spectroscopies

This section presents the Raman spectroscopy results for the AC+C and AC+Sq systems. The operando measurements were performed using a specific setup, as illustrated below, with excitation provided by a 514 nm green laser. The electrochemical cell was connected to a potentiostat, as illustrated in Figure 3.

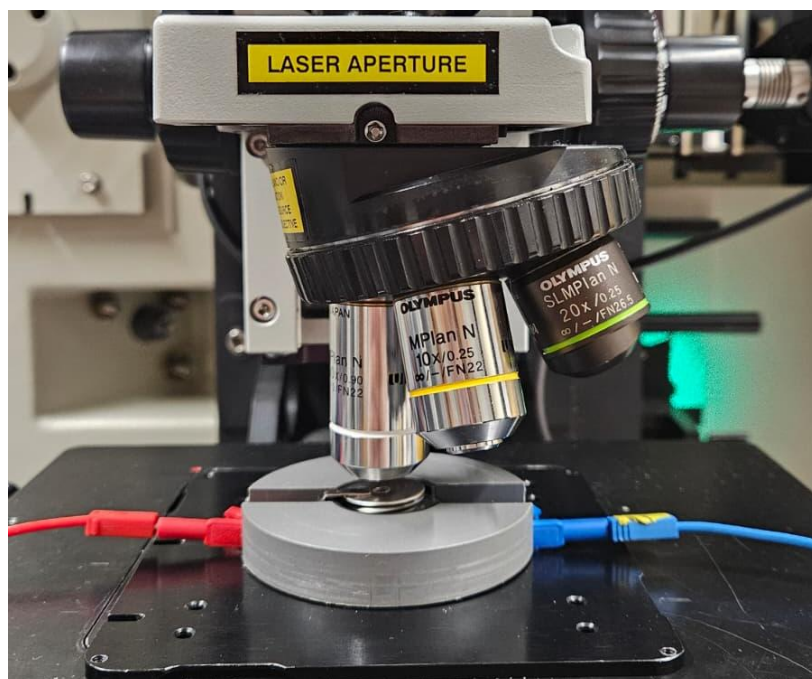


Figure 3: Photograph of the operando Raman spectroscopy configuration coupled to an electrochemical potentiostat.

Figure 4 presents the Raman spectra of (i) commercial  $\text{Na}_2\text{C}_5\text{O}_5$ , (ii) the electrolyte  $\text{NaPF}_6$  in EC:PC, and (iii) operando measurements recorded at different applied potentials vs.  $\text{Na}/\text{Na}^+$ , where contributions from both  $\text{Na}_2\text{C}_5\text{O}_5$  and the electrolyte are observed.

The Raman spectrum of commercial  $\text{Na}_2\text{C}_5\text{O}_5$  exhibits well-defined vibrational features characteristic of the croconate structure, with several dominant bands. The region below  $500\text{ cm}^{-1}$  is attributed to interactions between  $\text{Na}^+$  ions and the carbon framework, as well as collective lattice motions of the crystal structure. The band around  $600\text{ cm}^{-1}$  is associated with symmetric vibrational modes of the croconate. A strong band near  $1600\text{ cm}^{-1}$  is assigned to significant electron delocalisation across the conjugated carbon network, reflecting highly delocalized electronic states within the material.

In comparison, the Raman spectrum of  $\text{NaPF}_6$  in EC:PC electrolyte is dominated by broad, weak signals. These can be assigned to vibrational modes of the solvent molecules, EC and PC, as well as characteristic vibrations of the  $\text{PF}_6^-$  anion, in particular P-F stretching modes. These contributions form a diffuse background that overlaps with the active material signals during operando measurements.

Under operando conditions (3 V, 3.5 V, and 3.6 V), the characteristic Raman features of  $\text{Na}_2\text{C}_5\text{O}_5$  remain clearly observable, indicating that the croconate framework is largely preserved within this potential window. The spectra show a composite response arising from the simultaneous contributions of the active material and the electrolyte, with only minor variations in peak intensities, suggesting ongoing but limited electrochemical interactions involving  $\text{Na}^+$ .

At higher potential (3.79 V), a pronounced decrease in Raman intensity is observed, together with a progressive attenuation of the croconate-related bands. This shows the electrochemical oxidation of  $\text{Na}_2\text{C}_5\text{O}_5$ , leading to great electronic changes. At this potential, the Raman signals of  $\text{Na}_2\text{C}_5\text{O}_5$  are strongly reduced, consistent with the transformation of the material.

Overall, the results demonstrate that  $\text{Na}_2\text{C}_5\text{O}_5$  is stable in the intermediate potential range, while clear changes appear at higher potentials due to its oxidation.

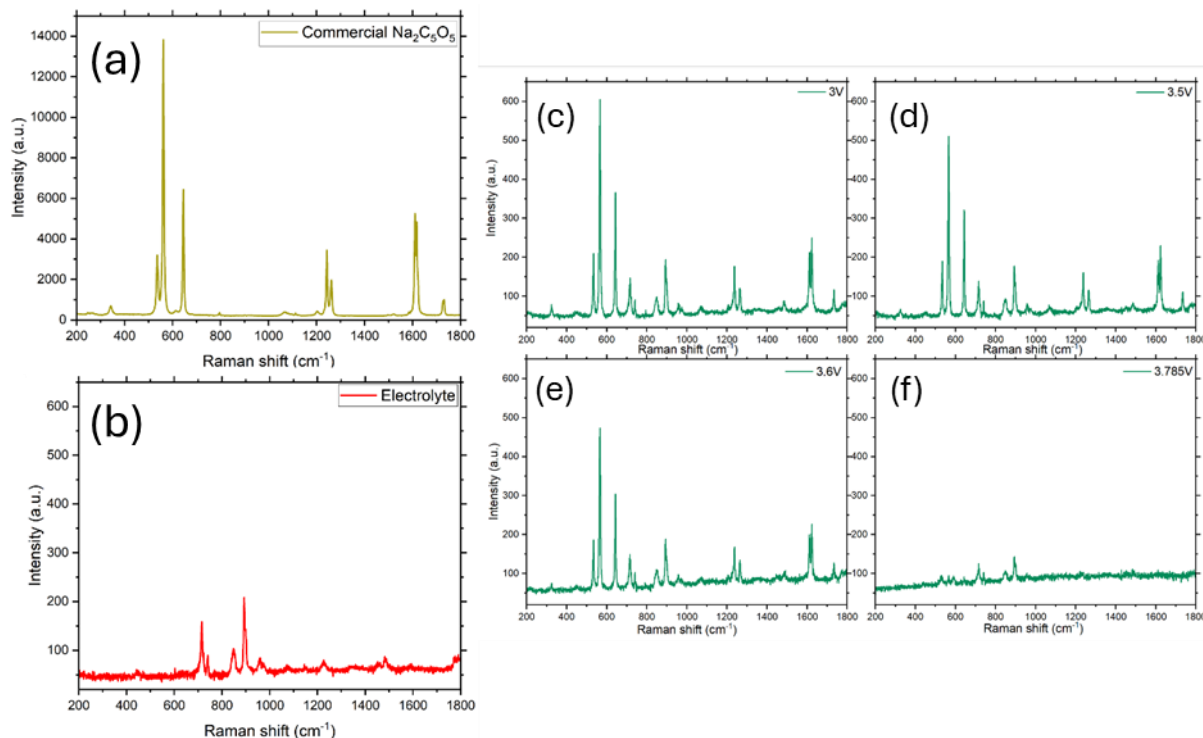


Figure 4: Raman spectroscopy of commercial  $\text{Na}_2\text{C}_5\text{O}_5$ : comparison with  $\text{NaPF}_6$  in EC:PC electrolyte (b) and operando evolution under different potentials vs Na: 3 V (c), 3.5 V (d), 3.6 V (e), 3.77 V (f).

Figure 5 presents the Raman spectra of  $\text{Na}_2\text{C}_4\text{O}_4$  as reference (pristine powder) and under operando electrochemical conditions at different applied potentials vs Na. The electrolyte spectrum is shown independently as a reference in order to clearly distinguish its vibrational contributions from those of the active material. The Raman spectrum of pristine  $\text{Na}_2\text{C}_4\text{O}_4$  powder exhibits well-defined and intense vibrational features characteristic of the squarate framework, confirming a highly ordered crystalline structure. The most prominent spectral features are distributed across several regions. Below  $500\text{ cm}^{-1}$ , weak low-frequency modes are associated with lattice vibrations and collective motions of the inorganic framework. In the  $500\text{--}800\text{ cm}^{-1}$  range, bands are attributed to skeletal deformations involving  $\text{Na}^+$  oxygen interactions and coupled motions of the carbon-oxygen backbone. The region between approximately  $900$  and  $1200\text{ cm}^{-1}$  is assigned to C–O stretching-type vibrations within the oxalate/squarate units. The most intense contributions, located in the  $1300\text{--}1700\text{ cm}^{-1}$  range, correspond to symmetric and asymmetric stretching modes of the carbonyl and conjugated C–C/C–O framework, which are highly sensitive to the electronic structure of the material.

Under operando conditions (3.0 V, 3.5 V, 3.61 V), the Raman spectra show a progressive loss of the characteristic  $\text{Na}_2\text{C}_4\text{O}_4$  vibrational features. The signals rapidly decrease, and the spectra become dominated by contributions from the  $\text{NaPF}_6$  EC:PC electrolyte and the carbon electrode. This indicates that the crystalline  $\text{Na}_2\text{C}_4\text{O}_4$  phase is no longer present at the electrode surface, consistent with its rapid dissolution in the electrolyte. As a result, the measured signal mainly reflects the liquid electrolyte environment, with only the AC contribution remaining. Optical microscopy observations support this evolution, showing morphological changes consistent with material disappearance during cycling (see Figure 6).

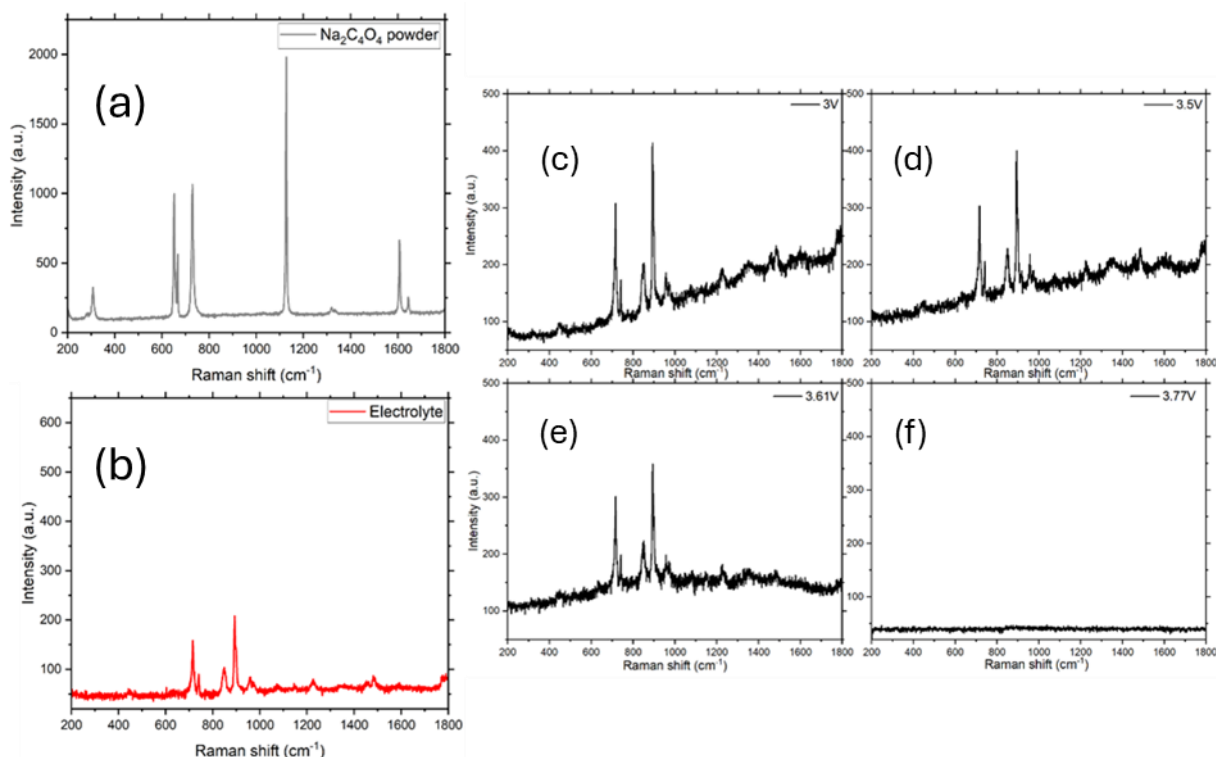


Figure 5: Raman spectroscopy of prepared  $\text{Na}_2\text{C}_4\text{O}_4$  (a): comparison with  $\text{NaPF}_6$  in EC:PC electrolyte (b) and operando evolution under different potentials vs Na: 3 V (c), 3.5 V (d), 3.6 V (e), 3.77 V (f).

At a higher potential (3.77 V), the Raman spectra show an almost complete disappearance of all signals. This is accompanied by a strong distortion of the baseline and a significant reduction in spectral quality. Such behaviour is attributed to a combination of effects, including local changes in the interfacial environment. In particular, the appearance of gas evolution is strongly suggested, most likely corresponding to  $\text{CO}_2$  formation, as already confirmed by complementary experimental techniques and optical microscopy, where  $\text{CO}_2$  bubble formation is directly observed. In addition, the pronounced baseline shift observed at high potential is indicative of significant changes in the optical response of the interface, likely related to local heating effects induced by laser illumination, as well as increased disorder and dynamic surface restructuring during oxidation.

Figure 6 illustrates the dissolution behaviour of  $\text{Na}_2\text{C}_4\text{O}_4$  upon contact with the electrolyte. In image (a), white  $\text{Na}_2\text{C}_4\text{O}_4$  crystals are clearly observed on the brown AC background. After the addition of the  $\text{NaPF}_6$  EC:PC electrolyte, image (b) shows the disappearance of these white crystals, indicating the dissolution of  $\text{Na}_2\text{C}_4\text{O}_4$  in the carbonate-based electrolyte. The remaining visible brown spots correspond to the AC particles, which appear due to the contrast in the optical image. During the experiment, recrystallisation of the salt was also observed upon electrolyte drying, indicating that the dissolution process is reversible and associated with a dissolution/precipitation equilibrium rather than irreversible oxidation or degradation of the active material.

This behaviour is consistent with the known solubility of sodium oxocarbon salts in polar carbonate solvents. A similar phenomenon was reported by Gambe et al. [1] for  $\text{Na}_2\text{C}_5\text{O}_5$ , where significant dissolution of the active material was observed in conventional carbonate electrolytes. To mitigate this issue, the authors employed acetonitrile-based electrolytes, which improved the electrochemical stability of the system.

The stronger dissolution tendency observed for Na-based squarates compared to analogous Li-based systems can be rationalised by the larger ionic radius and lower charge density of Na compared to Li.

As a result, the interaction between Na and the  $C_4O_4$  anion is weaker, which facilitates dissociation and dissolution in highly polar solvents such as EC and PC that strongly solvate Na ions. In contrast, Li-based squarate systems generally exhibit lower solubility because the smaller Li ion interacts more strongly with the oxocarbon anion. This may explain why dissolution was not reported in some Li-ion squarate studies performed under similar conditions [2].

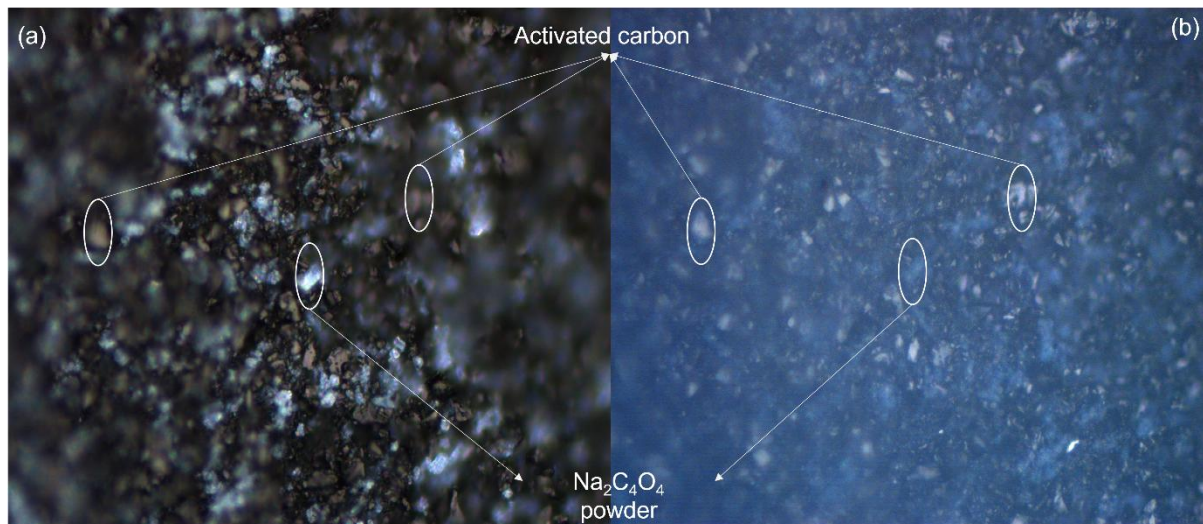


Figure 5: Optical microscopy images of  $Na_2C_4O_4$  before and after electrolyte addition.

#### 2.4.2 UV-visible spectroscopy

As part of the post-mortem investigation of sacrificial salts, and more specifically  $Na_2C_5O_5$ , the detection of neutral  $C_5O_5$  formed in the electrolyte is considered essential to validate the proposed oxidation mechanism. UV-Visible spectroscopy was selected as a promising detection technique. However, no reference UV-Visible spectrum of neutral  $C_5O_5$  has been reported in the literature so far, making it necessary to establish a reliable spectroscopic signature prior to any experimental identification in the electrolyte. Because of the very high cost of the compound (approximately €2600  $g^{-1}$ ) and the complexity associated with the synthesis of the neutral species, which requires highly controlled experimental conditions, theoretical calculations were prioritised in order to minimise material consumption while improving the understanding of its optical properties. These preliminary measurements aim to evaluate the detectability of the expected  $C_5O_5$  signal before moving toward complete experimental validation.

In this context, DFT calculations were performed to simulate the UV-Visible behaviour of different chemical forms of the system. Geometry optimisations and UV-Visible spectra simulations were successfully carried out for  $Na_2C_5O_5$ ,  $C_5O_5^{2-}$ , and neutral  $C_5O_5$  in different solvent environments, including DMC, acetonitrile, and water-containing systems. The corresponding results are presented in Figure 7. These calculations made it possible to evaluate the influence of both the sodium counter-ion and the solvent environment on the peak positions and spectral intensities. The simulated spectra provide a solid theoretical basis for the interpretation of future experimental measurements and for the identification of neutral  $C_5O_5$  in the electrolyte.

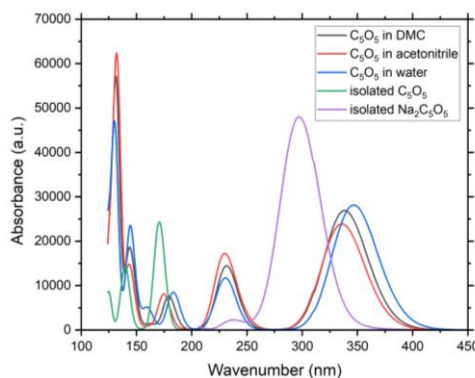


Figure 6: DFT simulation of UV-Visible absorption spectra for  $Na_2C_5O_5$  and  $C_5O_5$  species.

In parallel, the experimental setup is currently being prepared and adapted to enable operando UV-visible measurements directly on the electrochemical cells, as represented in Figure 8. The image shows a UV-visible spectrophotometry cuvette used in an electrochemical setup. Stainless steel components act as electrodes for electrical conductivity measurements. Teflon spacers are positioned both at the bottom and at the top of the cell to ensure proper separation and electrical insulation between the two electrodes. The entire assembly is immersed in the  $\text{NaPF}_6$  EC:PC electrolyte solution, enabling electrochemical processes under controlled optical conditions.

The after-operando sample of AC + sodium croconate was analysed as part of an ongoing optimisation study aimed at identifying the best experimental conditions. The evolution of the solution's colouration, induced during the experiment, was monitored using UV-visible spectroscopy in order to detect and quantify optical changes associated with the electrochemical processes.

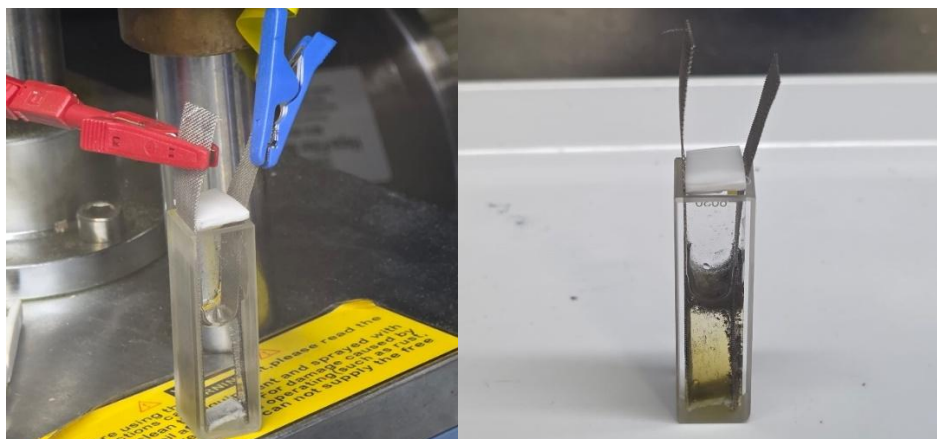


Figure 7: UV-visible spectroscopy cell during (left) and after (right) operando measurements.

## 2.5 BET-surface area on positive electrode

### 2.5.1 BET

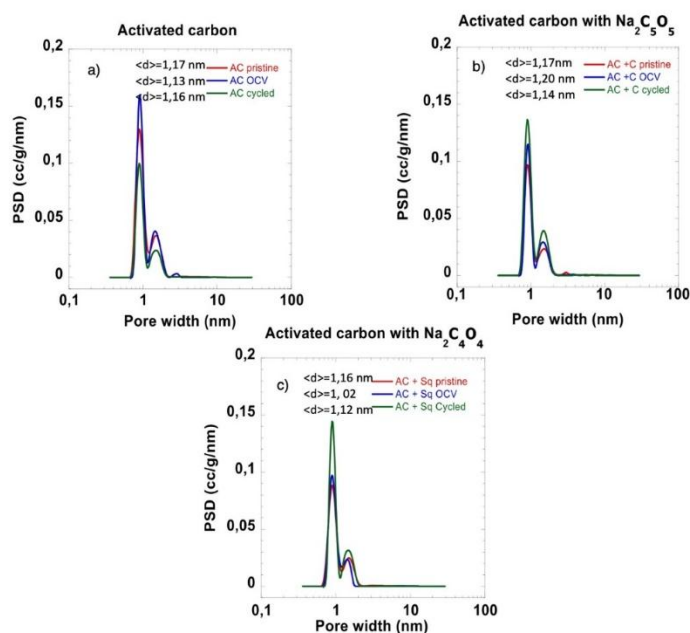


Figure 8: Pore size distribution of a) Activated carbon electrode, b) Activated Carbon +  $\text{Na}_2\text{C}_5\text{O}_5$ , c) Activated Carbon +  $\text{Na}_2\text{C}_4\text{O}_4$

The study investigates the impact of sacrificial salts on electrode properties using Argon physisorption (Micromeritics ASAP 2020). Self-standing electrodes were fabricated from a mixture of activated carbon, either disodium croconate ( $\text{Na}_2\text{C}_5\text{O}_5$ ) or disodium squarate ( $\text{Na}_2\text{C}_4\text{O}_4$ ), and PTFE as a binder, and were compared to electrodes composed solely of activated carbon. The objective was to determine whether the specific surface area of the positive electrode changes upon cycling. Then, for each formulation, there are three kinds of electrode: pristine, exposed to the electrolyte at the OCV for 7 hours and cycled at 0.06 mV/s from 2.0V to 4.2V vs  $\text{Na}^+/\text{Na}$ .

First of all, the pore size distribution plots in Figure 9 (sorted by electrode formulation) show a predominantly microporous distribution, with an average pore diameter of  $\sim 1.2$  nm for pristine AC, AC+C, and AC+Sq. Interestingly, the salt did not alter the pore-size distribution of the electrode, which may support the hypothesis that the sacrificial salts are located at the entrances of the largest pores, thereby blocking access to the smaller pores. This aligns with the assumption that, in the porous network of activated carbon, larger pores feed somehow the smaller ones. The same conclusion applies to the OCV and the cycled electrodes, where no significant change in pore size distribution is observed.

Figure 10 shows that no matter the formulation or the treatment of the electrode, the argon physisorption isotherm type is I(b). This is typical of microporous carbon.

However, the main difference lies in the specific surface area, which is related to the gas quantity adsorbed. The activated carbon pristine electrode manifests a higher specific surface than both the AC+C and the AC+Sq electrodes. This result is expected considering the low specific surface of sacrificial salt itself in comparison with activated carbon (Figure 10 a). Thus, the addition of a sacrificial salt limits access to the total surface area.

The specific surface areas measured after being in contact with the electrolyte are the same as those observed for pristine, except for the AC+Sq electrode. Indeed, the adsorbed quantity drops from  $300\text{cm}^3/\text{g}$  to  $250\text{cm}^3/\text{g}$ . Therefore, although no polarisation was applied, disodium squarate might react with the electrolyte and block a part of the pores (Figure 10 b).

Finally, after the first oxidation, the pristine AC electrode exhibits a lower quantity adsorbed ( $\sim 290\text{cm}^3/\text{g}$ ). The observed behaviour is likely due to electrolyte oxidation blocking part of the pores. In contrast, the activated carbon combined with disodium croconate (AC+C) exhibited the highest adsorbed quantity ( $\sim 410\text{cm}^3/\text{g}$ ), followed by activated carbon combined with disodium squarate (AC+Sq) ( $\sim 350\text{cm}^3/\text{g}$ ). This suggests that the sacrificial salt oxidises before the electrolyte, thereby protecting the electrode during the initial oxidation from electrolyte-induced pore blocking. Interestingly, disodium croconate gives a better specific surface than disodium squarate and, consequently, should give better capacity.

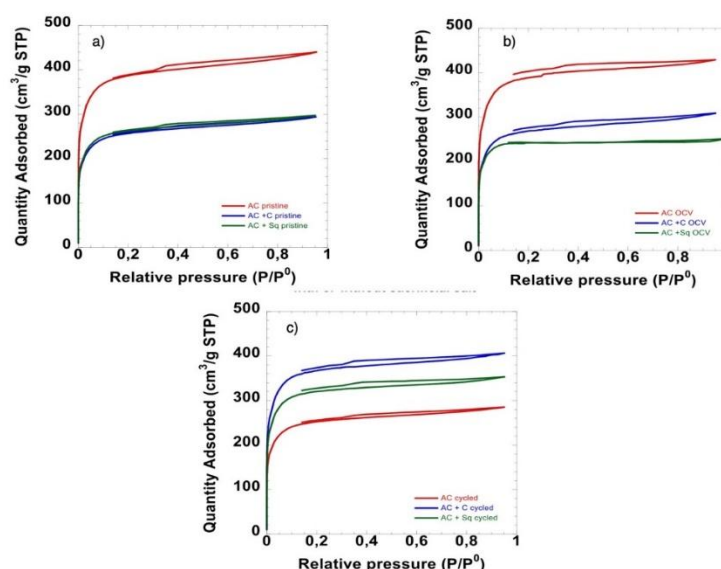


Figure 9: Isotherm physisorption of a) pristine electrodes, b) OCV electrodes, c) cycled electrodes

## 2.6 eDilato for electrode-electrolyte investigations

### 2.6.1 E-dilatometry on activated with sacrificial salt

#### 2.6.1.1 Electrode preparation

The objective was to monitor changes in electrode volume, and thus electrode density, upon cycling in the presence of a sacrificial salt. A significant decrease in electrode density is expected to affect the cycling performance of the positive electrode, leading to reduced specific capacity and impaired electrical conductivity. In a first step, the electrodes were prepared by mixing activated carbon (YP-50F), the sacrificial salt (either disodium croconate ( $\text{Na}_2\text{C}_5\text{O}_5$ ) or disodium squarate ( $\text{Na}_2\text{C}_4\text{O}_4$ ) and conductive carbon (C45) in a PVdF solution of NMP with a final ratio of 60:30:5:5. Then, the slurry was cast on an aluminium foil, dried and finally cut into an  $\varnothing 8\text{mm}$  circle. Then, the electrode previously made will be placed in an E-dilatometry cell as a working electrode. Both the counter and the reference electrode are made from a sodium metal foil. The cell is filled with 400  $\mu\text{L}$  of GEN0 electrolyte (1M  $\text{NaPF}_6$  in EC: PC). Finally, both the dilation signal and the current are recorded during cyclic voltammetry from 2V to 4.2 V vs  $\text{Na}^+/\text{Na}$  with a scan rate of 0.1 mV/s.

#### 2.6.1.2 E-dilatometry as an innovative way to track gas emission

Here, E-dilatometry is used as an innovative means to track both volume change and potential gas emissions from the oxidation of the sacrificial salt. Indeed, a large amount of gas should be detected by moving the sensor as shown in Figure 11. Then, E-dilatometry could detect any volume change in the electrode during and after the first oxidation

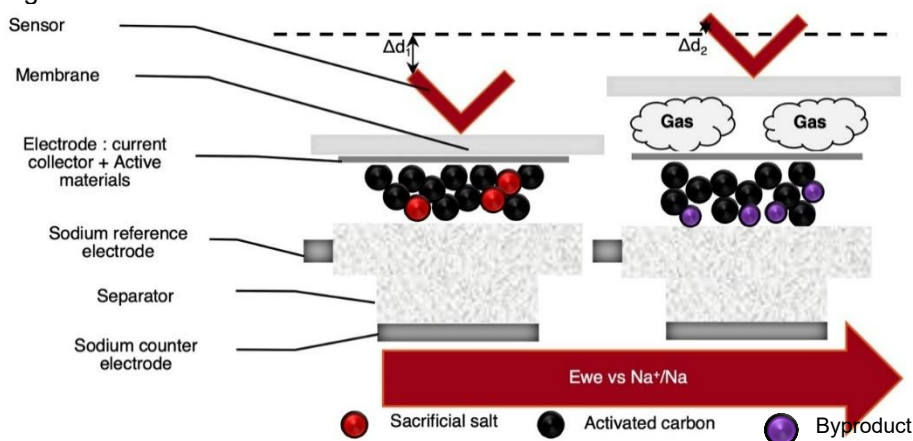


Figure 10: Experimental setup of the e-dilatometer for gas emission

In Figure 12, are presented cyclic voltammetry analysis, coupled with volume change measurements, revealed distinct behaviors between the pristine activated carbon (AC) electrode and the AC electrode with disodium croconate (AC+C) – regarding the activated carbon electrode with disodium squarate (AC+Sq), reliable measurements could not be obtained due to the excessive gas release upon cycling, which saturated the sensor and prevented accurate data acquisition.

The pristine AC electrode exhibited no dilation peak associated with gas production, displaying only volume variations correlated with the electroadsorption of  $\text{PF}_6^-$ . On the other hand, the electrode containing disodium croconate (AC+C) reveals a voltammogram with two redox peaks, respectively at 3.6V and 3.8V vs  $\text{Na}^+/\text{Na}$ , manifesting the salt oxidation reaction. These redox peaks are correlated with a negative volume variation of the electrode, although no gas emission is detected during the first cycle. It leads to the conclusion that the product of disodium croconate oxidation may be solvated in the electrolyte. Eventually, the salt oxidation and the dissolution of the product might affect the structure of the electrode.

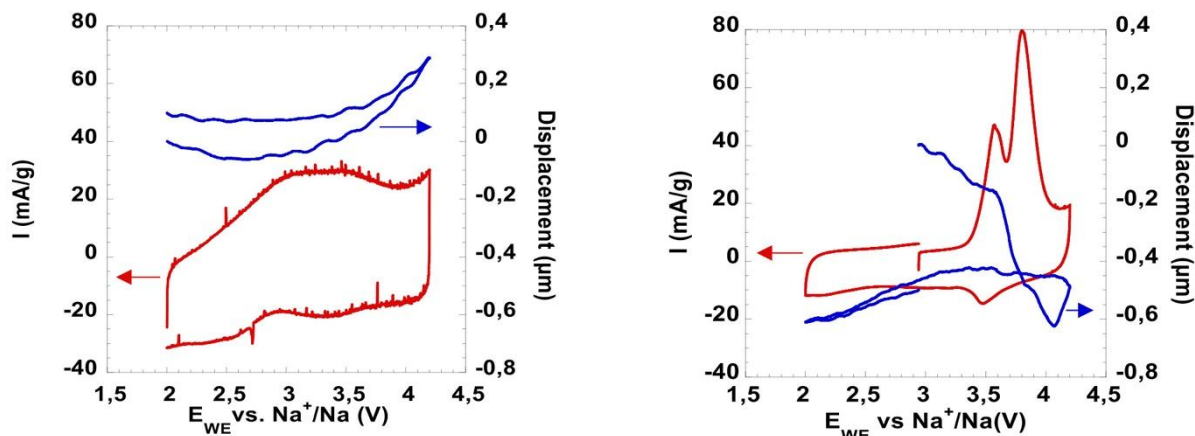


Figure 11: Volume change of AC electrode in 1M NaPF6 in EC: PC (Left) and volume change of AC + Na<sub>2</sub>C<sub>5</sub>O<sub>5</sub> electrode in 1M NaPF6 in EC: PC

However, the next few cycles show an exponential increase in volume, particularly for high potential. Such potentials can lead to the oxidation of the disodium croconate. The last cycle shows some random current peaks typical of gas inside the E-dilatometry cell (Figure 13) — that may be due to a degradation of the electrical contacts. A hypothesis would be the decarbonylation of high-potential cyclopentanepentone (C<sub>5</sub>O<sub>5</sub>) coming from the oxidation of disodium croconate. Nonetheless, it's important to underline the difference in pressure and in electrolyte volume between the E-dilatometer cell and the usual cell (Coincell, SwageLok, ...), which might influence the kinetics of gas formation.

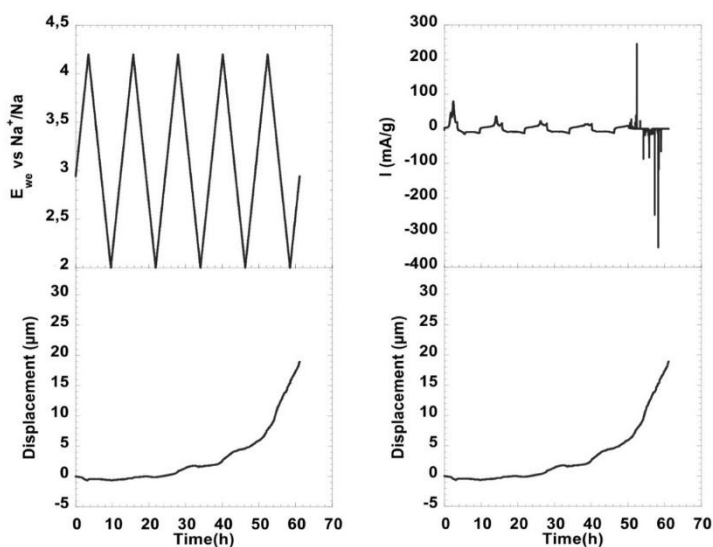


Figure 12: Volume increase over time vs potential (Left) or current (right)

## 2.6.2 Differential Electrochemical Mass Spectrometry (DEMS)

The primary objective of this study was to investigate the gas evolution behaviour of systems based on disodium croconate salt (Na<sub>2</sub>C<sub>5</sub>O<sub>5</sub>) in comparison with disodium squarate salt (Na<sub>2</sub>C<sub>4</sub>O<sub>4</sub>). Differential/On-line Electrochemical Mass Spectrometry (DEMS/OEMS) is an advanced electrochemical characterisation technique that effectively combines electrochemical analysis with mass spectrometry. This method enables the accurate real-time detection and identification of gases evolved during electrochemical processes. By correlating electrochemical signals with the mass-resolved gas evolution, DEMS serves as a powerful operando tool for understanding reaction mechanisms, side reactions and their onset potentials.

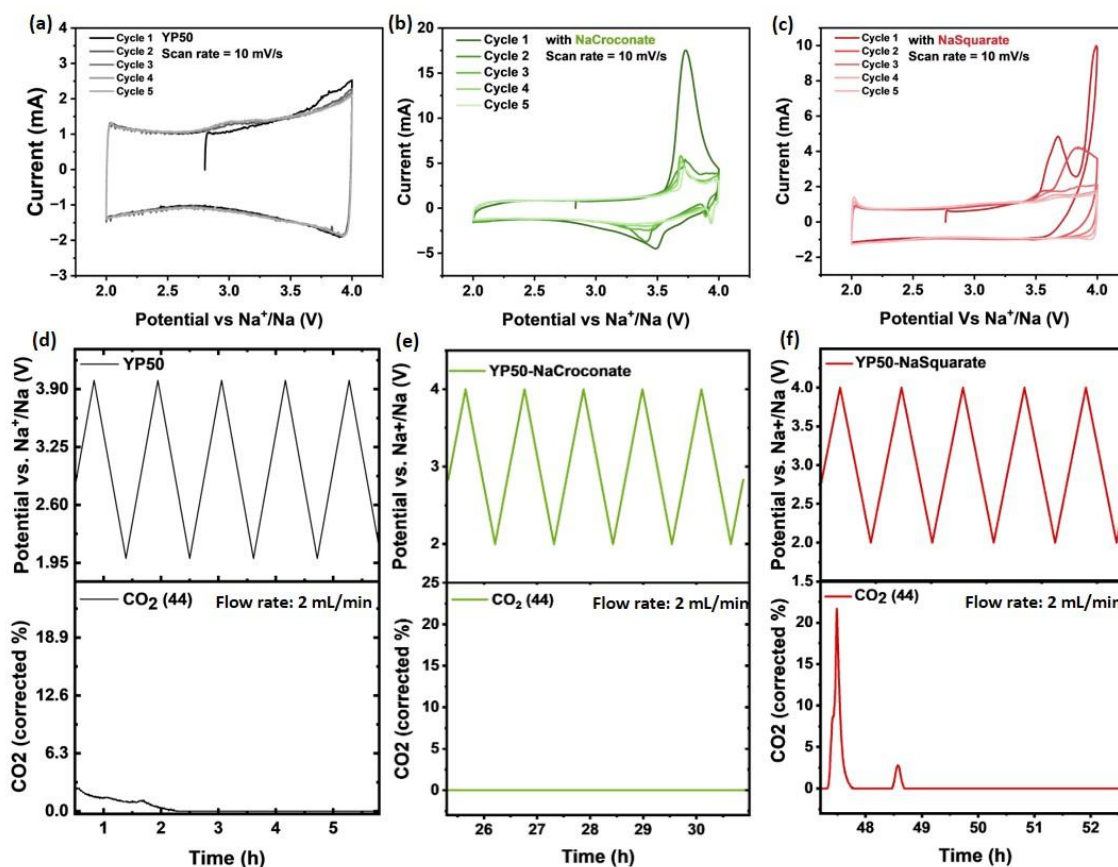


Figure 13: Differential Electrochemical Mass Spectrometry analysis of AC half cells. Cyclic voltammogram of AC half cells with (a) pristine AC electrode, (b) AC with sodium croconate sacrificial salt and (c) AC with sodium squarate sacrificial salt. DEMS spectra showing  $\text{CO}_2$  evolution in AC half cells with (d) pristine AC electrode, (e) AC with sodium croconate sacrificial salt and (f) AC with sodium squarate sacrificial salt during cyclic voltammetry.

To gain insight into the differences in gas evolution behaviour between the two sacrificial salts, disodium croconate and disodium squarate, activated carbon (AC) half-cells (PAT-Cell-Gas) containing the respective sacrificial salts were assembled and compared with a reference AC half-cell containing a pristine AC electrode. The cells were fabricated with freestanding AC electrodes (12 mm diameter, 175 micrometre thickness) as the working electrode, oversized activated carbon as the counter electrode and sodium metal as the reference. 150 microliter of 1 M  $\text{NaPF}_6$  in EC:PC (1:1) was used as the electrolyte. Cyclic voltammetry measurements (from 2 V to 4 V vs.  $\text{Na}^+/\text{Na}$ ) were subsequently performed on these AC half-cells, while  $\text{CO}_2$  evolution was simultaneously analysed using DEMS (Fig. 14a, b, c). The carrier gas used for the experiment was He, and the flow was precisely controlled by a mass flow controller (MFC). Prior to the measurements, the cells were allowed to rest for 24 h to ensure complete wetting of the electrode materials by the electrolyte. Before initiating the electrochemical measurements, the cells were purged with He gas for 15 min. For the AC half cells cycled with pristine AC electrode and AC electrode containing sodium croconate sacrificial salt, no  $\text{CO}_2$  evolution was observed after the background stabilisation. In contrast, for the AC half-cell with an electrode containing sodium squarate sacrificial salt, significant  $\text{CO}_2$  evolution is detected for the first two charge-discharge cycles. This can be correlated to the decomposition of the squarate during the initial charging cycles, which releases a large amount of  $\text{CO}_2$ . This supports the hypothesis that  $\text{CO}_2$  does not evolve in systems where sodium croconate is employed as sacrificial salt, thus preventing high pressure developed inside the electrochemical cell and breakage of the electrodes. This study supports the feasibility of using sodium croconate as a sacrificial salt compared to sodium squarate, which leads to a large amount of gas evolution.

### 2.6.3 XPS analysis

The electrode-electrolyte interaction is governed by SEI formation on the negative electrode. To probe the impact of the presodiation strategy on the SEI chemistry of HC anodes in a novel NaDFOB/GVL electrolyte system, XPS analysis was performed on desodiated electrodes subjected to ex situ electrochemical presodiation and in situ oxidation of the sacrificial  $\text{Na}_2\text{C}_4\text{O}_4$  salt. A pristine HC electrode was included as a chemical reference baseline.

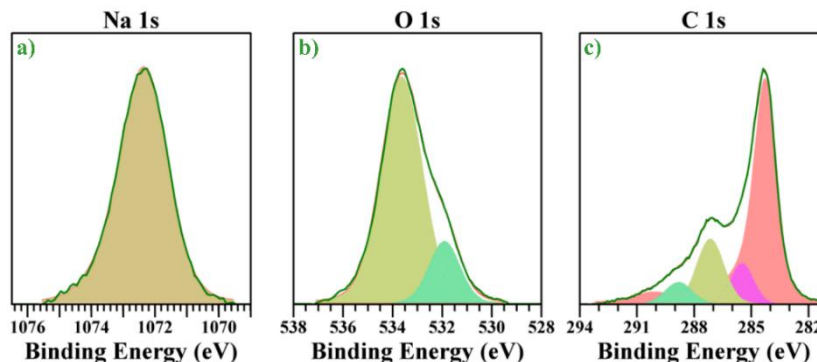


Figure 14: XPS high resolution spectra for the pristine hard carbon electrode.

Figure 15 presents the high-resolution XPS spectra of the pristine hard carbon-based electrode, which serves as a chemical reference for assessing the surface modifications introduced by each presodiation protocol. In the Na 1s region, a single peak at 1072.3 eV is identified and attributed to sodium within the CMC binder. The O 1s region is deconvoluted into two contributions: a peak at 533.6 eV associated with C—O bonds, and a peak at 531.9 eV attributed to C=O bonds. The C=O contribution originates primarily from the CMC binder, while the C—O signal reflects overlapping contributions from both the binder and surface functional groups inherent to the hard carbon. In the C 1s region, the dominant feature is a characteristic asymmetric peak at 284.2 eV, arising from the  $\text{sp}^2$ -hybridized C=C network of the hard carbon structure. Satellite peaks at 285.5, 287.1, and 288.8 eV are assigned to C—O functionalities and C—C bonds at the surface, as well as to C—O and C=O species consistent with those identified in the O 1s region, further confirming the presence of CMC binder residues at the electrode surface.

Having established the chemical fingerprint of the pristine electrode, the influence of the presodiation strategies on the HC electrode surface was systematically investigated. Figure 16 presents the high-resolution XPS spectra of desodiated electrodes subjected to each presodiation protocol: ex situ electrochemical presodiation (Figure 16 a–d) and in situ oxidation of the sacrificial salt (Figure 16 e–h).

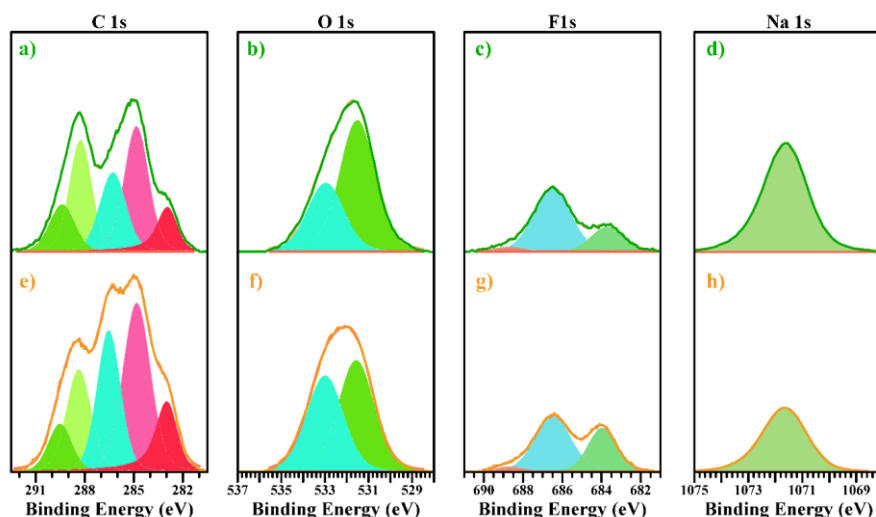


Figure 15: XPS high resolution spectra for desodiated electrodes after presodiation. (a–d) from ex situ electrochemically presodiated electrodes. (e–h) from electrodes presodiated by in situ oxidation of sacrificial salt.

In both electrode types, the Na 1s region exhibits a peak at 1071.6 eV — shifted to lower binding energy relative to the pristine electrode — attributed to the principal organic ( $\text{Na}-\text{C}-\text{O}$ ,  $\text{Na}-\text{C}=\text{O}$ ) and inorganic ( $\text{NaF}$ ) constituents of the SEI layer. In the C 1s region, the asymmetric  $\text{C}=\text{C}$  signal characteristic of the HC bulk appears at 282.9 eV, displaced toward lower binding energies as a consequence of the potential gradient established during SEI formation. A well-defined peak at 284.8 eV is assigned to  $\text{C}-\text{C}/\text{C}-\text{H}$  bonding, while additional features at 286.5, 288.3, and 289.4 eV correspond to  $\text{C}-\text{O}-\text{C}$ ,  $\text{O}-\text{C}=\text{O}$ , and  $-(\text{O}=\text{C})-\text{O}-(\text{C}=\text{O})-$  species, respectively, collectively representing the organic fraction of the SEI. These assignments are corroborated by the O 1s spectra, which exhibit peaks at 532.9 eV ( $\text{O}-\text{C}-\text{O}$ ) and 531.5 eV ( $\text{O}-\text{C}=\text{O}$ ). The F 1s region reveals two distinct contributions: a peak at 686.5 eV linked to NaDFOB decomposition products and surface residues, and a peak at 683.8 eV corresponding to NaF, indicative of inorganic SEI formation.

A comparative analysis of the SEI component ratios across both electrode types reveals notable differences in their surface chemistries. Organic species bearing  $\text{O}-\text{C}=\text{O}$  and  $-(\text{O}=\text{C})-\text{O}-(\text{C}=\text{O})-$  motifs, derived from electrolyte decomposition, are present in comparable quantities regardless of the presodiation route. However,  $\text{C}-\text{O}-\text{C}$  species and  $\text{C}-\text{C}$  bonding contributions are markedly more pronounced in the in situ sodiated electrode, consistent with the effective incorporation of oxidation products from the sacrificial salt and indicative of a structurally more developed SEI. Most strikingly, the NaF signal intensity for in situ sodiation is approximately twice that observed for ex situ sodiation, pointing to a higher degree of inorganic SEI ordering. This enriched inorganic character is likely responsible for the superior capacity retention observed in cells employing the in situ presodiation strategy, reinforcing its viability as a practical and scalable alternative to conventional electrochemical approaches.

### 3. Discussion and Conclusions

Using a comprehensive panel of analytical techniques, the expected reactions of the sacrificial salt candidates, di-sodium squarate and di-sodium croconate, were confirmed experimentally.

Di-sodium squarate leads to significant gas evolution as detected by *operando* microscopy and Raman analysis, differential Electrochemical Mass Spectrometry, and dilatometry. This leads to the swelling of the pouch cells as previously observed. Moreover, it seems that porosity was blocked concomitantly with gas evolution, as suggested by BET surface area measurements. The deposition of carbon from the oxidation of the sacrificial salt might be responsible for this behaviour.

Thanks to these characterisations, the accurate highlighting of these two drawbacks enables their overcoming during the cell fabrication process. However, this will require additional steps in the industrial process, such as outgassing after the first cycle and cell balancing for the loss of capacitance on the positive electrode after the first cycle.

The situation is quite different with the di-sodium croconate: no gas evolution has been detected, and the de-sodiated molecule (Cyclopentanepentone,  $\text{C}_5\text{O}_5$ ) is soluble in the electrolyte without detrimental side reactions (no shuttle effect was detected). Moreover, it seems that the presence of this molecule is beneficial for SEI formation on the negative hard carbon, leading to a more robust layer enriched in inorganic species which in turns is likely responsible for the superior capacity retention of the negative electrode. No additional steps are required to scale up the fabrication process, which will result in a significant gain in cell production from economic, safety, and timescale points of view. However, the higher cost of disodium croconate compared to squarate remains the main challenge to overcome.

## 4. Risk register

No risk has been detected for this deliverable.

| Risk No. | What is the risk | Probability of risk occurrence <sup>1</sup> | Effect of risk <sup>2</sup> | Solutions to overcome the risk |
|----------|------------------|---------------------------------------------|-----------------------------|--------------------------------|
|          |                  |                                             |                             |                                |
|          |                  |                                             |                             |                                |
|          |                  |                                             |                             |                                |

Table 1: Risk Register

## 5. References

[1] Gambe, Y., Kobayashi, H., & Honma, I. (2025). Acetonitrile-based highly concentrated electrolytes for high-power organic sodium-ion batteries. *ACS applied materials & interfaces*, 17(2), 3316-3323.

[2] Arnaiz, M., Shanmukaraj, D., Carriazo, D., Bhattacharjya, D., Villaverde, A., Armand, M., & Ajuria, J. (2020). A low-cost, transversal pre-metallation strategy enabling ultrafast and stable metal-ion capacitor technologies. *Energy & Environmental Science*, 13(8), 2441-2449.

<sup>1</sup> Probability risk will occur: 1 = high, 2 = medium, 3 = low

<sup>2</sup> 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.

| #   | 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 |

Table 2: Project Partners



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