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Graphene, MXene and ionic liquid-based sustainable supercapacitor

GREEN CAP

GREENCAP - Deliverable report

D3.2. – Electrodes for High Energy Density SCs

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Project summary

GREENCAP focuses on developing high-performance, sustainable cylindrical supercapacitors (SCs) that exhibit battery-like energy density, high power densities, and long cycle life, by utilising graphene and MXenes as electrode materials and ionic liquids (ILs) for high-voltage electrolytes. The use of 2D layered materials and ILs will enhance the specific surface area, ion accessibility, and charge storage while ensuring stability and safety across a wide temperature range.
The consortium consists of academic and industrial partners from seven European partners and Ukraine. GREENCAP addresses the energy storage sector, while also meeting the EU's climate-neutrality goals and the Action Plan on Critical Raw Materials (CRMs). GREENCAP will validate this SC

technology at an industrial scale (TRL 6) and develop a management system to optimize SC integration into high-end applications and the circular economy.

Publishable summary

The global transition toward electrification and renewable energy integration demands advanced energy storage technologies that can bridge the gap between high energy density and high power density. While lithium-ion batteries (LIBs) dominate the market due to their high energy content, their limitations in terms of rate capability, cycle life, and safety restrict their suitability for certain applications such as regenerative braking, power backup systems, and rapid charge-discharge energy management. In this context, electrochemical double-layer capacitors (EDLCs), or supercapacitors, have emerged as promising alternatives owing to their superior power density, fast charge-discharge capability, and exceptional cycling stability. However, their widespread adoption remains hindered by a comparatively low energy density, necessitating significant innovations in electrode materials and cell architectures.

Carbon-based materials such as activated carbon, carbon nanotubes, and graphene have been extensively studied as EDLC electrode materials due to their high surface area and electrical conductivity. Among these, curved graphene (CG) and few-layer graphene (FLG) have recently gained attention for their ability to combine accessible surface area with enhanced charge transport properties. Additionally, the development of two-dimensional transition metal carbides and nitrides—collectively known as MXenes—has opened new avenues for pseudocapacitive energy storage due to their metallic conductivity and surface redox activity.

This study, conducted within the framework of the GREENCAP project, aims to advance the performance of supercapacitor electrodes through the development of optimized formulations based on CG, FLG, and $Ti_3C_2T_x$ MXene. The research focuses on increasing active material loading, improving electrode mass balance, and integrating safer and higher-voltage electrolytes to meet the stringent energy density and safety requirements for real-world applications. The work presented here builds upon earlier material development efforts (WP1 and WP2) and serves as a foundation for device-level implementation in WP3 and WP4.

We report the fabrication and evaluation of a series of electrode architectures, including CG/FLG-based composites and MXene films, assessed in both organic and ionic liquid electrolytes. We further explore alternatives to conventional solvents such as acetonitrile (ACN) by introducing non-flammable gamma-valerolactone (GVL) systems. The results offer insights into the interdependence of material composition, electrode structure, and electrolyte compatibility, and demonstrate pathways toward energy-dense, scalable, and safe supercapacitor devices.

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Abbreviations & Definitions

Abbreviation	Explanation
ACN	Acetonitrile
CB	Carbon Black
CG	Curved Graphene
CMC	Carboxymethyl Cellulose
EDLC	Electric Double Layer Capacitor
FLG	Few-Layer Graphene
GVL	γ-Valerolactone
IL	Ionic Liquid
LIB	Lithium-Ion Battery
SBR	Styrene-Butadiene Rubber
SC	Supercapacitor
$TEABF_4$	Tetraethylammonium Tetrafluoroborate
UPS	Uninterruptible Power Supply
WP	Work Package

Item	Definition

1 Introduction

The increasing demand for efficient, sustainable, and high-performance energy storage systems has spurred intensive research into next-generation supercapacitors. These devices offer fast charge-discharge cycles, high power density, long cycle life, and a wide range of operating temperatures, making them attractive for applications in electric vehicles, grid balancing, uninterruptible power supplies (UPS), and portable electronics. However, their comparatively low energy density remains a limiting factor for broader adoption. Addressing this challenge requires the development of novel electrode materials and electrolytes that can simultaneously enhance energy density without compromising power delivery and cycle life.
This report presents comprehensive results from Work Package 3 (WP3) of the GREENCAP project, which focuses on the development and optimization of advanced electrode materials based on curved graphene (CG), few-layer graphene (FLG), and MXene. Building on the materials synthesized in WP1 and WP2, our objective in WP3 is to transition from material-level innovations to scalable electrode technologies suitable for practical device integration. The approach involves tailoring electrode formulations for higher mass loading, replacing traditional conductive additives with more efficient alternatives, and exploring safer and higher-voltage electrolyte systems.
A systematic study was undertaken to evaluate the effects of composition, mass balance, and electrolyte compatibility on electrochemical performance. Particular attention was given to the development of pouch and cylindrical cells that meet the GREENCAP targets for energy density (≥ 20 Wh/kg or ≥ 16 Wh/L) and capacitance (≥ 25 F), while ensuring safety and manufacturability. This report details the methodologies, test results, and key findings that contribute directly to the realization of these ambitious goals.

The following partners contributed in the development and preparation of the deliverable

Development of graphene-based electrodes:

BED, TUD, UNISTRA, FSU, UCAM, SKL, SM, SOLV

Development of MXene based electrodes:

BED, UNISTRA, TCD, TUD

Writing the deliverable

TUD, BED

2 Results & Discussion

2.1 Development of Graphene based electrodes

The overarching objective in electrode development is to realize high-energy-density supercapacitors with superior rate performance. To achieve this, efforts have been directed towards the development of novel graphene-based electrodes and optimizing their mass balance, ensuring that the materials developed in WP1 and WP2 contribute to the fabrication of high-performance pouch cells in WP3 and cylindrical cells in WP4.
In Task 3.1, the focus was on the optimization of the slurry formulation as a function of the electrode sheet resistance, while concurrently maximizing the active material mass loading and, consequently, the specific capacitance. This aim has been pursued by replacing carbon black as a conductive additive with few-layer graphene (FLG), which has a higher conductivity than the former. Consequently, it enabled to reduce the total amount of FLG and to increase the load of curved graphene (CG), used as the active material, whilst maintaining low value of sheet resistance (high electrical conductivity). Moreover, owing to the high intrinsic conductivity of curved graphene (CG) (refer to Periodic Report 1), slurry formulations were also developed without any conductive additives.
Initial electrode formulations were prepared using CG content at 85% and 95% (Table 1). Electrochemical performance was evaluated via floating tests using both an organic electrolyte (1 M $TEABF_4$ in ACN) and an ionic liquid electrolyte developed in WP1 (1 M N1113FSI in ACN).

Table 1. *The initial composition of the developed electrodes*

Entry	Composition	Electrolyte	Mass loading (mg cm^{-2})
1	CG: FLG:CMC/SBR (85:10:10)	1 M $TEABF_4$ in ACN	~ 1
2	CG: FLG:CMC/SBR (85:10:5)	1 M $TEABF_4$ in ACN	~ 1
3	CG: FLG:CMC/SBR (95:0:5)	1 M $N_{1113}FSI$/ACN	~ 1

- ***Electrode mass balance***

Using organic electrolytes, we observed that the stable voltage window can be extended from 2.4 V to 2.7–3.0 V through careful mass balancing between positive and negative electrodes. Specifically, increasing the mass of the positive electrode (m^+) relative to the total electrode mass ($m^- + m^+$) improved both floating and cycling stability. An optimal mass ratio of $m^+/(m^- + m^+) \approx 0.7$ was identified (**Figures 1a & 1b**).

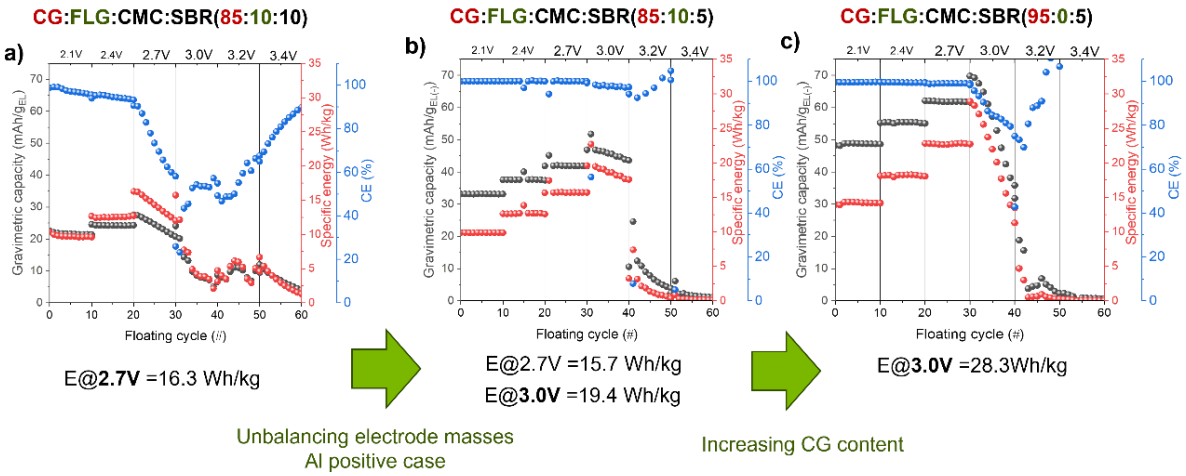

Figure 1. *Floating test for CG based electrodes using 1 M $TEABF_4$ in ACN. The performances were recorded at 1 A/g*

- ***Increase the active material and using ILs***

Additionally, increasing CG content while reducing/removing FLG led to enhanced energy density, achieving up to 28.3 Wh/kg with 1 M $TEABF_4$ in ACN and 33.2 Wh/kg with the IL-based electrolyte (**Figure 1c & Figure 2**).

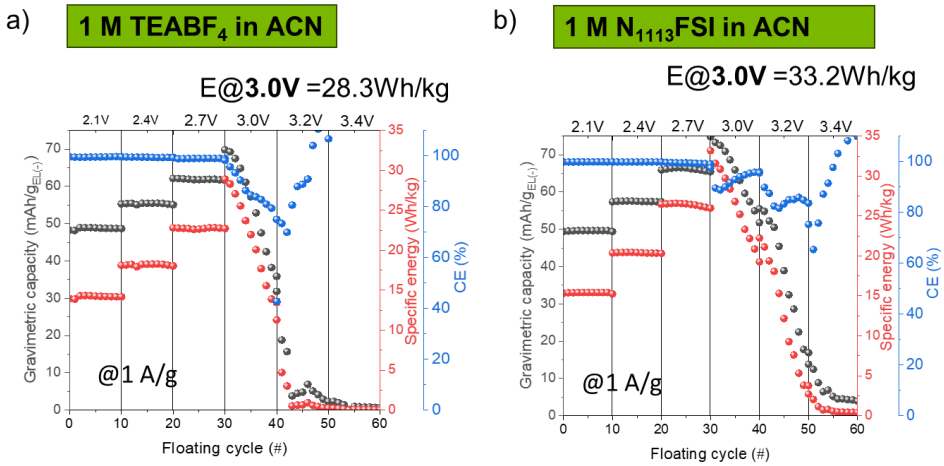

Figure 2*. Floating test for CG based electrodes using* ***a)*** *1 M $TEABF_4$ in ACN and* ***b)*** *1 M $N_{1113}FSI$ in ACN as the electrolytes. The performances were recorded at 1 A/g.*

- ***Towards High-Voltage and Safer Electrolytes***

Alternative solvents to ACN were explored for the formulation of non-flammable electrolytes, with gamma-valerolactone (GVL) showing promising stability at high voltage. When paired with 1 M $TEABF_4$, GVL enabled devices to operate at up to 3.0 V with favorable floating stability (**Figure 3**).

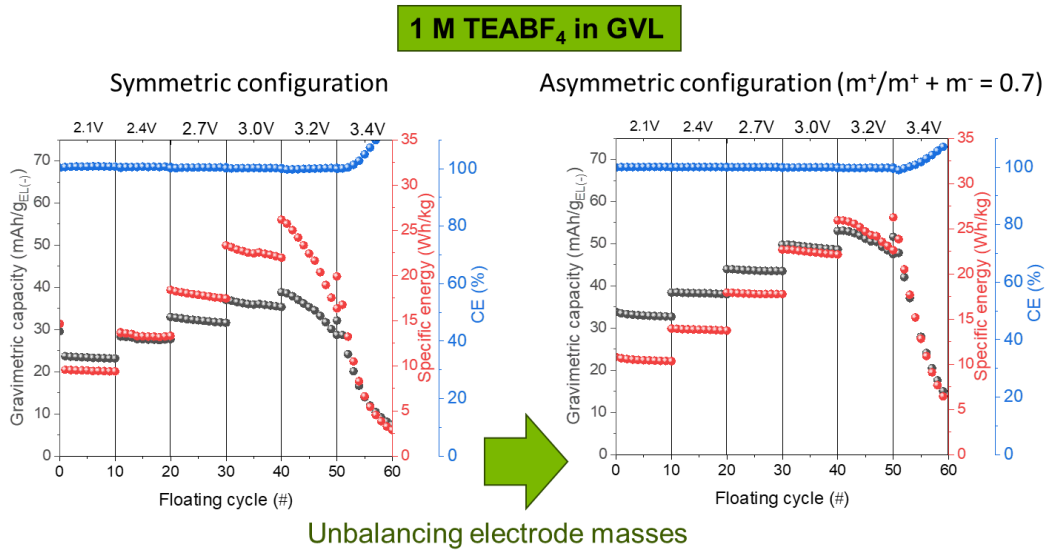

***Figure 3**. Floating test for EDLCs based on CG/CMC:SBR electrodes in coin cells using 1 M $TEABF_4$ in GVL as the electrolytes, showing the comparison between symmetric and asymmetric configurations. The performances were recorded at 1 A/g.*

Comparable performance was obtained with 1 M N1113FSI, although ACN-based devices still outperformed GVL overall (**Figure 4**). Nevertheless, the high coulombic efficiency of GVL-based systems highlights their potential for safer, high-voltage SCs.

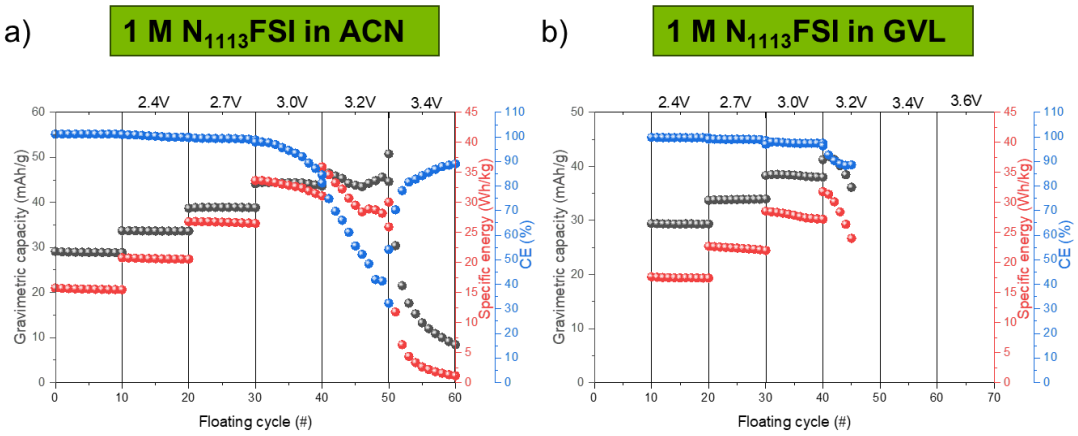

***Figure 4**. Floating tests for EDLCs based on CG/CMC:SBR electrodes in Swagelok cells using **a)** 1 M $N_{1113}FSI$ in ACN and **b)** 1 M $N_{1113}FSI$ in GVL as the electrolytes. The performances were recorded at 1 A/g.*

- ***Electrodes with Increased Mass Loading***

To further enhance performance, mass loading was increased by optimizing CG content and repeating the coating process (**Table 2**).

Table 2. The electrode compositions with high mass loading

Acronym	Composition	Electrolyte	Mass loading (mg cm^{-2})
G0	CG: FLG:CMC/SBR (90:5:5)	1 M $N_{1113}FSI$/ACN	3.66
G1	CG: FLG:CMC/SBR (94:2:4)	1 M $N_{1113}FSI$/ACN	4.72
G2	CG: FLG:CMC/SBR (95:0:5)	1 M $N_{1113}FSI$/ACN	8.25

The G2 electrode (95% CG, no FLG) achieved a mass loading of 8.25 mg/cm². However, performance at both high and low current densities declined, likely due to reduced ionic conductivity. Thus, FLG-containing formulations were prioritized.

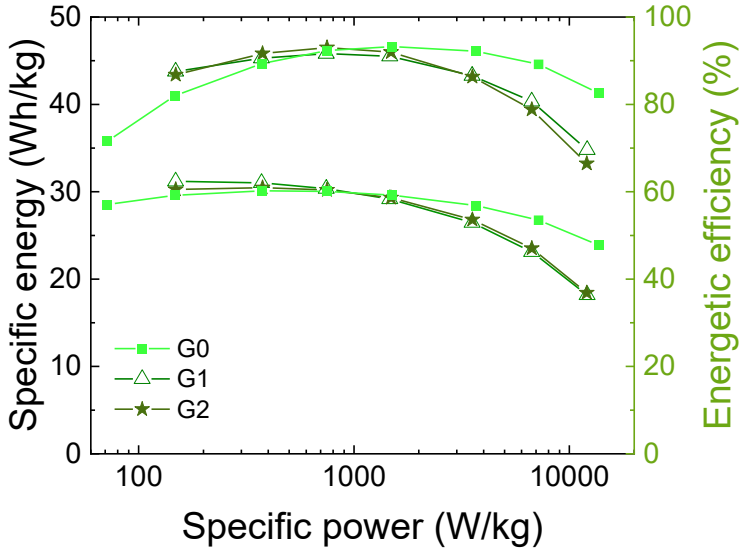

Figure 5. *The electrochemical performance of curved graphene/few-layer graphene electrodes in N1113FSI in ACN electrolyte at 3V by varying the mass loading.*

Detailed electrochemical evaluations (**Figures 5 & 6**) revealed that increasing mass loading from 3.66 to 4.72 mg/cm² improved specific capacitance from 95.6 F/g (71.7 F/cm³) to 100.7 F/g (75.5 F/cm³) at 0.2 A/g. These electrodes demonstrated excellent coulombic efficiency and rate capability and were subsequently used in WP3 pouch cell prototypes.

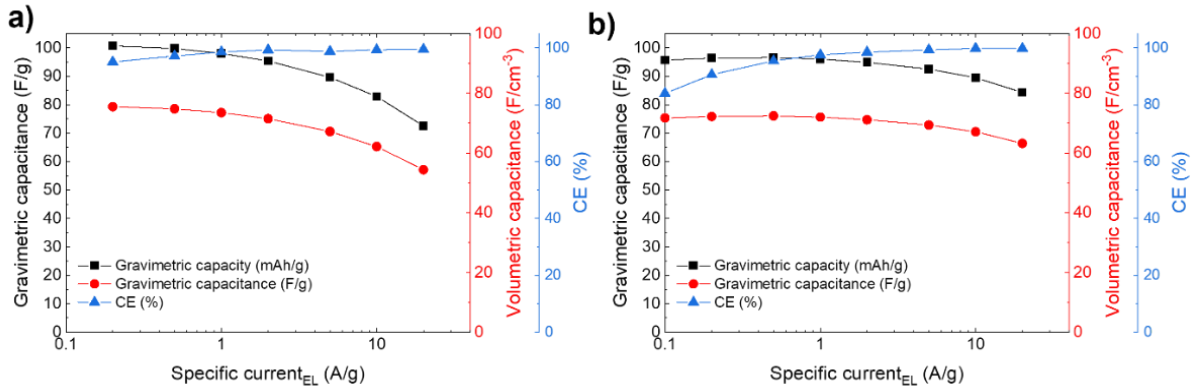

Figure 6. *The electrochemical performance of curved graphene/few-layer graphene electrodes in N_{1113}FSI in ACN electrolyte.*

2.2 Development of Mxene based electrodes

MXene electrode research explored two strategies: free-standing films and traditional slurry formulations, primarily for use in aqueous electrolytes.

- **Free-Standing MXene Film Electrodes**

Electrochemical evaluation of pristine $Ti_3C_2T_x$ MXene films in 3 M H_2SO_4 revealed a specific capacitance of 359.3 F/g and a volumetric capacitance of 194 F/cm³ at 20 mV/s. Capacitance decreased at higher scan rates, consistent with ion diffusion limitations (**Figure 7**).

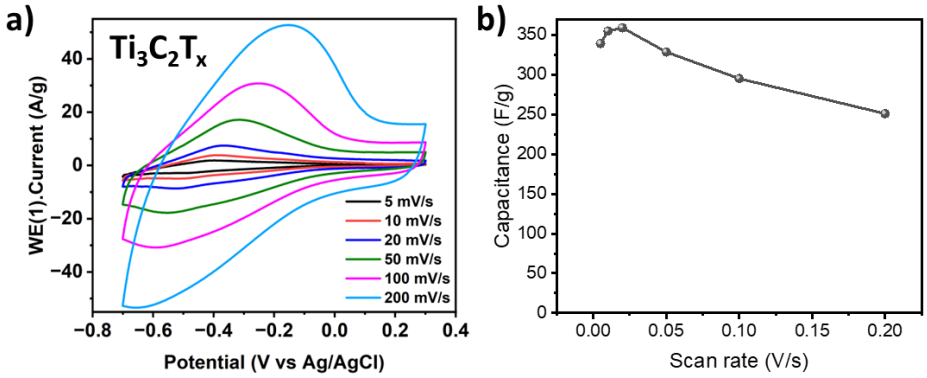

***Figure 7. a)** CV curves and **b)** specific capacitance of $Ti_3C_2T_x$ at different scan rates*

- **Slurry-Coated MXene Electrodes**

To align with industrial practice and facilitate technology transfer, slurry formulations comprising MXene:CB:CMC/SBR (80:10:10) were developed. Electrodes with a mass loading of 3.5 mg/cm² demonstrated ~300 F/g specific capacitance and robust rate performance (**Figure 8**). These are currently being scaled up for pouch cell development in upcoming reports.

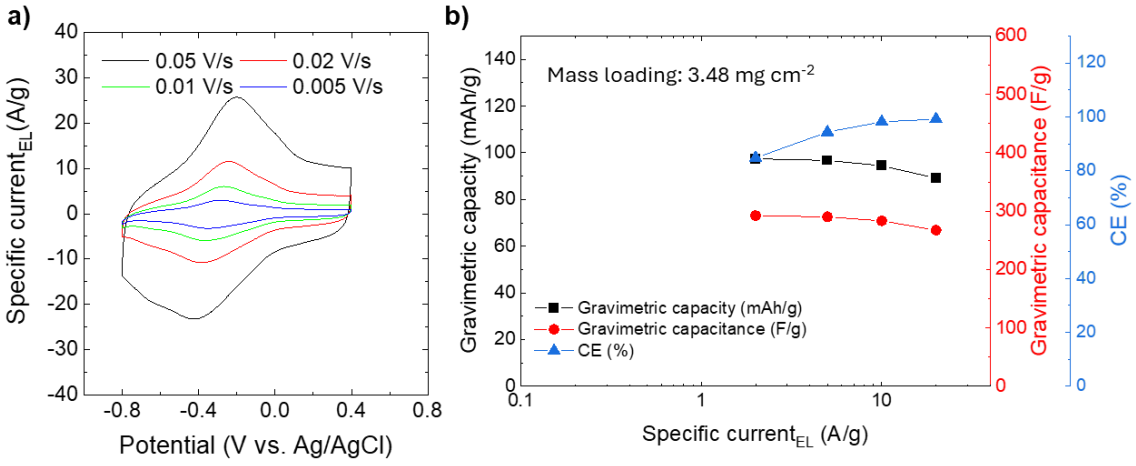

***Figure 8.** a) CV curves and b) specific capacitance of $Ti_3C_2T_x$ at different scan rates*

Based on this method, we are currently developing pouch cell prototypes and the results will be followed by the next reports.

2.3 Contribution to project (linked) Objectives

This deliverable directly supports the GREENCAP project goals, particularly WP3, by advancing the development of high gravimetric and volumetric capacitance electrodes. These achievements pave the way for 25 F pouch cells with energy densities exceeding 20 Wh/kg or 16 Wh/L.

2.4 Contribution to major project exploitable result

The insights and materials developed herein will also contribute to WP4 by facilitating the fabrication of cylindrical supercapacitors with strong commercial potential across diverse sectors, including stationary energy storage, data backup systems, and uninterruptible power supplies (UPS).

3 Conclusions and Recommendations

The work carried out in WP3 has yielded substantial progress toward the development of next-generation supercapacitor electrodes based on both graphene and MXene materials. Our investigations demonstrate that replacing traditional conductive additives with FLG—while optimizing the curved graphene content—can lead to electrode architectures with improved electronic conductivity, mechanical integrity, and electrochemical stability. Mass balancing strategies were shown to be critical for achieving wider voltage windows and improved floating and cycling performance, particularly when using organic and ionic liquid-based electrolytes.

Importantly, the incorporation of high-performance electrolytes, including the safer and non-flammable gamma-valerolactone (GVL), illustrates the feasibility of formulating supercapacitor systems with higher operating voltages (up to 3.0 V) without sacrificing stability. Although ACN-based systems still outperform GVL in terms of overall capacitance, the latter's safety profile makes it a promising candidate for commercial applications requiring enhanced thermal and electrochemical robustness.

Parallel development of MXene-based electrodes—using both free-standing films and industry-compatible slurry-cast methods—further broadened the scope of material solutions. These electrodes exhibited outstanding specific capacitance, particularly in acidic aqueous electrolytes, and showed good rate performance, reinforcing their potential for compact and high-power storage applications.

Taken together, the results reported herein represent a critical milestone in the GREENCAP project. They provide a strong foundation for the subsequent development of high-performance pouch cells (WP3) and cylindrical cells (WP4), with direct implications for the project's ultimate exploitation goals. Beyond academic value, the strategies and technologies demonstrated offer a clear pathway toward scalable, safe, and energy-dense supercapacitor systems suitable for a wide range of industrial applications.

4 Risks and interconnections

4.1 Risks/problems encountered

N/A

4.2 Interconnections with other deliverables

5 Deviations from Annex 1

N/A

6 References

7 Acknowledgements

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2	SOLV	SOLVIONIC
3	FSU	FRIEDRICH-SCHILLER-UNIVERSITAT JENA
4	SKL	SKELETON TECHNOLOGIES OU
5	TCD	THE PROVOST, FELLOWS, FOUNDATION SCHOLARS & THE OTHER MEMBERS OF BOARD, OF THE COLLEGE OF THE HOLY & UNDIVIDED TRINITY OF QUEEN ELIZABETH NEAR DUBLIN
6	TUD	TECHNISCHE UNIVERSITAET DRESDEN
7	UNISTRA	UNIVERSITE DE STRASBOURG
8	SM	SKELETON MATERIALS GMBH
9	UNR	UNIRESEARCH BV
10	CNR	CONSIGLIO NAZIONALE DELLE RICERCHE
11	UCAM	THE CHANCELLOR MASTERS AND SCHOLARS OF THE UNIVERSITY OF CAMBRIDGE
12	CU	Y CARBON LLC

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8 Appendix A - Quality Assurance Review Form

The following questions should be answered by all reviewers (WP Leader, reviewer, Project Coordinator) as part of the Quality Assurance procedure. Questions answered with NO should be motivated. The deliverable author will update the draft based on the comments. When all reviewers have answered all questions with YES, only then can the Deliverable be submitted to the EC.NOTE: This Quality Assurance form will be removed from Deliverables with dissemination level “Public” before publication.