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Graphene, MXene and ionic liquid-based sustainable supercapacitor

GREENCAP - Deliverable report

D1.2 – Novel CRM-free EMs and IL-based electrolytes for SCs (Publishable summary)

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Project overview

The GREENCAP project, funded under the Horizon Europe Programme, focuses on developing high-performance, sustainable supercapacitors (SCs) using advanced materials and green chemistry. The primary goals of the project include designing supercapacitors with improved performance and sustainability, developing prototypes for industrial-scale production, and utilizing Layered Two-Dimensional Materials (L2DMs) such as graphene and MXenes. The project also aims to integrate Ionic Liquids (ILs) due to their favorable electrochemical properties and environmental benefits.

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Abbreviations & Definitions

Abbreviation	Explanation
2D	2 Dimensional
CRM	Critical Raw Material
SLG	Single layer graphene
FLG	Few layers graphene
FSI	Bis(fluorosulfonyl)imide
IL	Ionic Liquids
L2DM	Layered 2D material
EM	Electrode Material
SC	Supercapacitor
TFO	Triflate
TFSI	bis(trifluoromethanesulfonyl)imide
CG	curved graphene
WJM	wet-jet milling
AC	activated carbon
HPH	High-Pressure Homogenisation
CFD	Computational Fluid Dynamics
FFBR	Frit Fluidized Bed Reactor

1 Introduction

The deliverable D1.2 outlines the efforts in creating novel Critical Raw Material (CRM)-free Electrode Materials (Ems) and IL-based electrolytes for SCs. The objectives of the project emphasize scalable production methods for electrode materials and electrolytes, prioritizing the elimination of CRMs, implementing low-environmental-footprint processes, and establishing comprehensive characterization and quality control protocols.

Key achievements include:

- **Production of Few-Layer Graphene (FLG)**: The project successfully replaced harmful solvents like N-Methyl-2-pyrrolidone (NMP) with sustainable water-based media for the production of FLG, improving its synthesis sustainability.

- **Electrochemical Exfoliation of Synthetic Graphite**: A novel method for the electrochemical exfoliation of synthetic graphite has been developed. This method utilizes dilute aqueous inorganic salt solutions and electric potential to induce delamination of graphite layers, leading to the production of graphene flakes.

- **Synthesis of CRM-Free MXenes**: Various CRM-free MXenes have been synthesized using mild etching and molten salt methods. This development minimizes reliance on critical raw materials and enhances the potential for sustainable, high-performance Ems.

- **Formulation of Ionic Liquids (ILs)**: The project has developed a range of aprotic ILs aimed at enhancing energy storage capacity and electrochemical performance of SCs. Protonated ILs were also synthesized specifically for use with MXene-based electrodes to improve performance.

- **Upscaling of Electrolyte Production**: One particular IL, 1 M N1113 FSI in ACN, is currently being upscaled to the kilogram scale for use in the first prototypes of supercapacitors.

2 Methods and core part of the report

The deliverable details various methods employed for the synthesis and production of electrode materials and electrolytes. This includes:

- **Wet-Jet Milling**: A process used for producing FLG by exfoliating graphite in water, refined to optimize yield and sustainability.

- **Electrochemical Exfoliation**: A technique involving the intercalation of ions between graphite layers to produce high-quality graphene, with significant yield improvements noted in the use of synthetic graphite foil.

- **MXene Synthesis**: The synthesis processes for MXenes involved mild etching with HCl and LiF, as well as molten salt methods, providing various MXenes with potential for high-performance applications.

- **Ionic Liquid Production**: Two-step processes for producing aprotic and protonated ILs were established, ensuring high purity and quality for use in SCs.

3 Results

The deliverable highlights the successful outcomes of the project in several key areas:

- **FLG Production**: The new water-based method has shown significant improvements in yield, while reducing the environmental impact associated with traditional methods.

- **Synthetic Graphite Exfoliation**: The innovative electrochemical methods have resulted in high-quality graphene with yields exceeding 80% for synthetic graphite foil, demonstrating the method's scalability.

- **MXene Developments**: The synthesis of new MXenes has expanded the material selection available for SC applications, with successful production of multiple types confirmed through characterization methods. Seven types of MAX phases were used: Ti_2AlC, Ti_3AlC_2, Ti_3AlCN, Mo_2Ga_2C, Mo_2GaC, $(Mo_{2/3}Y_{1/3})_2AlC$, $Mo_2Ti_2AlC_3$
  We have been successful in producing Ti3C2Tx, Mo2CTx, and Ti3CNTx via the mild etching method. Molten salt synthesis of selected MXenes has also been successful. So far, Ti3C2Tx, Ti2CTx, Ti3C2Tx, Mo2CTx, Mo1.33CTx, and Mo2Ti2C3Tx have been produced using molten salt etching procedures. Two combinations of salts have been used: CuCl2, KCl, and NaCl, which produces Cl terminated MXenes, and CuBr2, KBr, and NaBr, which produces Br terminated MXenes.

- **Electrolyte Innovations**: The formulations of ILs have demonstrated promising electrochemical performance, with specific ILs showing potential for enhancing SC performance metrics such as energy density and cycle stability.

3.1 Contribution to project (linked) Objectives

This deliverable significantly contributes to GREENCAP's objectives by advancing the development of scalable, CRM-free materials for SCs. The report outlines progress towards creating high-performance energy storage devices that adhere to sustainable manufacturing standards.

1. **Electrode Materials**: The successful optimization and synthesis of CRM-free Ems, including FLG and MXenes, represent a major step towards sustainable production.

2. **Electrolyte Development**: The creation of high-performing ILs tailored for use with advanced electrode materials contributes directly to improving SC performance, addressing both energy density and stability.

3. **Manufacturing Processes**: The report details the development of new, scalable production processes, paving the way for industrial applications and large-scale manufacturing of supercapacitors.

- **Electrolyte Innovations**: The formulations of ILs have demonstrated promising electrochemical performance, with specific ILs showing potential for enhancing SC performance metrics such as energy density and cycle stability.

4 Conclusion and Recommendation

The deliverable D1.2 encapsulates significant advancements in the GREENCAP project, focusing on the production of sustainable, high-performance materials for supercapacitors. The innovative methodologies and materials developed provide a strong foundation for future commercialization and scientific exploration in the field of energy storage. The outcomes not only align with the project's goals but also offer insights into the potential impact of sustainable practices in energy storage technologies.

5 Deviations from Annex 1

No deviations to report

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:

#	Partner short name	Partner Full Name
1	BED	BEDIMENSIONAL SPA
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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7 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.

Question	WP Leader	Reviewer	Project Coordinator
	Prof. Valeria Nicolosi (TCD)	Boyang Mao (UCAM)	Francesco Bonaccorso (BeD)
1. *Do you accept this Deliverable as it is?*	Yes	Yes	Yes
2. *Is the Deliverable complete?* - *All required chapters?* - *Use of relevant templates?*	Yes	Yes	Yes
3. *Does the Deliverable correspond to the DoA?* - *All relevant actions preformed and reported?*	Yes	Yes	Yes
4. *Is the Deliverable in line with the GREENCAP objectives?* - *WP objectives* - *Task Objectives*	Yes	Yes	Yes
5. *Is the technical quality sufficient?* - *Inputs and assumptions correct/clear?* - *Data, calculations, and motivations correct/clear?* - *Outputs and conclusions correct/clear?*	Yes	Yes	Yes
6. *Is created and potential IP identified and are protection measures in place?*	Yes	Yes	Yes
7. *Is the Risk Procedure followed and reported?*	Yes	Yes	Yes
8. *Is the reporting quality sufficient?* - *Clear language* - *Clear argumentation* - *Consistency* - *Structure*	Yes	Yes	Yes