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Graphene, MXene and ionic liquid-based sustainable supercapacitor



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D1.1 – Quality control for CRM-free SC materials



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Summary

This deliverable describes the protocols developed in WP1 for the quality assessment of all the supercapacitor (SC) materials, including electrode materials and ionic liquids (ILs), defining specifications and quality control (QC) procedures to ensure the material uniformity required for their subsequent functionalization/hybridization processes (WP2) and application in SC manufacturing (WP3 and WP4). When needed, these protocols will be updated throughout the project lifetime and will provide the basic information to define material certification strategies pursued in WP4 (Task 4.1).

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Abbreviations & Definitions

Abbreviation	Explanation
2D	Two-dimensional
AFM	Atomic force microscopy
BET	Brunauer-Emmett-Teller
CRM	Critical Raw Material
DOI	Digital Object Identifier
EDX	Energy-dispersive X-ray spectroscopy
EM	Electrode material
FLG	Few-layer graphene
FWHM	Full width at half maximum
GA	Grant Agreement
HPH	High-pressure homogenization
IC	Ion chromatography
IL	Ionic liquid
KF	Karl Fischer
L2DM	Layered 2D material
MIC	Material Identifier Code
MTA	Material Transfer Agreement
NMP	N-Methyl-2-pyrrolidone
PET	Polyethylene terephthalate
QC	Quality Control
SC	Supercapacitor
SEM	Scanning electron microscopy
SLG	Single-layer graphene
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
WJM	Wet-jet milling
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

1 Introduction

This document contains the guidelines for the Quality Control (QC) units of the work package (WP) 1 partners to characterise the supercapacitor (SC) materials used during the execution of the project. In particular, graphene and other layered two-dimensional (2D) materials (L2DM), used for the design of high-capacity electrode materials, and ionic-liquids (ILs), used for the formulation of high-voltage electrolytes. The document describes the protocols developed in WP1 for the QC assessment of all the SC materials, defining specifications and quality control procedures to ensure the material uniformity required for the development of the work to be carried out in the other WPs. These include functionalization/hybridization processes (WP2) and application in SC manufacturing (WP3 and WP4). These protocols will represent, by defining the set of actions for analysts to follow to guarantee homogeneous measurement criteria of quality, the basic information to pursue material certification targeted in WP4 (Task 4.1). Section 2 of this document provides the methods for the characterisation of graphene and other L2DM, indications on how to register, prepare and characterize the samples, and the basic tools to analyse the data. Section 3 is dedicated to the procedures used to characterize IL-based electrolytes, ensuring SC quality grade.

2 Graphene and other L2DMs

2.1 Normative reference

The QC procedures developed in WP1 for graphene are based on the ISO/TS 21356-1:2021 Nanotechnologies — Structural characterisation of graphene. The ISO standard indicates the process for the characterisation of the material following long-time investing methods to analyse small batches. However, the partners recognised that the ISO protocols can be readapted to fulfil a prompt characterization of material batches produced through innovative process at laboratory scale, as well as to meet production needs in terms of prompt deliveries at industrial level. The QC protocols reported hereafter uses the nomenclature attained in the ISO/TS 80004-13:2017 Nanotechnologies — Vocabulary — Part 13: Graphene and related two-dimensional (2D) materials. For other L2DMs, *e.g.*, MXenes, specific standards have not been defined yet. Starting from protocols reported for graphene, characterization guidelines reported here are also applied to other L2DMs beyond graphene, considering their structural and chemical characteristics.

2.2 Terms and definition

For this document, the terms and definitions given in ISO/TS 80004-1:2015, ISO/TS 80004-2:2015, ISO/TS 80004-6:2021, ISO/TS 80004-13:2017, and ISO/TS 21356-1:2021 will be applied. Those are briefly listed below.

Two-dimensional material: material consisting of one or several layers with the atoms in each layer covalently bonded to neighbouring atoms in the same layer, which has one dimension, its thickness, in the nanoscale or smaller and the other two dimensions generally at larger scales.

Note 1 to entry: the number of layers when a 2D material becomes a bulk material varies depending on the material being measured and its properties.

Note 2 to entry: interlayer bonding is distinct from and weaker than intralayer bonding.

Note 3 to entry: each layer may contain more than one element.

Layer: discrete material is restricted in one dimension, within or at the surface of a condensed phase.

Aggregate: a particle comprising bonded or fused particles where the resulting external surface area is significantly smaller than the sum of surface areas of the individual components.

Note 1 to entry: the forces holding an aggregate together are strong forces, for example, covalent or ionic bonds or those resulting from sintering, complex physical entanglement, or otherwise combined former primary particles.

Note 2 to entry: aggregates are also termed secondary particles, and the source particles are termed primary particles.

Graphene layer, single-layer graphene (SLG), monolayer graphene: a single layer of carbon atoms with each atom bound to three neighbours in a honeycomb structure.

Graphite: the element carbon's allotropic form consists of graphene layers stacked parallel to each other in a three-dimensional (3D), crystalline, long-range order.

Bilayer graphene: 2D material consisting of two well-defined stacked graphene layers.

Few-layer graphene (FLG): 2D material consisting of three to ten well-defined stacked graphene layers.

Lateral size, flake size: Lateral dimensions of a 2D material flake.

Note 1 to entry: If the flake is approximately circular, this is typically measured using an equivalent circular diameter or, if not, *via* x, y measurements along and perpendicular to the longest side.

2.3 Quality control of CRM-free precursor materials

To produce graphene through CRM-free top-down approaches (*e.g.*, wet-jet milling -WJM-, high-pressure homogenization -HPH- and electrochemical exfoliation), natural graphite commonly used as the graphene precursor must be replaced by synthetic graphite. Synthetic graphite is typically produced by heating petroleum coke to high temperatures, at which gradually transforms into crystalline graphite. However, coke transforms into graphitic microstructure and the graphitization may not be complete. Thus, the synthetic graphite may still exhibit crystalline disorder. The quality of the synthetic graphite is usually measured using a parameter commonly known as the degree of graphitization. The degree of graphitization is a measure of how similar the synthetic graphite is compared to natural/pristine graphite. As the disordered carbon graphitizes, the *d*-spacing gradually decreases towards the crystalline graphite *d*-spacing. By measuring the d_{002} interplanar spacing of the synthetic graphite, the degree of graphitization (*g*) can be estimated by the equation:[1]

$$g(\%) = \frac{0.3440 - d_{002}}{0.3440 - 0.3354}$$

In GREENCAP, each batch of graphite sources is characterized by QC units of the partners by means of X-ray diffraction (XRD) to measure the *g*(%), as it can directly measure the interplanar *d*-spacings to ensure the reproducibility of structural properties of the exfoliated materials. In addition, crystallite size has an influence on the diffraction intensity. More in detail, the full width at half maximums (FWHMs) of diffraction peaks increases with decreasing crystallite size.[1] Overall, the analysis of *g*(%) and FWHM of the (002) peak for graphite sources are QC procedures used to ensure that the quality of starting graphite does not vary from batch to batch (**Figure 2-1**), which, in turn, ensure the reproducibility of the characteristics of the exfoliated samples.

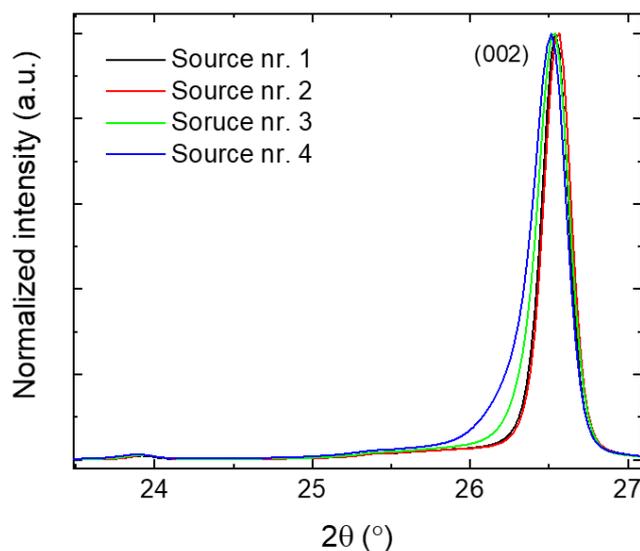


Figure 2-1 XRD patterns measured by BeDimensional (BED) on four different synthetic graphite sources used to produce FLG through WJM exfoliation method.

Beyond XRD analysis, X-ray fluorescence (XRF) measurements and X-ray photoelectron spectroscopy (XPS) represent effective techniques to determine the compositional characteristics of graphite sources, including the presence of impurities.[2],[3] The latter can be associated with catalysts that are used to lower the graphitization temperature and include boron, phosphorus, and nitrogen, but also metals.[4] At this stage, most GREENCAP partners preferred to keep confidential the information related to the synthetic graphite sources. Technical University of Dresden (TUD) is currently using synthetic graphite supplied by Sigma Aldrich to produce of graphene through electrochemical exfoliation (**Figure 2-2**). The TUD team has identified additional suppliers that produce graphite foils from synthetic graphite, including Stanford Advanced Materials (USA), JONES TECH PLC (USA), Harog Technology (China), and Nano Research Elements (India). Their products have been already purchased and will be characterized by exploiting the above-discussed techniques before performing their exfoliation.

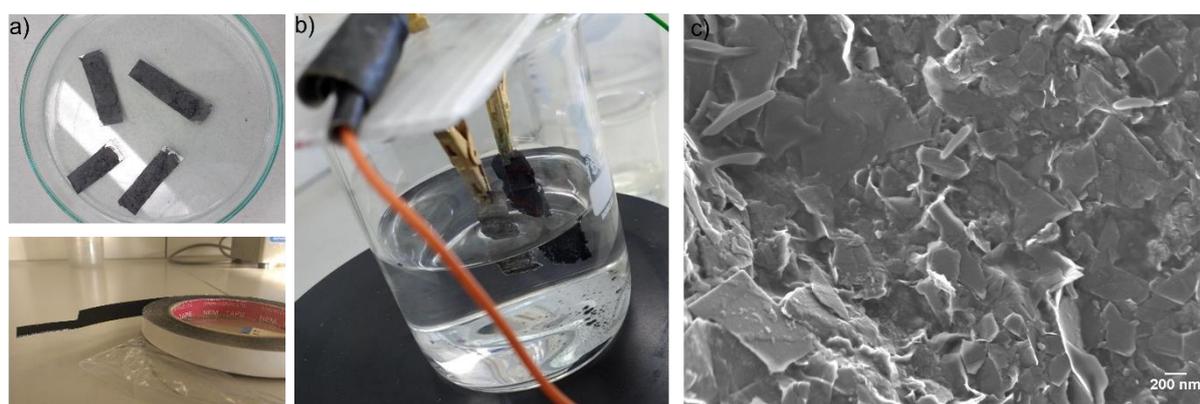


Figure 2-2 a) Preparation of synthetic graphite electrodes on polyethylene terephthalate (PET) and conductive tape substrates b) Electrochemical exfoliation of synthetic graphite-based electrodes c) Scanning electron microscopy (SEM) image of produced graphene from synthetic graphite electrodes.

Curved graphene is synthesized from silicon carbide (SiC) by Skeleton Materials (SM), according to its proprietary patented technology. The SM QC unit has developed specific protocols, including compositional and structural characterizations, to ensure batch-to-batch reproducibility of curved graphene's precursors. Lastly, for MXenes, the quality of the MAX phase precursors is evaluated

through both structural (XRD) and compositional analyses (*e.g.*, XPS). For Ti_3AlC_2 MAX phases, TUD and Trinity College Dublin (TCD) have identified different providers of MAX phases (*e.g.*, Ti_3AlC_2 and Mo_2Ga_2C), including Jilin 11 Technology Co., Ltd. (China) and Carbon Ukraine (Ukraine). The partners TUD and TCD have currently proved that, after etching and delamination (**Figure 2-3a-d**), the $Ti_3C_2T_x$ MXene flakes produced from the Carbon Ukraine MAX phase (**Figure 2-3d**) possess satisfactory quality in terms of lateral size and thickness. Also, Carbon Ukraine's MAX phases have led to a high concentration of the MXenes aqueous solutions, indicating satisfactory etching and delamination yields. The etching and delamination, by mild molten salt procedures, of CRM-free MAX phases, *e.g.*, Mo_2Ga_2C , have been preliminary performed and is currently under optimization (**Figure 2-3e-f**). Since the specifications of MAX phases needed to obtain high-quality MXenes have not been defined yet, the QC protocols for these types of precursors will be defined during the next phases of the project.

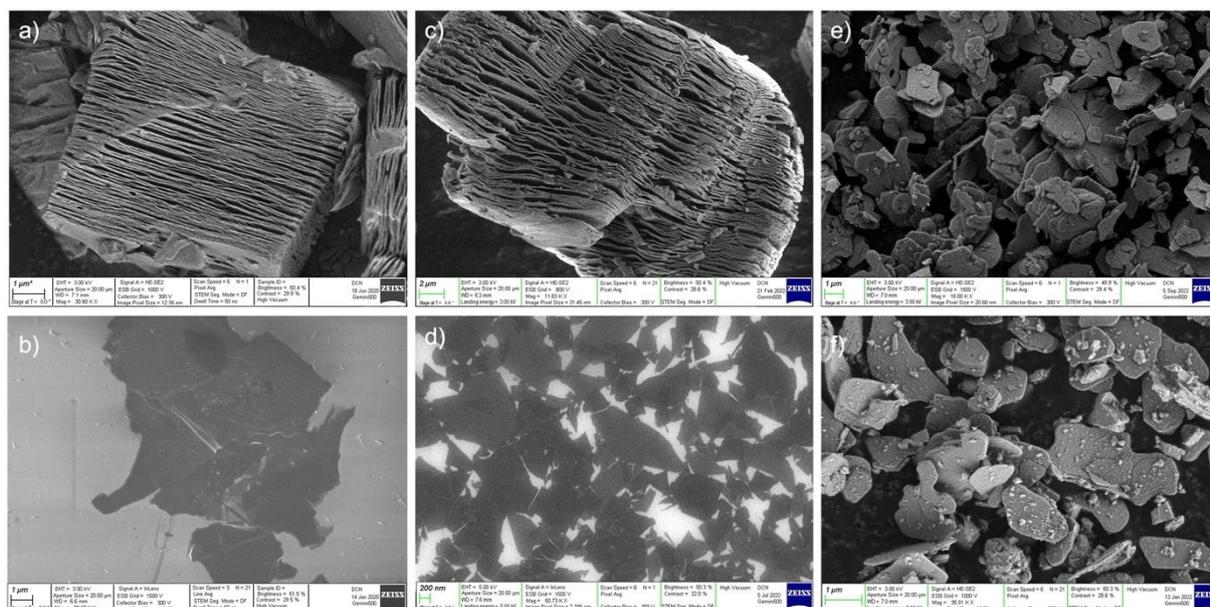


Figure 2-3 a) Etched and b) delaminated $Ti_3C_2T_x$ MXene from Jilin 11 Technology Co., Ltd. (China). c) Etched and d) delaminated $Ti_3C_2T_x$ MXene from Carbon Ukraine (Ukraine). e) Etched Mo_2C MXene and its precursor f) Mo_2Ga_2C from Jilin 11 Technology Co., Ltd. (China).

2.4 Quality and control flowchart diagram for L2DMs

This section presents the series of measurements and procedures necessary to assess the quality of the L2DMs, thus morphological and structural properties of these materials, as produced through the methods described in GREENCAP Grant Agreement (GA) No. 101091572. Noteworthy, the characterisation methods may depend on the physical state of the sample, *i.e.*, powder or liquid dispersion. An example of QC flowchart diagram is shown in **Figure 2-4** and describes the characterisation steps to perform once the sample is produced before to be used for the realization of SC electrodes in GREENCAP. These protocols represent a readjustment of the ISO/TS 21356-1:2021 standard reported for graphene and are here generalized for all the L2DMs investigated in GREENCAP. The next subsections describe in detail every characterisation step, providing indications regarding the sample registration, sample preparation method, sample measurement, data analysis and reporting. As described in the following subsections, the "Quality control threshold" are specifically set for each L2DM, depending on its functional role in the SC electrode. For samples in powder form, a thermogravimetric analysis (TGA) is carried out to quantify the presence of solvent residuals or impurities originated by the production method. The content of impurities (*e.g.*, O) can be also

measured through XPS and other compositional analysis (*e.g.*, XRF). The morphological characteristics of the L2DMs (statistical distribution of size and thickness) are assessed through atomic force microscopy (AFM), transmission electron microscopy (TEM) and SEM. The thickness of exfoliated graphite samples is also assessed by Raman spectroscopy, as described in ISO/TS 21356-1:2021. The structural quality of the L2DMs is evaluated by means of Raman spectroscopy, XRD and Fourier-transform infrared (FTIR) spectroscopy. Gas sorption measurements are used to determine the specific surface area (*e.g.*, *via* Brunauer-Emmett-Teller -BET- analysis) and pore size distribution, which are key-features of the L2DMs used as the electrode active materials (*e.g.*, curved graphene).

Some brief guidelines for a correct reading and interpretation of the flowchart are reported here:

- read the flow chart by following the lines with arrows from box to box. The lines with arrows determine the flow through the graph. However, the flow reported in **Figure 2-3** is representative, and the characterization steps can follow a different order depending on the L2DM;
- the rectangles show the type of characterization;
- the yellow diamonds stand for decisional steps. The decision determines which arrow (red or green) is followed. The arrows end in two boxes, indicate acceptable or not acceptable samples, respectively, according to partners' QC units.

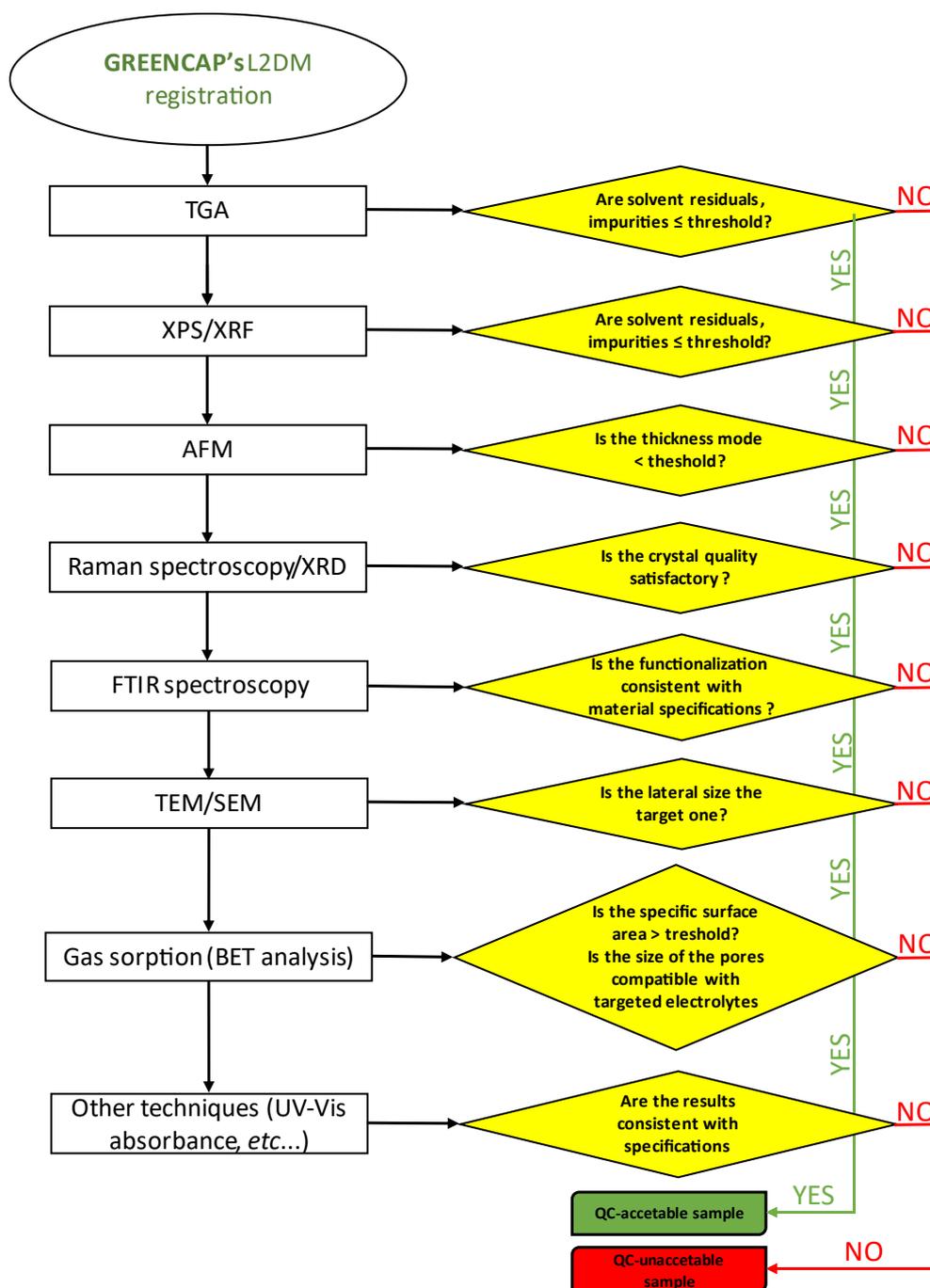


Figure 2-4 Representative QC flowchart diagram used to ensure the quality and reproducibility of L2DMs amongst different production batches.

2.4.1 GREENCAP's L2DM registration

As indicated in the QC flowchart diagram (**Figure 2-4**), an L2DM batch produced for GREENCAP project is registered in the internal database of the partner producing the sample. Afterwards, the batch of L2DMs is characterized through appropriate protocols before to be used by the same partner, or to be delivered to other partners. The request of materials amongst the partners is regulated by the Material Transfer Agreement (MTA), as reported in the Consortium Agreement. Recommended registration procedures is:

- name the L2DM batch with a Material Identifier Code (MIC). The format of MIC is internally defined by each partner, so that can be easily attributed to material characteristics, including: chemical name of the material, production parameters, number of batch, etc...
- upload the MIC in a spreadsheet file (e.g., Excel), notifying the material quantity and its state (powder or liquid dispersion), as well as the date of the delivery of the sample to the QC unit. Production parameters and other details can also be reported in the form of notes in this file.

2.4.2 Thermogravimetric analysis

The amount of solvent residual and impurities present on the as-produced powders can be generally assessed through TGA measurements. The TGA technique determines the change in the sample mass as a function of temperature or time under different gas atmosphere conditions (e.g., N₂, Ar and air). Other thermal properties can be also assessed combining differential scanning calorimetry (DSC) to TGA. The DSC method can measure the amount of heat involved in endothermic/exothermic processes of the sample tested during the temperature heating process and the parameter measured is the enthalpy change. **Figure 2-5** reports a representative TGA curve measured for a batch of FLG produced by BED through the wet-jet milling (WJM) method.

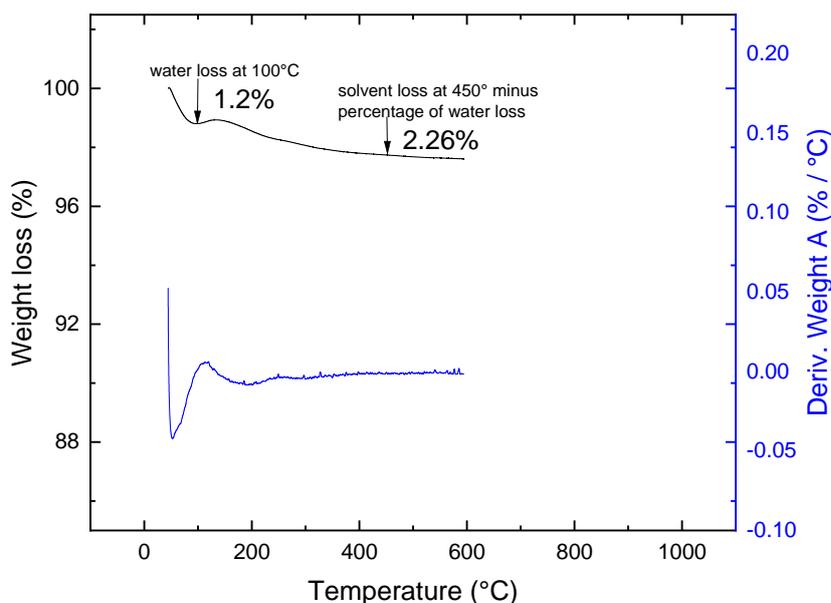


Figure 2-5 TGA curve of a representative FLG (powder) batch produced by BED through the WJM method. This batch was not considered acceptable by the BED's QC unit since it contained an excessive amount of solvent above BED's threshold value.

2.4.3 X-ray photoelectron spectroscopy and XRF

X-ray photoelectron spectroscopy and XRF are used to assess the chemical composition of L2DMs, including the presence of functionalities originated by the production processes (or the presence of impurities). These techniques are extremely important to ensure the expected purity of L2DMs such as pristine graphene, including FLG produced by WJM and HPH exfoliation methods. Importantly, XPS measurements can effectively check the presence of solvents residual, as previously proved for the case of N-Methyl-2-pyrrolidone (NMP) solvent by the analysis of the N 1s XPS spectrum. In fact, the band peaking at ~400.0 eV is associated to the amide groups (-N-(C=O)).[5] Meanwhile, XRF is a rapid

tool to evaluate the presence of metal impurities, which may also derive by the impurities already present in the native graphite sources, as discussed in Section 2.3.

2.4.4 Atomic force microscopy

Atomic force microscopy is used to determine the statistical distribution of the thickness of L2DMs in each production batch. For graphene-based samples, the sample preparation, sample measurements, and data analysis can generally follow the ISO/TS 21356-1:2021, even though the entire ISO protocols can be simplified to excessively time-consuming procedures. The AFM samples can be prepared by depositing L2DM dispersion on mica substrates. The concentration and the solvent of the L2DM dispersion must be optimized to obtain isolated flakes, as needed to acquire reliable thickness data (**Figure 2-6**).

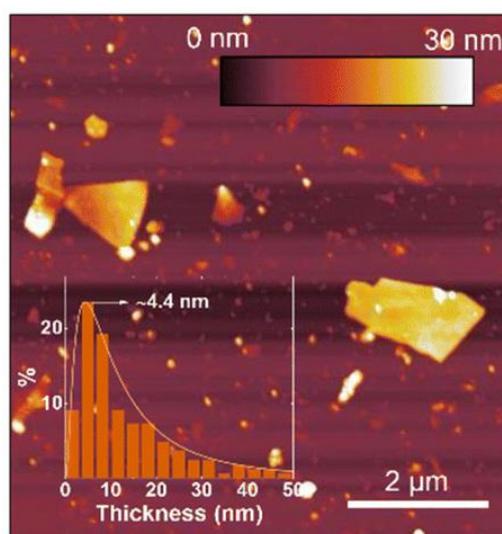


Figure 2-6 AFM image of WJM-produced FLG produced by BED by means of the WJM exfoliation method (without any additional purification step). The inset panel shows the statistical analysis of the thickness data ($n = 200$, log-normal fit).[6]

2.4.5 Raman spectroscopy, XRD and FTIR spectroscopy

Raman spectroscopy and XRD can be used to assess the structural quality of L2DMs. For the specific case of graphene, the Raman spectrum shows, as fingerprints, G ($\sim 1585 \text{ cm}^{-1}$), D ($\sim 1380 \text{ cm}^{-1}$), D' ($\sim 1620 \text{ cm}^{-1}$) and 2D ($\sim 2700 \text{ cm}^{-1}$) peaks.[7],[8] The G peak corresponds to the E_{2g} phonon at the Brillouin zone centre. The D peak is due to the breathing modes of sp^2 rings and requires a defect for its activation by double resonance.[7],[8] Double resonance occurs as an intra-valley process, *i.e.*, connecting two points belonging to the same cone around K or K', giving origin to the D' peak.[9] The 2D peak is the second order of the D peak, even though no defects are required for the activation of two phonons with the same momentum.[7],[8] The thickness of the graphene flakes can be estimated by the analysis of the 2D peak (**Figure 2-7**).

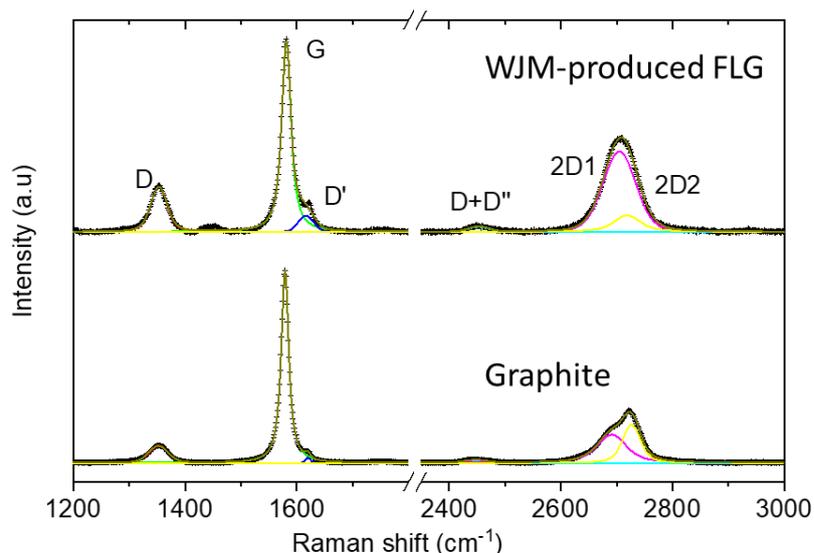


Figure 2-7 Comparison between the Raman spectra (normalized on $I(G)$) of the graphite and BED's WJM-produced graphene flakes, with their multi-peak Lorentzian fitting showing the contribution of the individual modes ($2D_1$ and $2D_2$).

More in detail, graphite features a 2D peak given by two contributions, named $2D_1$ and $2D_2$.^[7] The intensity of the $2D_2$ is *ca.* twice that of $2D_1$.^{[7],[8]} Multi-layer graphene exhibits a 2D peak with intensity and lineshape similar to those of the graphite.^{[7][8]} Few-layer graphene, instead, has a $2D_1$ peak more intense than the $2D_2$.^{[7][8]} Lastly, SLG exhibits a 2D peak composed of a single sharp contribution, which is attributed to $2D_1$.^{[7],[8]} Thus, in the $I(2D_1)/I(G)$ vs. $I(2D_2)/I(G)$ plot, where $I(X)$ indicate the intensity of the peak X, the data that fall above the line ($I(2D_2) = I(2D_1)$) correspond to FLG, while those below (*i.e.*, $I(2D_2) < I(2D_1)$) indicate multi-layer flakes (indistinguishable from graphite). Also, when intrinsic defects are located at the edges of graphene flakes and, in absence of defective basal plane, $I(D)/I(G)$ varies inversely with the crystal size. However, defects can occur also on the basal planes of the flakes. For such flakes, the $I(D)/I(G)$ correlates with the amount of disorder. To evaluate the crystal quality of the graphene flakes, the plot of $I(D)/I(G)$ vs. $FWHM(G)$, in which $FWHM(G)$ refers to the full width half maximum of the peak G, can be used to evaluate the existence and nature of defects.^{[10],[11],[12]} When the plot of $I(D)/I(G)$ vs. $FWHM(G)$ does not show a linear correlation, defects in the basal plane can be excluded, and defects are mainly associated to the edges of the flakes. The analysis of XRD patterns can be used to discriminate pristine graphene from its derivative, such as graphene oxide and reduced graphene oxide. Meanwhile FTIR spectroscopy is an effective non-destructive tool to evaluate the structural quality of graphitic materials.^[13] Adsorbed water molecules may determine the appearance of weak bands in the FTIR spectrum of graphitic samples, while additional peaks beyond those of ideal graphite may refer to reactants used for the production processes of graphene.^[13] Lastly, FTIR spectroscopy is commonly used to determine the presence of functional groups in graphene derivatives. Consequently, FTIR spectroscopy will be extremely useful for the QC of the graphene derivatives that will be produced in Task 2.1 of WP2 (“Chemical functionalization of electrode materials”).

Also, as for the case of native graphite, $g(\%)$ and the FWHM of the (002) peak can be used as parameters to evaluate the structural quality and the size of the crystallites in the exfoliated samples.^[1] Raman spectroscopy, XRD, and FTIR spectroscopy can be used to assess the crystallinity and the presence of functional groups of other L2DMs, including MXenes. **Figure 2-8** shows the XRD patterns of representative MAX phase (Ti_3AlC_2) and the corresponding MXene ($Ti_3C_2T_x$). After the

etching process, the (002) peak of Ti_3AlC_2 located at $\sim 9.5^\circ$ downshifts to $\sim 8^\circ$ (multilayer $Ti_3C_2T_x$). Tetramethylammonium hydroxide (TMAOH)/ tetrabutylammonium hydroxide (TBAOH) intercalation can lead to the exfoliation of multi-layer $Ti_3C_2T_x$ into single-/few-layer $Ti_3C_2T_x$, accompanied with the further downshift of (002) peak to $\sim 7.8^\circ$.

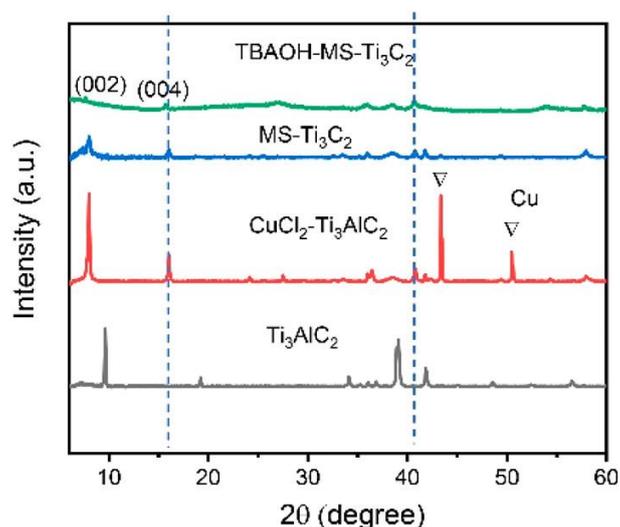


Figure 2-8 XRD patterns of a representative MAX phase (Ti_3AlC_2) and the corresponding multilayer and single-/few-layer MXenes ($Ti_3C_2T_x$).

2.4.6 Transmission/scanning electron microscopies

In GREENCAP, TEM and SEM measurements are performed to statistically evaluate the lateral size of the L2DMs, as well as their overall morphology and structural characteristics, *e.g.*, presence of defects. Also, TEM can be coupled with energy-dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) to provide compositional information, evaluate eventual oxidation or degradation of the material post-exfoliation, and assess the presence/nature of possible impurities.

The reproducibility of the morphological characteristics of L2DMs is pivotal to tailor the porosity of the electrode materials, aiming at maximizing the electrochemically accessible surface area of the SC electrodes. **Figure 2-9** shows the TEM analysis of a representative batch of FLG produced by BED through the WJM exfoliation method.

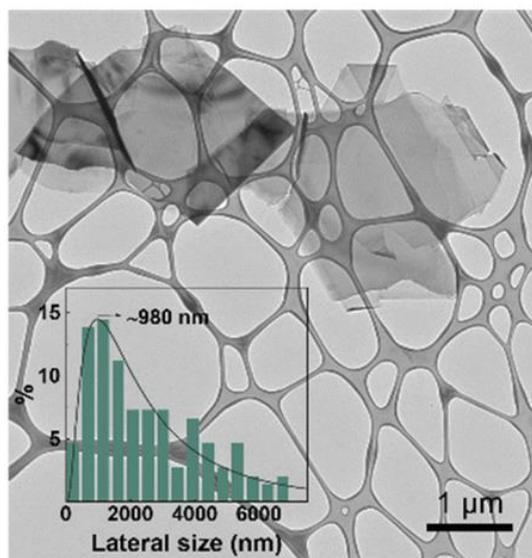


Figure 2-9 TEM image of representative FLG produced by BED by means of the WJM exfoliation method. The inset panel shows the statistical analysis of the lateral size data ($n = 200$, log-normal fit).[6]

Alternatively, the lateral size of the L2DMs can be also evaluated by SEM, which can be coupled with EDX to provide compositional information. Also, SEM analysis can be used to preliminary assess the effectiveness of the exfoliation methods used to produce novel L2DMs, as shown in **Figure 2-10** for the case of $Ti_3C_2T_x$ production by means of the Lewis acid etching of the Ti_3AlC_2 MAX phase.

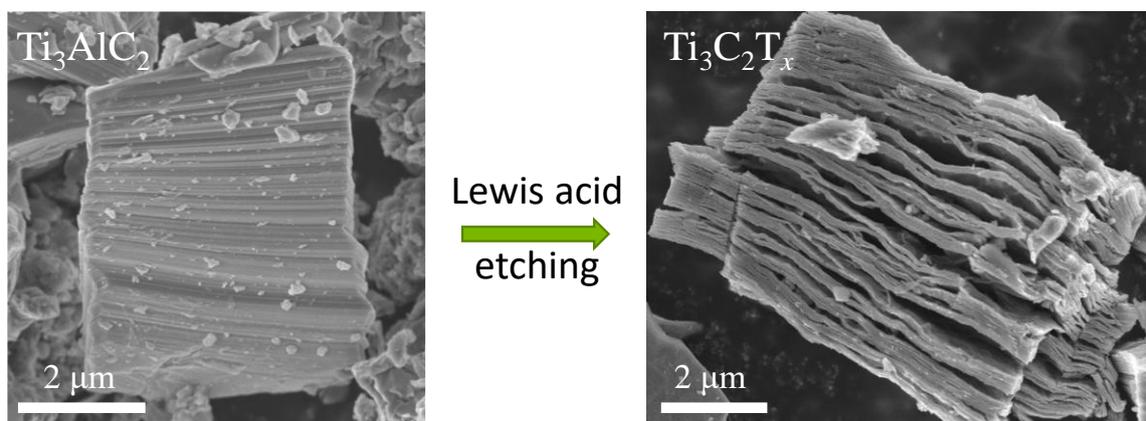


Figure 2-10 SEM images showing the effectiveness of Lewis acid etching of the Ti_3AlC_2 MAX phase into multi-layer $Ti_3C_2T_x$.

2.4.7 Gas sorption

Gas sorption measurements are performed on L2DM powders to determine their specific surface area, *e.g.*, via BET method, as well as the pore size distribution.[14] This information is particularly important when L2DMs are used as the active materials in SC devices. **Figure 2-11a** reports the BET surface area data measured by SM for its curved graphene, produced through either a fluidized bed reactor (FBR) or a frit fluidized bed reactor (FFBR). The latter reactor represents an optimized design compared to the former. These data are correlated to the Cl_2 effective conversion rate (**Figure 2-11b**), according to its proprietary production process (not described in this deliverable).

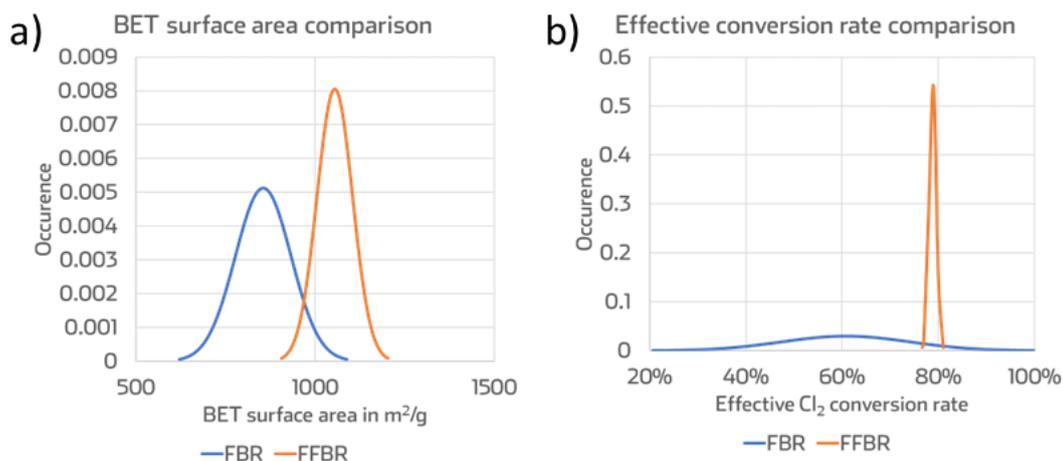


Figure 2-11 Comparison of the characteristics of graphene produced by SM by means of FBR and FFBR. a) BET surface area and b) Cl₂ effective conversion rate data.

2.4.8 Other techniques

To assess the compositional, structural, morphological, electrical, electrochemical, and other physical properties of L2DMs, other type of techniques can be used upon request for specific purposes related to SC activities. However, at this stage, these techniques may not all be included within the QC protocols since they can be excessively time-consuming. Even though these techniques are listed here below, they will be mainly used within WP1 to perform a multiscale characterization of the most promising L2DMs to be used for the realization of SC electrodes. These techniques are:

- Spectroscopic techniques such UV/visible spectroscopy, Auger electron, electron energy loss, reflection high-energy energy loss, ultraviolet photoelectron (UPS), inverse photoelectron, secondary electron, and photoelectron spectroscopies combined with synchrotron light sources. They will serve to extend the analysis of the composition properties of the L2DMs.
- Wide-angle X-ray scattering and grazing incidence X-ray diffraction. They will be used to extend the structural characterization of L2DMs performed through XRD and Raman spectroscopy by the QC units.
- High-resolution transmission electron and scanning transmission electron microscopies. They will provide an in-depth characterization of the morphological properties of L2DMs, after their preliminary evaluation by QC units through TEM, AFM and SEM.
- Scanning tunnelling spectroscopy and conductive-AFM measurements. They will be used to correlate the structural and electronic properties.
- Kelvin probe force microscopy and macroscopic Kelvin probe measurements to attain information related to the work function and electronic properties of L2DMs.

2.4.9 Additional notes

GREENCAP partners that are developing L2DMs in WP1 are currently optimizing the production processes to eliminate/reduce the use of CRMs, while avoiding the use of toxic/hazardous materials. These activities are subject matter of Task 1.1 of WP1, as described in the GA No. 101091572. In this

context, some partners are implementing specific process step to improve the overall quality and reproducibility of GREENCAP's L2DMs, as shown in **Figure 2-12** for the representative case of curved graphene produced by SM. Potential refinement processes for curved graphene include carbon washing and high temperature vacuum treatments.



Figure 2-12 a) Curved graphene production process steps before the GREENCAP project, b) Curved graphene production processes steps during the GREENCAP project where additional refinement step is considered.

Noteworthy, the quality of materials upscaled at industrial level will be also assessed through electrochemical characterization in SC devices. To evaluate the main electrical characteristics of an SC, namely electrical series resistance (ESR) and capacitance (or capacity), Skeleton Technologies (SKL) uses the 5-cycle method¹ (**Figure 2-13**):

- the cell is charged to 2.85 V and then discharged to 1.425 V with a constant current,
- at 1.425 V a 5 s duration current cut is applied,
- five such cycles are performed before the cell is discharged back to 0 V.

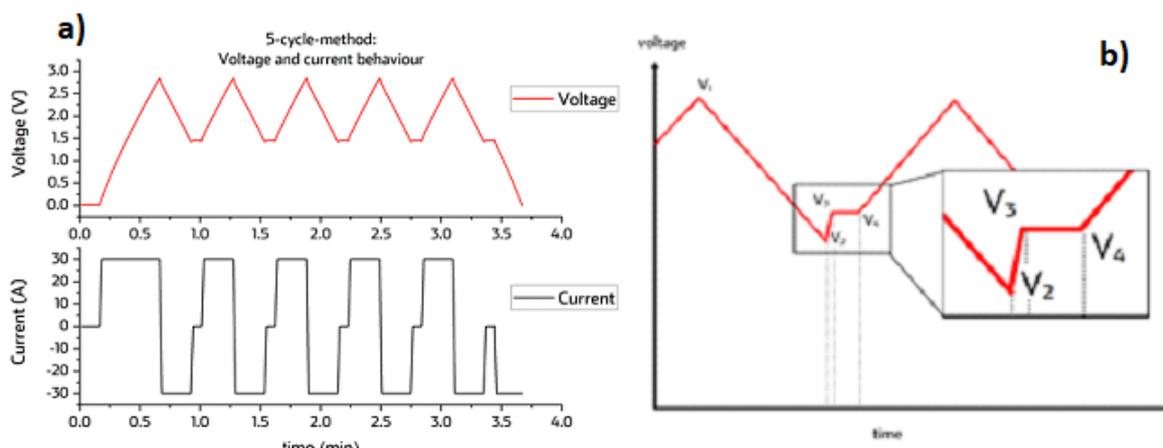


Figure 2-13 a) 5-cycle method, b) detailed view of the time-voltage profile right after discharging to half voltage.

The capacitance is calculated from the discharge cycle according to Equation 1:

$$Capacitance = \frac{I * (t_2 - t_1)}{(V_1 - V_2)} \quad (1)$$

in which t_1 is at point V_1 , and t_2 is at point V_2 .

¹ The applied DC current depends on the cell size.

The ESR_{10ms} and ESR_{1s} are determined according to Equations 2 and 3, in which V_2 is 1.425 V, V_3 is measured at $t_3=0.01$ seconds after current-cut, and V_4 is measured at $t_4=1$ second after current-cut.

$$ESR_{10ms} = \frac{(V_3 - V_2)}{I} \quad (2)$$

$$ESR_{1s} = \frac{(V_4 - V_2)}{I} \quad (3)$$

in which ESR_{10ms} is output as internal resistance after each loop (after discharging).

Another important characteristic for supercapacitors is self-discharge. As compared to batteries, supercapacitors display rather extensive self-discharge due to the electrical field type of energy storage process. The extent of self-discharge is mainly dependent on the temperature and the cell voltage, as well as the charge/discharge current and voltage hold steps "history" of the cell.

Table 2-1 Example protocol of self-discharge test.

Temperature, °C	V _{start}		
	1.9 V	2.1 V	2.3 V
60	I _{CC} = 15 A V _{hold} = 15 minutes		
65			
75			
85			

The goal of the test is to define a specific test duration until reaching a defined voltage at open circuit potential. Self-discharge tests are mandatory for series production. However, this can be a serious bottleneck for quality control at series production as the self-discharge tests are highly time consuming. This is a challenge to overcome when upscaling production. Other electrochemical protocols for the characterization of SCs have been agreed by partners and will be subject matter of WP3.

3 Ionic liquids

Achieving both high quality and consistently pure products requires strong expertise and knowledge in ILs. Based on over 20 years of expertise, Solvionic (SOLV) has developed a unique know-how on the purification and QC of ILs. This section presents a flow chart (**Figure 3-1**) of the QC process used by SOLV to verify the purity of ILs before their use as electrolytes for SCs.

Starting with the production process, each product is assigned a unique batch number and its own file used for traceability throughout the processing of the product. Next, at different intermediary steps, the level of any impurity will be quantified using ion chromatography (IC) as the main tool. After the final drying process, the water content will be assessed using the Karl Fischer (KF) method. Finally, once the product reaches the sufficient level of purity and water content (99.9% purity and <20 ppm water), it is then conditioned using a protective atmosphere. At this point, ILs will be ready for use within SCs or to be shipped to other GREENCAP partners.

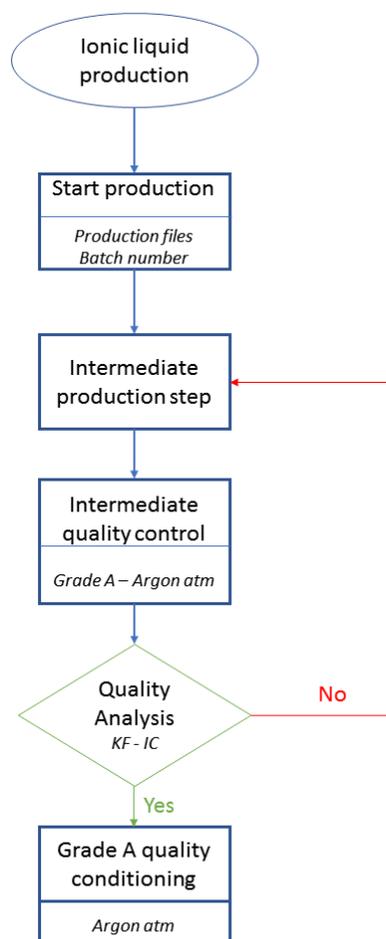


Figure 3-1 QC flowchart used to ensure the purity of ILs.

4 Conclusion

The GREENCAP consortium applies QC procedures to ensure the material uniformity required for their subsequent functionalization/hybridization processes and application in SC manufacturing. This document describes the set of characterizations that are routinely carried out by QC units of partners producing SC materials, including electrode materials and ILs. Concerning graphene-based materials, generally, the QC procedures follow those described in international standards, *e.g.*, ISO/TS 21356-1:2021 Nanotechnologies — Structural characterisation of graphene. However, GREENCAP partners recognize the need to readapt ISO guidelines to ensure prompt QC actions on time on research samples, according to the timeline expected by the project. In addition, QC procedures are here defined also for L2DMs beyond graphene and its derivatives, as well as for ILs, for which there are no standards yet. Consequently, the current QC procedures will subsequently be updated, depending on the set of materials developed for GREENCAP. These procedures may serve as basis for the development of future QC international standards of L2DMs and ILs.

5 Risk and Deviations from Annex 1

No risks have arisen related to this deliverable. There are no deviations from the description of this deliverable as given in Annex I of the GA.

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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

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