FREE4LiB

Deliverable 3.3

Development, testing and validation of recycling solutions for cathode and black mass at lab-scale

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Feasible Recovery of critical raw materials through a new circular Ecosystem for a Li-Ion Battery cross-value chain in Europe

WP3 - Recycling technologies and materials re-using for Li-batteries

D3.3 - Development, testing and validation of recycling solutions for cathode and black mass at lab-scale

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Versions

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05/07/2024	1	CSIC, LUREDERRA, EURECAT	first draft of the document
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30/08/2024	4	CSIC, CARTIF	final document

Contents

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List of Abbreviations

ACRONYMS	DESCRIPTION
BM	Black Mass
AA	Atomic adsorption
XRD	X-Ray diffraction
SEM	Scanning electron microscopy
EDX	Energy dispersive X-ray
NADES	Natural deep eutectic solvents
CAM	Cathode active material
ICP-MS	Inductively coupled plasma mass spectrometry

1. Executive summary

This deliverable collects some of the results of WP3, which main objective is screening technologies around LIBs recycling & remanufacturing and test them at lab scale (TRL 3-4), including the develop a battery pack dismantling line supported by robots, the recovery of valuable materials (metal oxides, plastics and metals) from spent LIBs through different recycling techs, and materials re-using: validate valorized materials to battery value chain, and validate the use of recycled materials in alternative uses.

More specifically, the document presents the results obtained for the development, testing and validation of recycling solutions for cathode and black mass at lab-scale. The research aim is to obtain valuable products from black mass and cathode materials using 3 different technologies.

This document will explain 3 different recycling routes based on different technological approaches:

- Hydrometallurgical treatment from black mass.
- A combined pyro+hydrometallurgical treatment from black mass.
- Direct cathode recycling

The hydrometallurgical treatment from black mass consists of the leaching of black mass by different acids. After the optimization of the process the best conditions to recover the valuable metals are malic acid + O_3, in these leaching conditions, the leaching of contaminant metals (Cu and Fe) is not complete, what helps to the posterior recovery of the interest metals. Once metals are solved, and to recover the target metals, an oxalic acid precipitation was performed, to recover Ni, Mn and Co oxalates. This precursor will be used to synthetize cathode materials NMC622 and LMNO type. To improve the separation of the metals, a liquid-liquid separation step is added to recover Co as CoSO4. This precursor will be used to synthetize LMNO cathodes.

The combined pyro+hydrometallurgical treatment is based on perform a pyrometallurgical step to recover lithium from black mass. Once the lithium is recovered, the same process described in hydrometallurgical treatment is carried out from the residue of lithium recovery.

The direct recycling method converts end-of-life (EOL) cathode materials into battery-grade materials with minimal energy consumption and environmental impact, preserving the material structure. A crucial step in this process is re-lithiation, which restores the lithium stoichiometry of the cathode materials. Spent cathode active materials, both foil and powder, undergo re-lithiation using two technologies: hydrothermal and electrochemical.

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In the metal recovery industry, a novel direct cathode recycling process utilizing NADES has been developed, demonstrating promising results. Compared to citric acid, another recognized green solvent, NADES exhibits superior metal recovery rates. However, NADES does suffer from increased viscosity at higher solid-liquid ratios, which was not reported for citric acid. Despite this drawback, the final recovery rates of lithium, cobalt, and nickel surpass the targets set by the latest EC battery directive, highlighting NADES's substantial potential in sustainable metal recycling.

2. Introduction

This document aims to present the results obtained for the development, testing and validation of recycling solutions for cathode and black mass at lab-scale. The research aim is to obtain valuable products from black mass and cathode materials using 3 different technologies.

This deliverable explains 3 different recycling routes based on different technological approaches:

- Hydrometallurgical treatment from black mass.
- A combined pyro+hydrometallurgical treatment from black mass.
- Direct cathode recycling

As mentioned before, the different process from cathode recycling and black mass recycling, will result in materials that could be used as precursors of new materials to be used in batteries, and that will be tested during the project.

In order to investigate recycling solutions for black mass at lab scale to recover the principal metals that black masses contain, two different approaches were assessed. Hydrometallurgical treatment of black mass, as well as combined pyro-hydrometallurgical process were analysed. Both of them consist of several steps that were investigated. and and show the flow diagrams for the hydrometallurgical process and for the combined pyro-hydrometallurgical process carried out, as well as the recovery for each metal. From the materials obtained, the preparation of precursor by Flame Spray Pyrolysis was carried out.

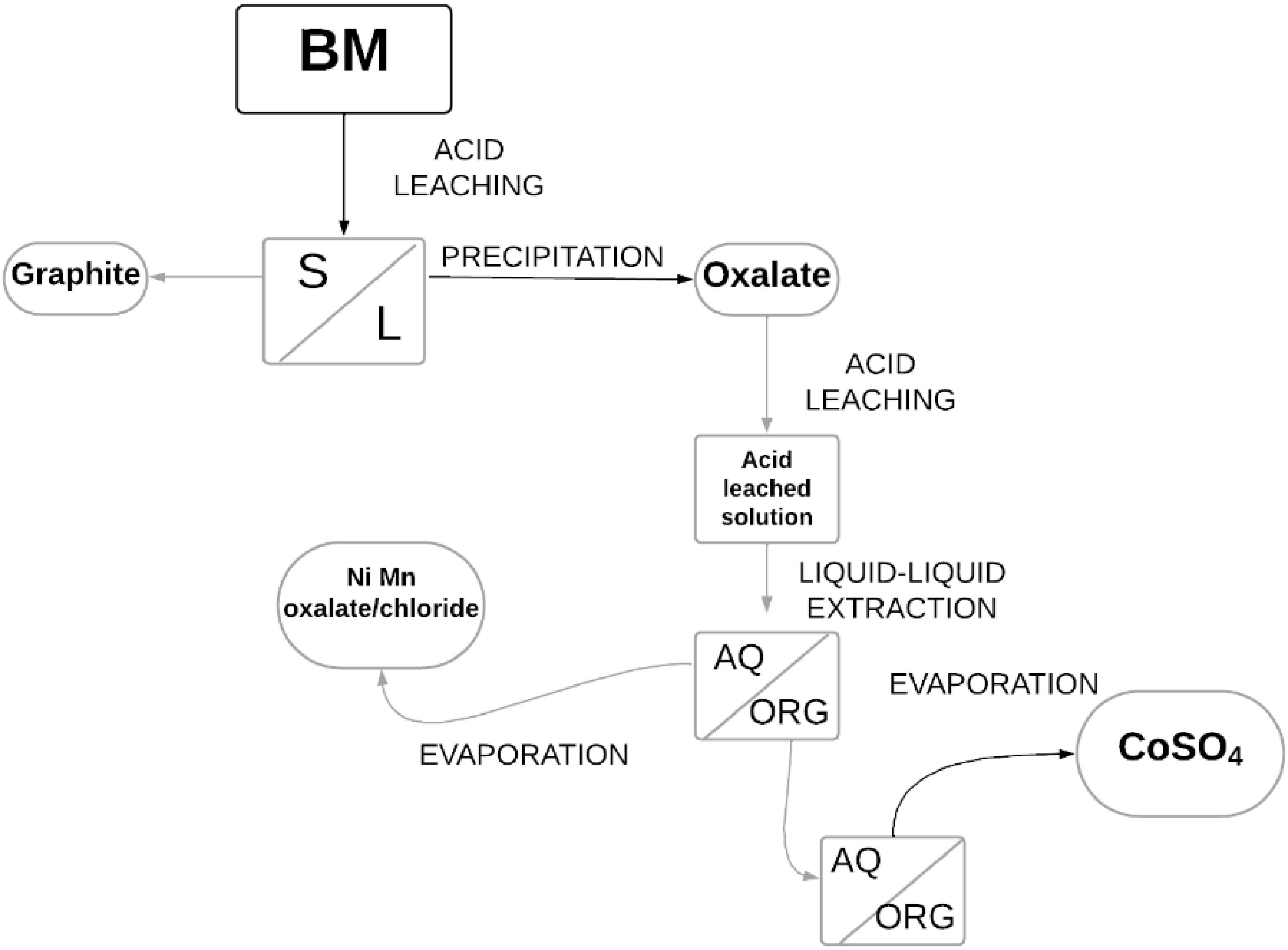

Figure 1. Flow diagram for the hydrometallurgical process.

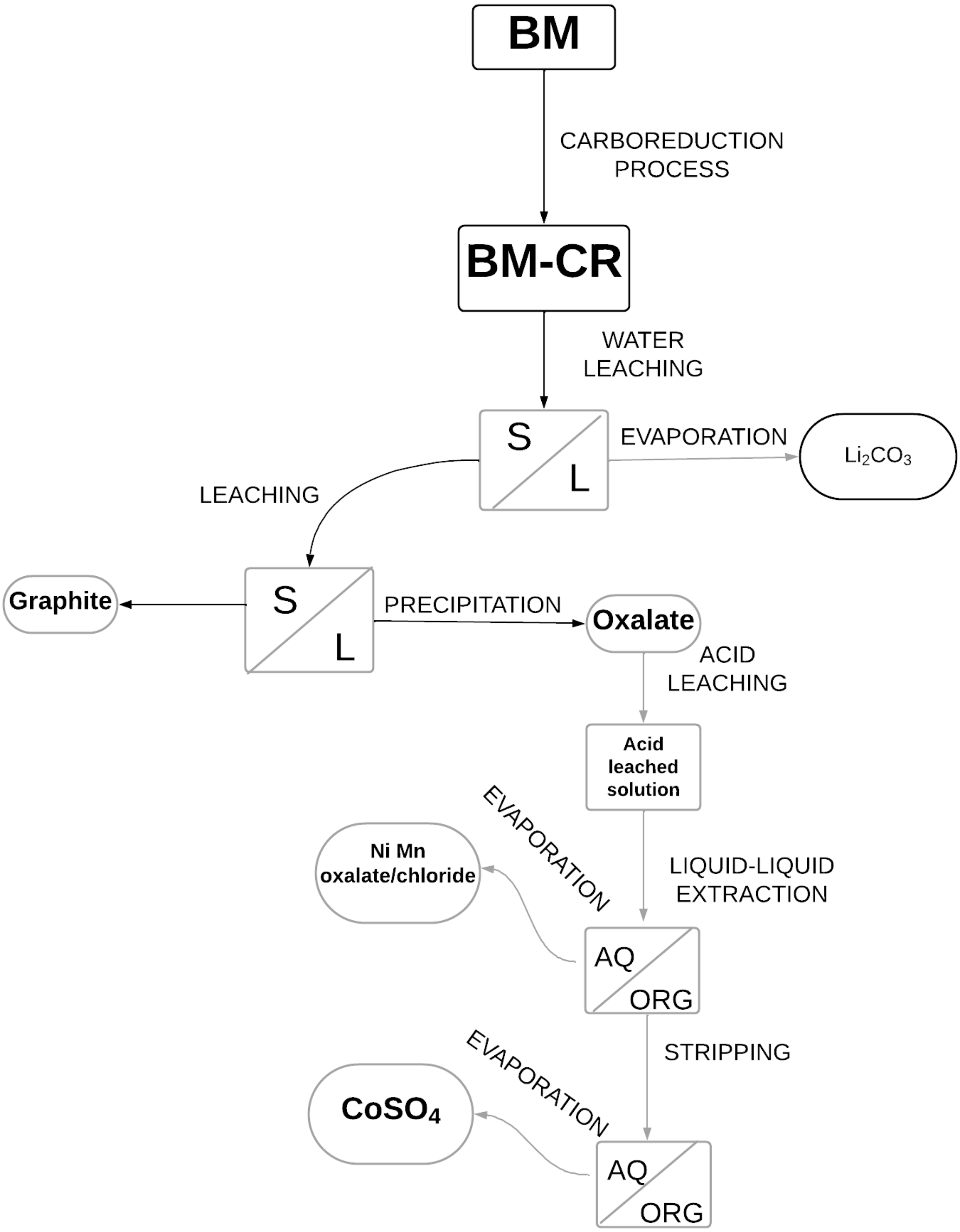

Figure 2. Flow diagram for the combined pyro-hydrometallurgical process.

Another approach for the recovery of active materials from EOL LIBs is the direct cathode recycling.

Inorganic acids are commonly used in metal recovery processes, despite their economic and environmental impact. In recent years green solvents are being studied as a much greener and economic alternative. Natural deep eutectic

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solvents (NADES) are an outstanding alternative with an enormous potential due to its chemical characteristics, its low environmental impact, and its price.

Direct recycling technologies typically involve regeneration of spent cathodes by restoring their composition and crystal structure. Lithium salts, as lithium sources, have shown potential for recovering degraded cathode active materials (CAM) their original stoichiometric ratio and crystal structure.

In this project, a novel approach for recycling cathode materials from end-of-life lithium-ion batteries are demonstrated and analysed (Figure 3). Two recycling process, hydrothermal and electrochemical re-lithiation, have been carry out in an aqueous electrolyte, followed by heat treatment.

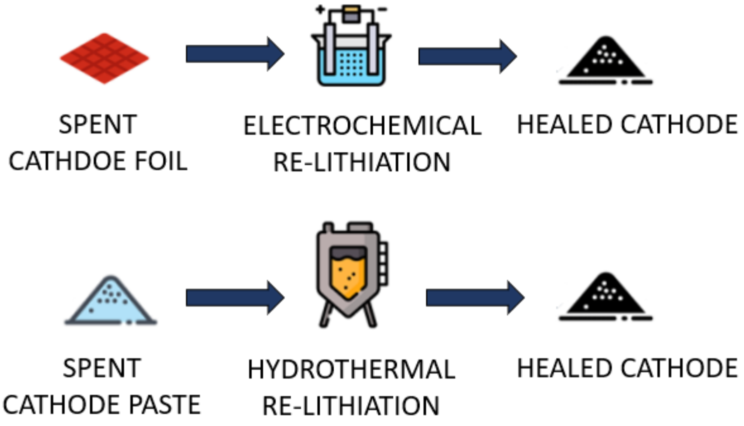

Figure 3. Re-lithiation technologies to restore cathode active material.

NADES are a class of solvents made from natural compounds that, when mixed in specific ratios, form a eutectic mixture with a melting point significantly lower than either of the individual components. These solvents are known for their ability to dissolve a wide range of substances, making them useful in various applications. NADES are generally non-toxic, biodegradable and are stable under a wide range of conditions, including different temperatures and pH levels. These solvents are considered environmentally friendly alternatives to traditional organic solvents, aligning with principles of green chemistry.

In this project, a stage of NADES leaching followed by a selective precipitation step to recover valuable compounds will be developed (Figure 4).

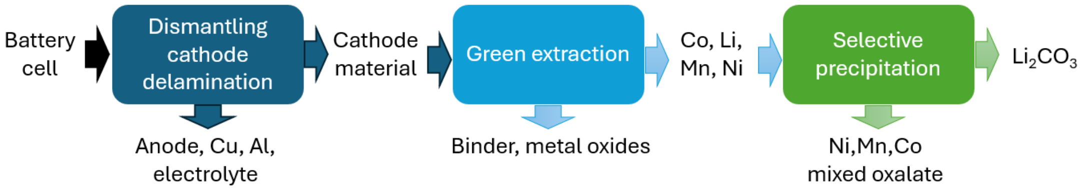

Figure 4. Process based on NADES for cathode direct recycling.

3. Recycling solutions for black mass at lab scale

3.1 Black mass characterization

Three different black masses were received (BMs) from ACC (BM01) and FRA (BM02 and BM03). BM01 comes from a thermo-mechanical pre-treatment process, while BM02 and BM03 come from an electrohydraulic fragmentation process. BMs were characterized by different techniques, such as, atomic absorption (AA) to determine the chemical composition, total carbon content to determine the percentage of graphite from anode, X-Ray Diffraction (XRD) to characterize the mineralogy, and Scanning Electron Microscopy (SEM) to characterize the morphology.

Results of AA and total carbon content, shows differences of composition depending on the source of the BM, and even slight differences when BM come from the same procedure, especially for contaminant elements from cases and collectors, such as Cu, Al and Fe, as it can be observed in . Comparing the two pre-treatment processes, the content of valuable metals (Li, Co, Ni, Mn) increase when electrohydraulic fragmentation is used. The opposite happens for contaminant metals (Al, Fe), that decrease for this process. Regarding Cu, the behaviour seems to be different from the rest of contaminant elements, the electrohydraulic fragmentation process increases the content of Cu in the BM. In terms of chemical composition, the electrohydraulic fragmentation appears to be a better option for the recovery of valuable metals.

Table 1. Chemical composition of BMs determined by AA.

% (w/w)	BM01	BM02	BM03
Li	3.6	3.22	2.75
Ni	11.3	16.70	16.58

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Co	3.3	5.45	5.15
Mn	3.9	5.06	4.20
Al	1.6	0.57	1.01
Fe	0.03	0.01	1.35
Cu	0.5	1.22	3.23
C_{total}	54.2	53.4	40.3

Regarding mineralogical composition, a clear difference between both pre-treatment process can be also seen. In the case of thermo-mechanical treatment (BM01, 5a), a decomposition of the spinel phase typical of NMC622 cathodes ($LiNi_{0.6}Mn_{0.2}Co_{0.2}O_4$) it can be observed, that can be proved by the presence of the metal oxides, and lithium carbonate. The presence of graphite it could be also detected. In the case of BMs from electrohydraulic fragmentation (BM02 5b & BM03 5c), the spinel phase is detected together with graphite.

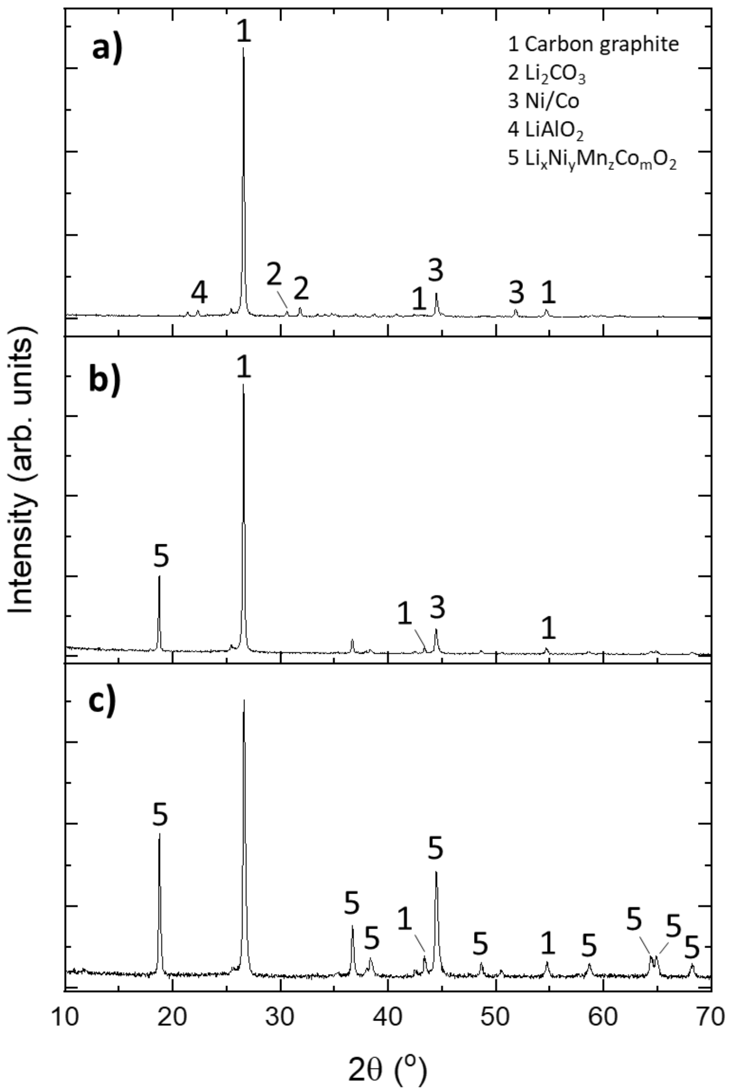

Figure 5. XRD for (a) BM01, (b) BM02, and (c) BM03 black masses.

In order to evaluate the influence on the pre-treatment on the microstructure of the samples, the black masses which are obtained by a thermomechanical pre-treatment process (BM01, 6), as well as an electrohydraulic fragmentation process (BM03, 7) were analysed by SEM.

Particles agglomerates were found in both cases, where two different morphologies can be appreciated. A globular morphology can be observed, which can be due to the presence of carbon-graphite from anodic fraction. On the other hand, particles agglomerates with polyhedral shape can also be appreciated probably due to the presence of the metal-oxides.

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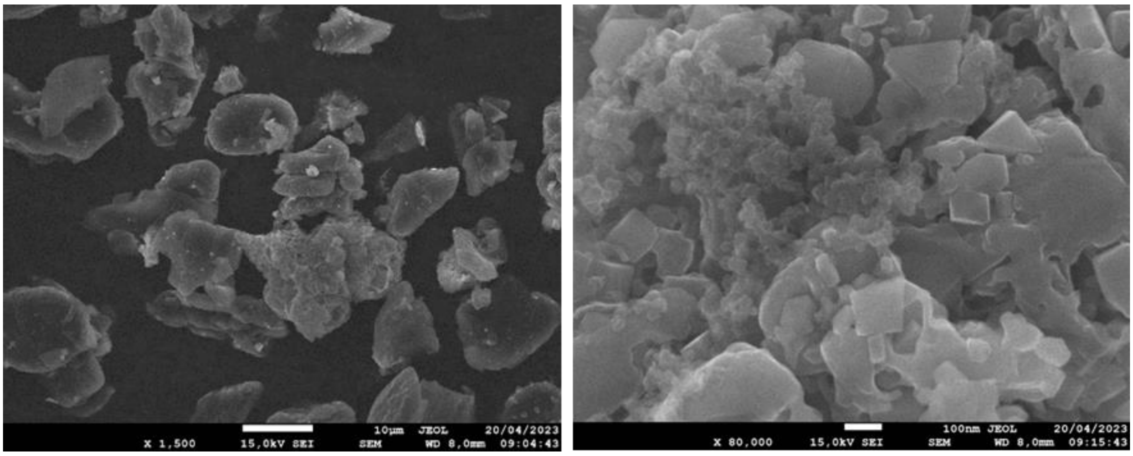

Figure 6. SEM images of BM01 black mass.

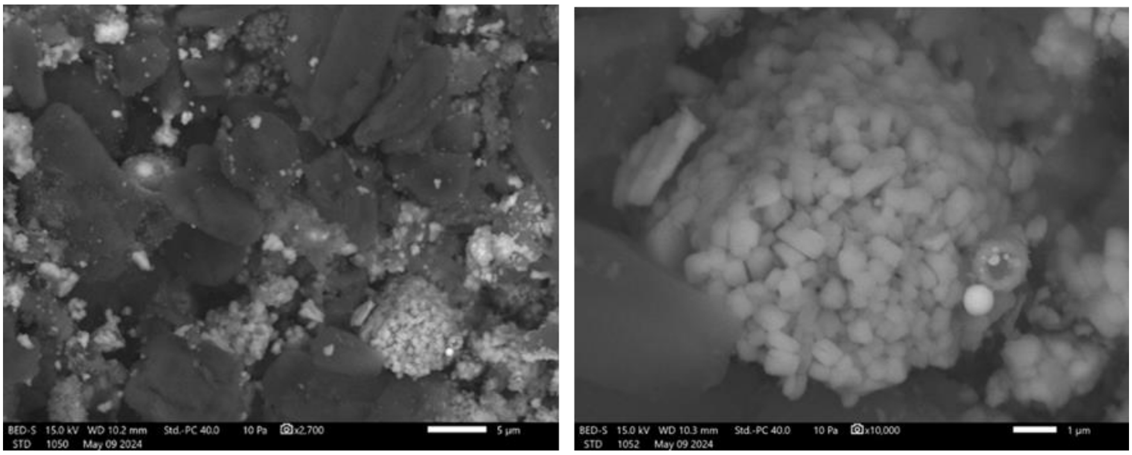

Figure 7. SEM images of BM03 black mass.

3.2 Hydrometallurgical treatment of black mass

Based on previous knowledge of CSIC, the hydrometallurgical process consists of an oxidant acid leaching of BMs, using organic and inorganic acids, with the objective of dissolve all valuable metals. shows conditions employed for each BM. Metals recovery percentage for each metal using the experimental different conditions are shown in 8.

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Table 2. Leaching conditions.

Reference	BM	[Acid] (M)	Temperature (ºC)	t (h)	Oxidant
L1	BM01	H_2SO_4, 2M	70	2	-
L2	BM01	H_2SO_4, 2M	70	2	O_3
L3	BM01	Citric acid, 1.25M	70	2	-
L4	BM01	Citric acid, 1.25M	70	2	O_3
L5	BM01	Malic acid, 1.5M	70	2	H_2O_2 5%
L6	BM01	Malic acid, 1.5M	70	2	O_3
L7	BM01	HCl, 10M	70	2	-
L8	BM02	Malic acid, 1.5M	70	2	O_3
L9	BM03	H_2SO_4, 2M	70	2	O_3
L10	BM03	Malic acid, 1.5M	70	2	O_3

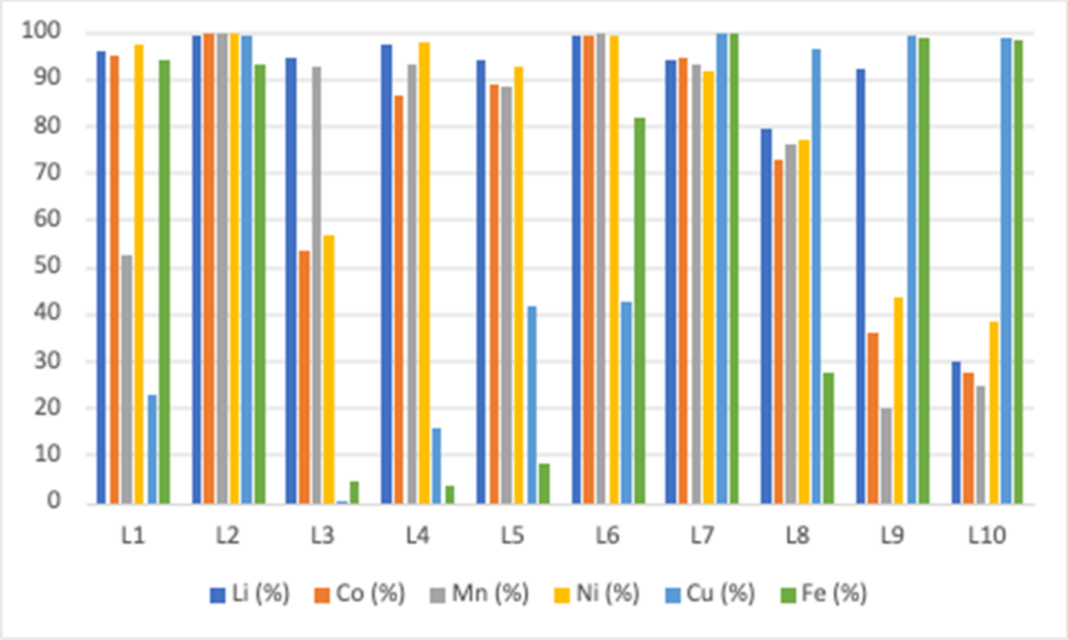

Figure 8. Leaching yield (%).

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The best conditions to leach valuable metals (Li, Ni, Co and Mn) are malic acid + O_3, in these leaching conditions, the leaching of contaminant metals (Cu and Fe) is not complete, what helps to the posterior recovery of the interest metals. For this reason, malic acid leaching using O3 as oxidant was selected for the subsequent tests. In addition, it should be noted that subsequent tests were carried out using BM01 and BM03 as initial BMs to analyze the influence of different pretreatment used.

Once metals are solved, and to recover the target metals, an oxalic acid precipitation was performed, to recover Ni, Mn and Co oxalates leading to PRE03, according to reaction:

$$Me^{2+} + C_2O_4^{2-} \leftrightarrow MeC_2O_4$$

Most lithium and other trivalent metals remain in the dissolution.

The precursors obtained from both BMs analysed (PRE03, 9) were characterized by AA and XRD (10). As expected, all diffraction maxima can be indexed to metal oxalates mainly nickel, cobalt and manganese. To calculate the composition of the solid, the obtained powder was subjected to a digestion process using aqua regia mixture until total dissolution. As mentioned before () the main components of the precursors are Ni, Mn and Co, with small quantities of impurities about 0,2% (Li, Cu and Fe).

Figure 9. Ni, Mn, Co oxalate (PRE03).

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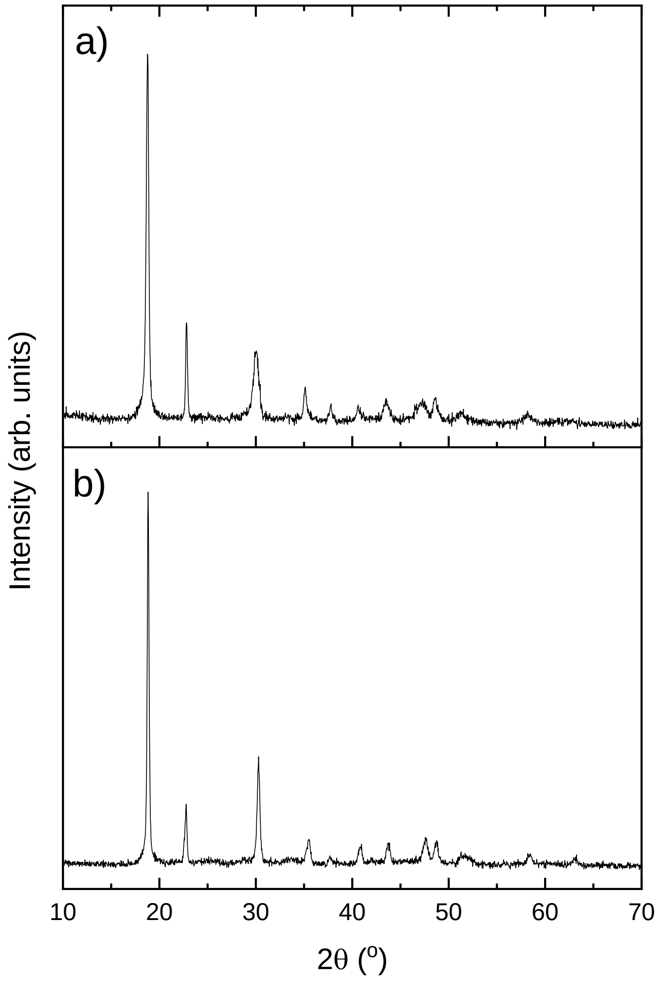

Figure 10. Ni, Mn, Co oxalates (PRE03) from (a) BM01 and (b) BM03.

Table 3. Chemical composition of PRE03.

% (w/w)	PRE03 from BM01	PRE03 from BM03
Li	0.24	0.11
Ni	16.05	14.47
Co	5.90	5.57
Mn	6.83	4.43
Al	-	-

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Fe	<0.01	<0.01
Cu	<0.01	4.78

This precursor (PRE03) will be used to synthetize cathode materials NMC622 and LMNO type.

To be able to synthesise low cobalt content cathodes, liquid-liquid separation was performed to separated Co. For this, the obtaining Ni, Mn, Co oxalate was leached using hydrochloric acid with a 10 M concentration. Acidic leaching was carried out using mechanical agitation at 60-80 °C until oxalate was total dissolved. The concentration of each leaching solution is showed in . The final solution was subjected to liquid-liquid separation process. The reagent used, a deep eutectic solvent selective to Co. Before performing liquid-liquid separation an acid leaching is needed.

Table 4. Chemical composition of dissolved oxalate leaching.

Concentration (g/L)	PRE03_dissol from BM01	PRE03_dissol from BM03
Li	0.10	0.09
Ni	6.42	6.01
Co	2.29	2.17
Mn	2.71	1.84

This dissolution (PRE03_dissol) was then put in contact with DES (1a), leading to PRE05 from BM01 and BM03, respectively. Once the organic phase is loaded with Co, the stripping of Co into an aqueous phase is performed using H_2SO_4 0.5M (1b).

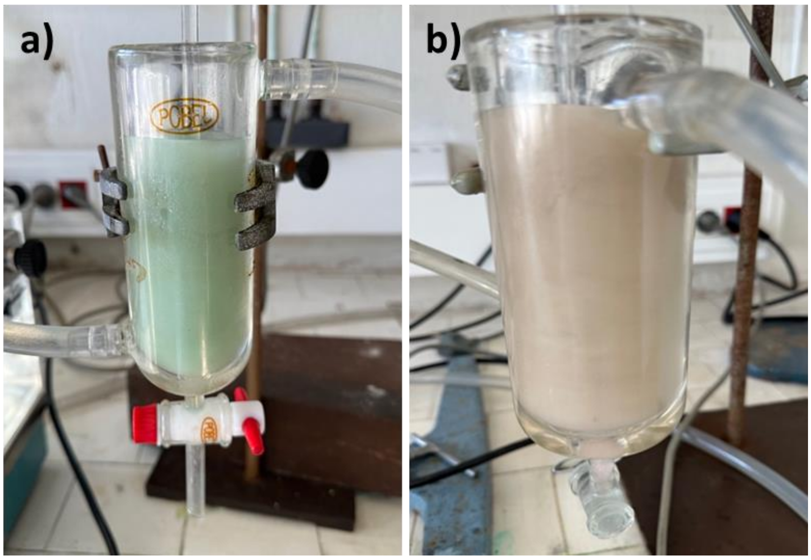

Figure 31. Extraction and re-extraction steps.

This aqueous solution containing Co, was evaporated using a rotavapor, and $CoSO_4$ was obtained (2). $CoSO_4$ (PRE04) was characterized by XRD and SEM (4). As it can be observed in 3, $CoSO_4.H_2O$ is the only mineralogical phase detected.

Figure 42. Photography of cobalt sulphate obtained.

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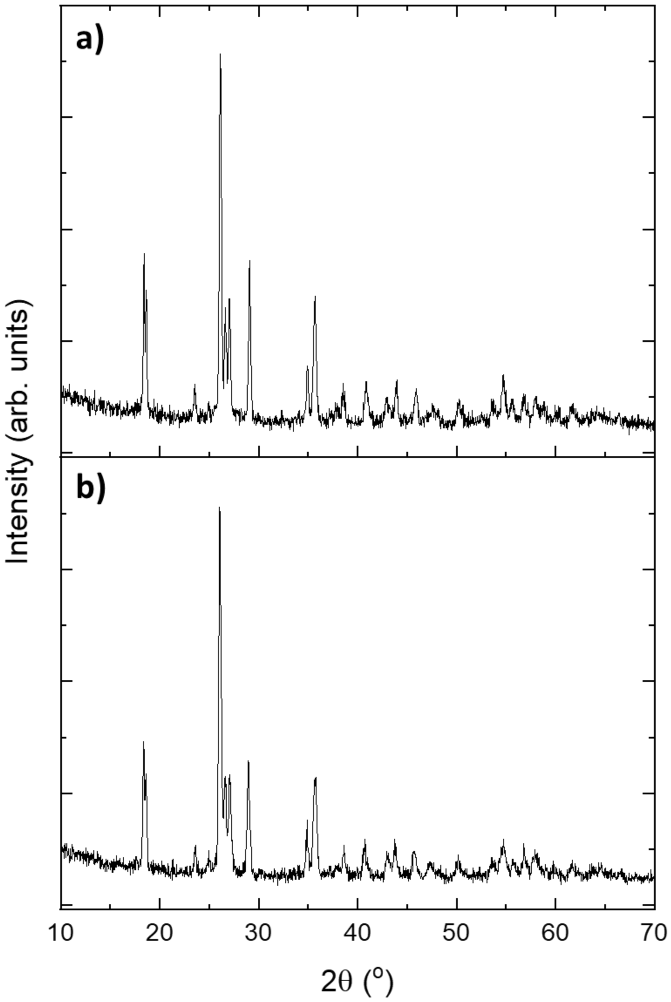

Figure 53. XRD patterns for $CoSO_4$ from (a) BM01 and (b) BM03.

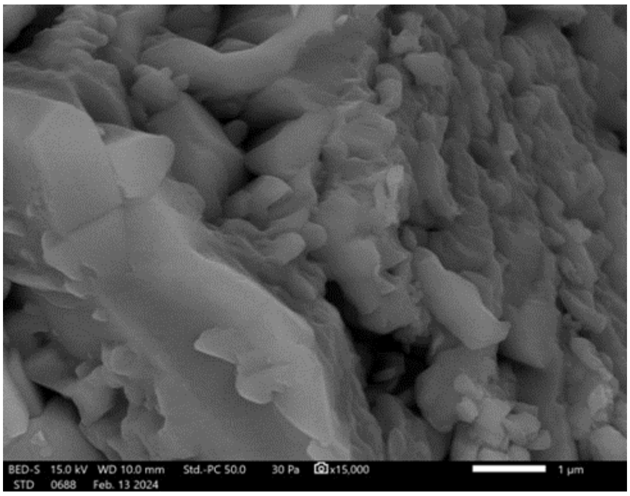

Figure 64. SEM image of $CoSO_4$.

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Despite this, after the digestion of both solids obtained small amounts of other impurities were also detected by AAS, as can be appreciated in .

Table 5. Chemical composition of $CoSO_4$ obtained from BM01 and BM03.

% (w/w)	PRE04 from BM01	PRE04 from BM03
Li	0.01	0.01
Ni	0.75	0.79
Co	13.41	17.68
Mn	5.06	5.99
Cu	-	7.81

Then, the aqueous phases after the separation of the Co-loaded organic phases were evaporated until the final Ni/Mn-precursors solids were reached. The chemical compositions of the solids were calculated from AA measurements after the digestion of the powders (see). XRD patterns are shown in 5. In these cases, metal oxalates/chlorides were obtained.

Table 6. Chemical composition of oxalate/chloride obtained after Co extraction.

% (w/w)	PRE05 from BM01	PRE05 from BM03
Li	0.36	0.33
Ni	20.28	22.15
Co	0.69	0.58
Mn	6.54	4.49
Cu	-	1.16

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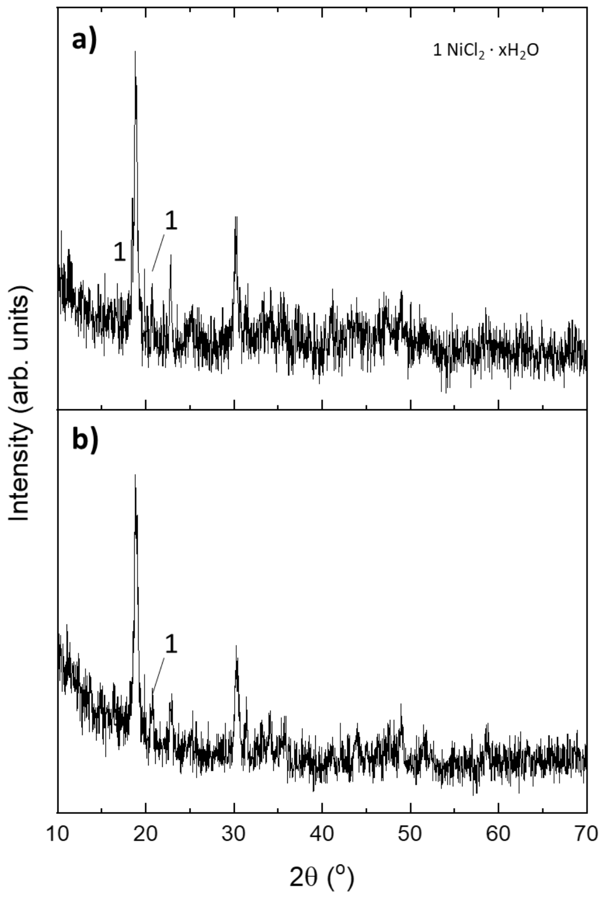

Figure 75. XRD patterns for PRE05 from (a) BM01, and (b) BM03.

3.2.1 Flame spray pyrolysis

One of the study routes for the recycling of black mass, considered in FREE4LIB project, is the conversion of this material into optimum and suitable metallic precursors to use on the Flame Spray Pyrolysis equipment. Through this technology, new recycled cathode materials would be synthesised. For a great development of this activity, a close contact between partners involved in the recycling process is essential. In that sense, Lurederra is in charge of the preparation of optimum recycled precursors for the FSP, while CSIC and CARTIF are the suppliers of recycled materials.

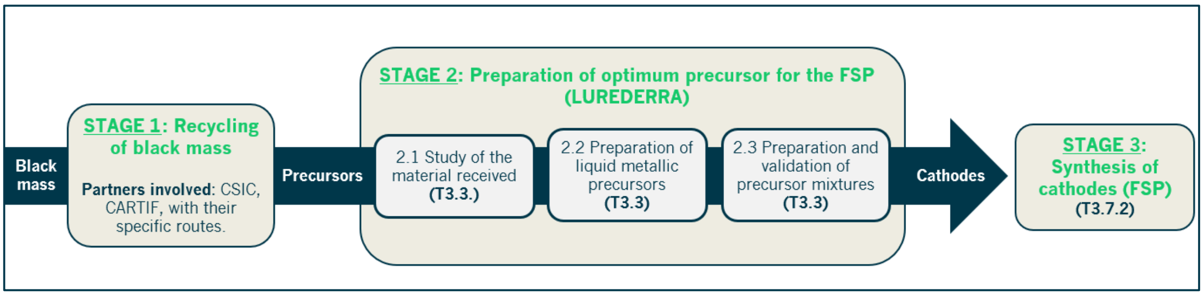

Figure 86. General overview of the process.

This section is divided in three sub-sections, introducing firstly, the main requirements a precursor should have to be useable on the FSP equipment. Second part refers to the different natures of samples studied and tested by Lurederra and the last part compiles and summarizes the conclusions achieved.

3.2.1.1 Main requirements

The Flame Spray Pyrolysis technology (FSP) is an industrially scalable technique for the development and production of nanoparticles. The process is based on the introduction of a liquid precursor mixture into a combustion chamber through a nozzle. This nozzle acts as an atomizer, dispersing the mixture and forming small droplets (a spray) which is burned in a flame and where the nanoparticles are formed very fast (7).

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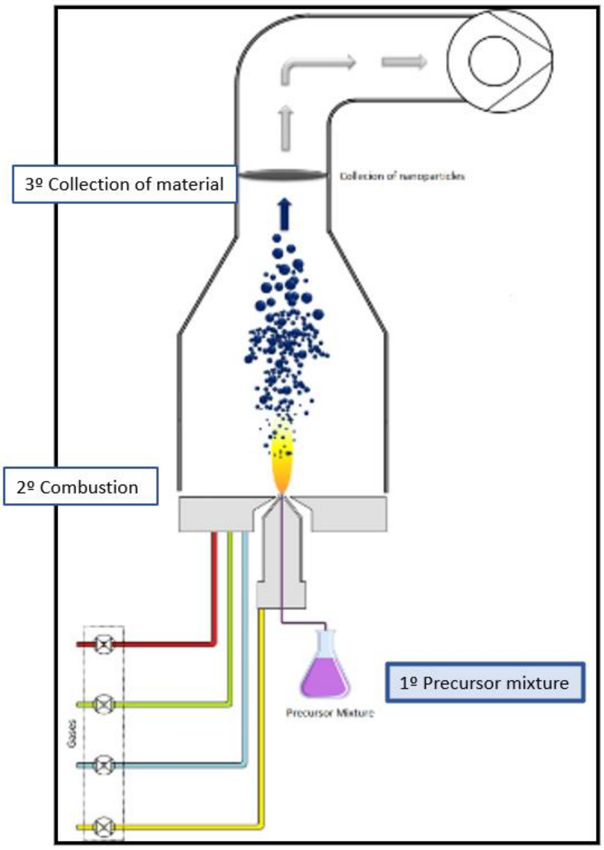

Figure 97. FSP equipment diagram with main stages: precursor mixture, combustion, and collection of material.

This section of the Deliverable 3.3, the activities are mainly related with the first stage of the process, preparation of precursor mixtures. The liquid precursor mixture refers to the solution of specific metallic compounds in a media. The formulation of these liquid mixtures is one of the most important steps for FSP particle synthesis. The selection of each of the materials (metal precursors and solvents) is crucial, because the products formed in the flame depends on it. There is a large number and a huge diversity of materials that can be used as source of metals, from organometallic nature like ethylhexanoates, acetylacetonates, butoxides, isopropoxides; to inorganic materials as nitrates, sulphates, and carbonates, among others. The physico-chemical properties and behaviour of each of these compounds, depend on its nature. Thus, getting the metals in the desired chemical structure is essential. At the end, suitable combustion enthalpies, melting/decomposition temperatures, miscibility, and chemical stability are characteristics that influence the overall particle formation in the flame which in turn determine the resultant particle properties.

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The target cathode compositions pre-defined in FREE4LIB project are NMC622, NMC811 and LiNMO, composed of nickel, manganese, cobalt, and lithium. Considering the information from literature, one important aspect to have in mind, is the specific low temperature conditions required for the production process in the FSP equipment. In that sense, to achieve this characteristic, several parameters of the precursor mixture are being adjusted. Main points to act are:

- **Quantify the metal composition of the material**. In this case, the recycled materials may need to be enriched with the other metal precursors to achieve the specific metal proportions of the desired cathodes. As source of enrichment, it would be possible to use both commercial and/or other recycled precursors. In both cases, the compatibility between them is an important study to carry out.
- **Capability to be solved in a liquid media.** A homogeneous solution is needed for being injected on the FSP equipment, in that sense, cations are required in a liquid media.
- **Capability of finetuning its physico-chemical properties.** Including viscosity, thermal properties as calorimetry...

The study starts by analysing the different metallic precursors available for the specific cations of interest. In this analysis, their physico-chemical properties are considered, focusing on the calorimetric properties, viscosity, and stability, as well as their compatibility with other precursors (in case of preparing a mixed oxide) and with the liquid media. The media is also another important point of study, as it gives the environment for the combustion.

With those precursors, specific precursor mixtures are prepared, optimised, and validated.

3.2.1.2 Recycled precursors

Since the start of this task, several recycled precursors have been received from different partners (CSIC and CARTIF). Depending on the progress on the recycling of black mass, materials with different chemical natures were obtained (oxides, carbonates, sulphates, oxalates...).

In this section, a detailed analysis of each type of recycled material received is explained, pointing out the difficulties that have been arise, and showing the work carried out, including best results up to now.

A) Mixture of metal oxides, metals, and graphite

As a product of the pyrometallurgical process of the black mass, CSIC obtained initially lithium carbonate and an insoluble residue containing other desired metals (Ni, Mn, and Co). Analysing the composition results provided by CSIC, it was identified that the residue was mainly based on graphite and a mixture of those metals and metallic oxides.

Figure 108. Residue from the leaching process.

Before working in deep with this black sample, a cleaning step to remove the graphite was required. Main reasons for carrying out this pre-treatment are that graphite is not part of the target cathode composition and additionally, if we keep it on the final precursor mixture, it may interfere on the formation of the particles or it could lead to the generation of potential impurities on the final material, since in the Flame Spray Pyrolysis the carbon is degraded.

Thus, different thermal treatments were studied, varying the temperature, as well as the duration of the test. In each case, the mass loss was calculated to know the efficiency of the conditions, as well as to be able to define and select the most favourable ones.

Table 7. % of mass loss obtained in the thermal treatment tested.

Step 1	Step 2	Step 3	Step 4
8.72	54.28	5	0.6

As shown on , most of the graphite is removed on *Step 2*, what means that following the thermal treatment of *Step 3* is enough for a preliminary cleaning of the residue. After that, several chemicals, digestion procedures and experimental conditions were tested trying to dissolve the resulted powder. In

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any case, a complete digestion of the sample was achieved. The mixture of chemical natures presents in this sample resulted in inhomogeneous behaviours that could not be managed for preparing FSP precursor mixtures (9).

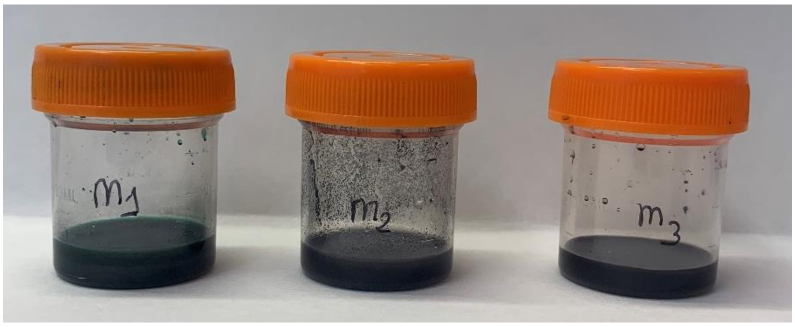

Figure 119. Solution tests of the residue.

B) Metal oxides

On the other hand, CARTIF supplied a cathode powder which was generated from a delamination process. This black powder was a mixture of metal oxides, with no graphite present on it, and basically, the composition was the pure cathode. Due to the similarity of this material to the previous one, an analogous procedure was followed. In this case, better results were achieved concerning the digestion process.

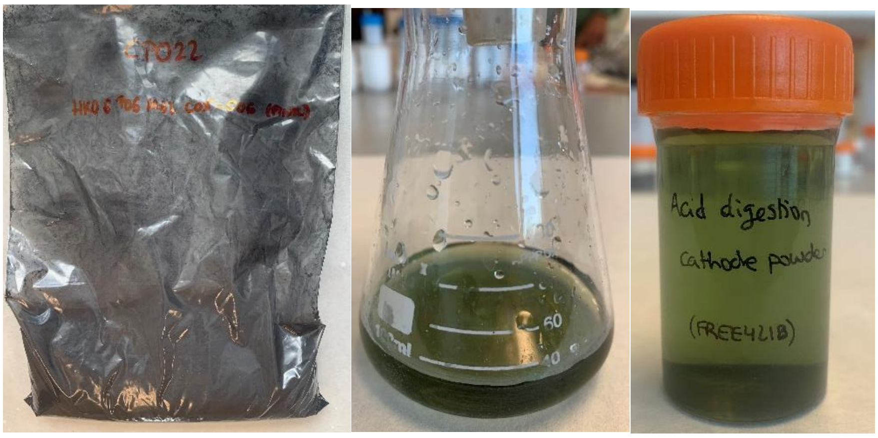

Figure 2012. Initial acid digestion of the cathode powder.

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Figure 131. Optimised acid digestion of the cathode powder.

Once a complete digestion was achieved (1), Lurederra went one step-forward to the preparation of the precursor mixture, the compatibility with several solvents was tested. As shown on 2. a clear, stable, and homogeneous solution was achieved, combining the digestion solution of the cathode powder with an alcoholic solvent.

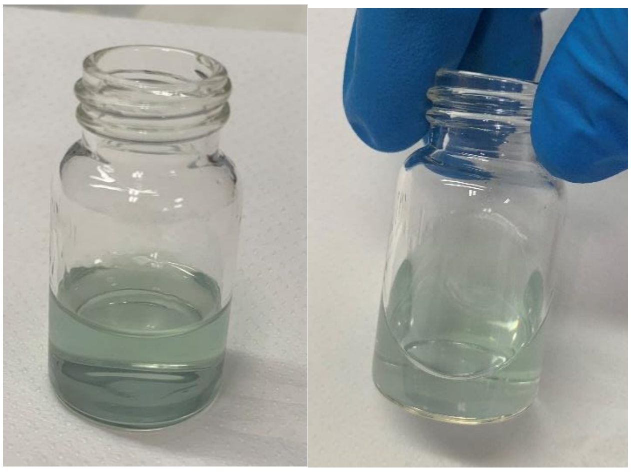

Figure 142. Combination of the digestion solution with an alcohol.

C) Metal carbonates

As mentioned before, CSIC managed to separate lithium from the rest of metals present on the black mass in form of lithium carbonate, through the pyrometallurgical process. Following a similar methodology, activities started with a thermal treatment to remove any possible impurity, avoiding the extra contamination that could be lead on the final cathode powder. From the different tests carried out, it was concluded that a light temperature was enough to completely clean the material.

Table 8. Mass loss of lithium carbonate on the selected thermal conditions.

Li_2CO_3 mass (g)	Temperature (°C)	% of mass loss
0.2135	450ªC	5.71

shows the optimum temperature for having the material cleaned. Next step was focused on studying the compatibility and behaviour of the powder in different liquid medias, testing alcohols and organic solvents, among others, as well as, several acids (organic and inorganic nature). The concentration of the solutions was one important factor that was adjusted in each of the cases.

Table 9. Compatibility tests of lithium carbonate on different media.

Acid	No solvent	Solvent 1	Solvent 2	Solvent 3
X	X	X	X	X
M1	OK	X	OK	X
M2	X	X	X	X
M3	OK	X	OK	OK

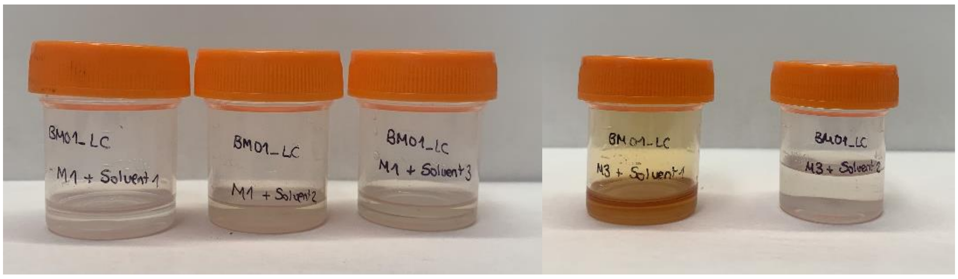

Figure 153. Solvent tests carried out with the lithium carbonate. Left) Two-phase solutions, Right) Homogeneous solutions.

As shown on and 3, complete solution of the powder and good compatibility results were achieved in several tests. The presence of a specific acid is required for helping the solution. In that sense, lithium carbonate could be used directly as a recycled lithium precursor. The most stable mixture was characterised, getting a calorimetry of 5624 cal/g.

On the other hand, it was considered to run an intermediate step, consisting on transforming the carbonate into another inorganic salt like nitrate, thus, getting a more easily-handled material, looking for avoiding the use of an acid. Two different chemical routes were studied to get lithium nitrate.

A) Chemical reaction with HCl. In the first stage of the reaction, lithium chloride was formed in the aqueous media. Then, adding silver nitrate, silver chloride precipitated and the lithium nitrate salt was kept on the solution. After a filtration step, the solution was dried to get the desired lithium salt.

$$Li_2CO_3 + 2HCl \rightarrow 2LiCl\,(ac) + H_2O + CO_2$$

$$LiCl + AgNO_3 \rightarrow AgCl\,(s) + LiNO_3\,(ac)$$

Figure 164. Lithium nitrate obtaining process from HCl reaction.

B) Chemical reaction with HNO_3. This route consists of a one-step reaction. Lithium nitrate is formed with the addition of HNO_3, and after a drying stage, a solid salt is reached.

$$Li_2CO_3 + 2HNO_3 \rightarrow 2LiNO_3 + H_2O + CO_2$$

Figure 175. Lithium nitrate obtaining process from HNO_3 reaction.

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Both salts generated were characterised to confirm the total transformation of the carbonate into the nitrate compound. In that sense, Lurederra, with the laboratory equipment available in their facilities, carried out an IR essay (6). The materials generated were compared with a commercial lithium nitrate, as well as, the starting sample (lithium carbonate).

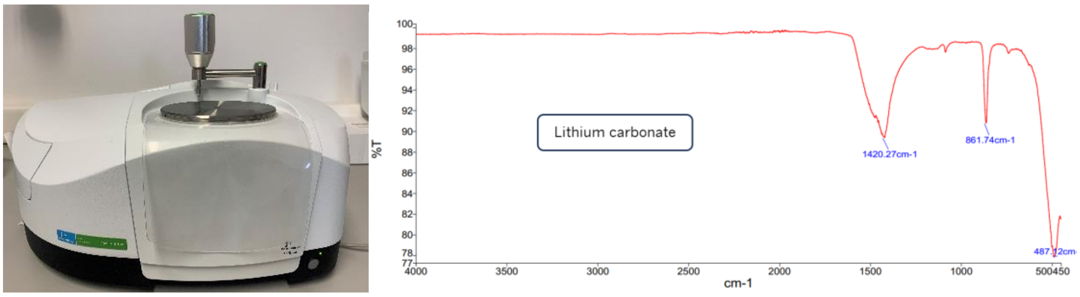

Figure 186. IR equipment and IR spectra of lithium carbonate sample (CSIC).

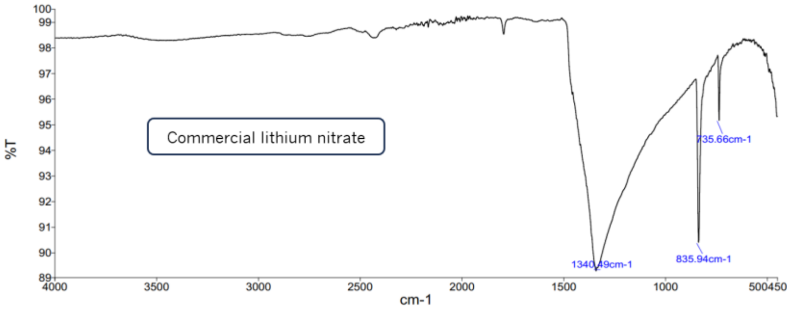

Figure 197. IR spectra from commercial lithium nitrate.

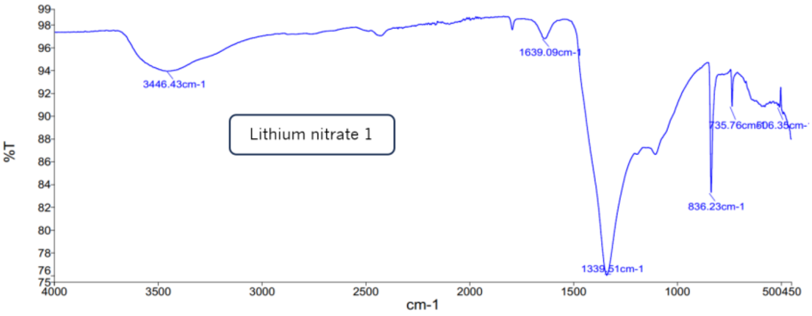

Figure 208. IR spectra from lithium nitrate obtained from chemical reaction with HCl.

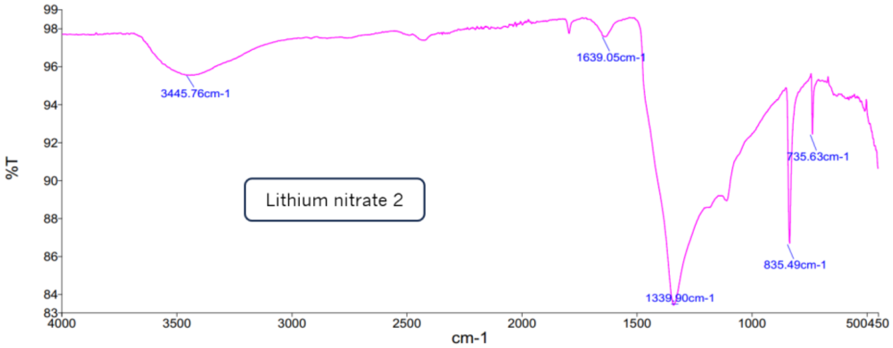

Figure 219. IR spectra from lithium nitrate obtained from chemical reaction with HNO_3.

As shown on the above pictures (6-9), a complete transformation of the lithium carbonate was achieved. After that, Lurederra proceeded to prepare a liquid recycled lithium precursor. This solution had the following physico-chemical properties: 0.25% of lithium content, viscosity of 1.8cP, calorimetry of 6753 cal/g and a good stability over time.

Figure 22. Steps of the conversion of recycled lithium carbonate into a liquid lithium recycled precursor.

Taking into consideration the results obtained, it was concluded that lithium carbonate was a suitable and versatile recycled material, since it could be used directly for FSP precursor mixture preparation by solution or transformation into nitrate. In any case, it could be used as main lithium precursor or for enriching other precursor materials with lithium content.

D) <u>Metal oxalates</u>

From the optimisation of the hydrometallurgical process carried out by CSIC, a new material was received. This material consisted of a mixture of metallic oxalates, mainly nickel oxalate, manganese oxalate and cobalt oxalates. A low proportion of lithium oxalate was also present on the powder. Preliminary research about the chemical behaviour of the respective individual oxalates was carried out, to clearly define the procedure to follow. Those salts have a low decomposition temperature, so no thermal treatment was done trying to avoid the conversion of those salts into the corresponding oxides.

Table 10. ICP results of mixed oxalates and adjustment of metal proportions to get the target new compositions.

wt%	%Ni	%Mn	%Co	%Li
Mixed oxalates	16.05	6.53	5.90	0.24
NMC622 target	+38.2	+10.4	+12.74	+10.0
NMC811 target	+55.4	+1.84	+3.90	+11.0

Lurederra proceeded with a direct acid digestion of the powder received. Several conditions were tested, varying the acids used (HCl, HNO_3, H_2O_2...), as well as the temperature.

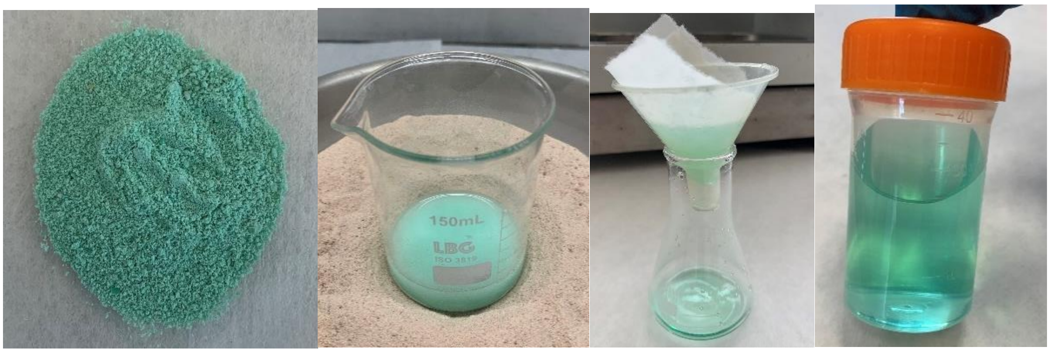

Figure 231. General overview of the acid digestion carried out for the mixed oxalates.

Finally, a complete and homogeneous digestion solution containing all the cations was achieved (). Then, tests of compatibility with different solvents were carried out, identifying the most favourable media for later finetuning the physico-chemical properties of the precursor mixture. On the following picture (), it is shown the result of mixing the oxalates solution with different medias. Although S3 showed a two-phase solution, the two other tests concluded in a good a homogeneous solution.

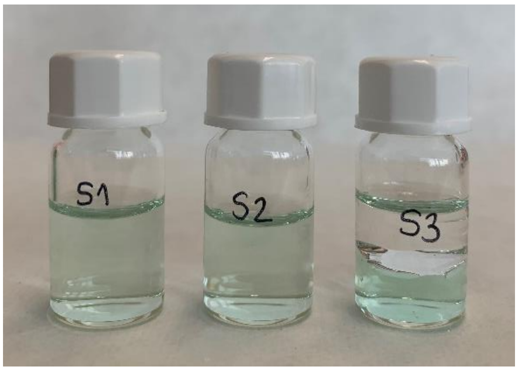

Figure 24. Compatibility tests with different media.

3.3 Combined pyro-hydrometallurgical process

As it was mentioned before, hydrometallurgical process has the disadvantage at the moment, that lithium remains in the solution. The research is on-going to recover also Li after precipitation process, but in order to recover Li from black mass a different recycling process was carried out. This process consists of a two steps process: a pyrometallurgical process followed by a hydrometallurgical process to recover most of the valuable metals contained in BM. It should be noted that the process was carried out from BM01 and BM03 black masses for comparison purposes.

The first step of the process, the pyrometallurgical one, was performed following a CSIC previous patent, that consists of perform a carbothermic reduction, using reducing agents at different temperatures, in the range of 700-850ºC.

To carry out the carbothermic reductions, different mixtures of each black mass and reducing agent, were prepared modifying the reducing agent proportion. The different proportions for each mixture of BM/reducing agent were completely homogenized. The mixtures were loaded in an alumina crucible and placed on a tubular Carbolite furnace at different temperatures. N_2 gas carrier was introduced in other to create an inert atmosphere. The samples were introduced into the furnace at a set temperature.

After the carboreduction reactions tests, the reduced black mass was leached using water at room temperature for 2 h considering the low solubility of lithium carbonate with a solid/liquid ratio of 200 g/L for selective Li recovery. After that, the final suspensions were filtered, and the obtained solutions were evaporated until a white solid (Li_2CO_3, PRE01) was achieved. For this purpose, the solid residue obtained in the first leaching reaction is subjected to a new water leaching process under the same conditions as in the previous leaching. After a new filtration, the liquid obtained is evaporated obtaining a new white solid (Li_2CO_3, PRE01) which is subsequently characterized. In all evaporation stages, the water obtained is reused in the water leaching operations. Finally, after this last water leaching, a final solid (PRE02) is obtained from which the rest of the metals contained in the black mass. The final solid will be used for further Ni, Co, and Mn recovery processes.

Both precursors were characterized by AA and XRD. Particles agglomerates was found from the SEM micrographs after the carboreduction step, and water leaching ().

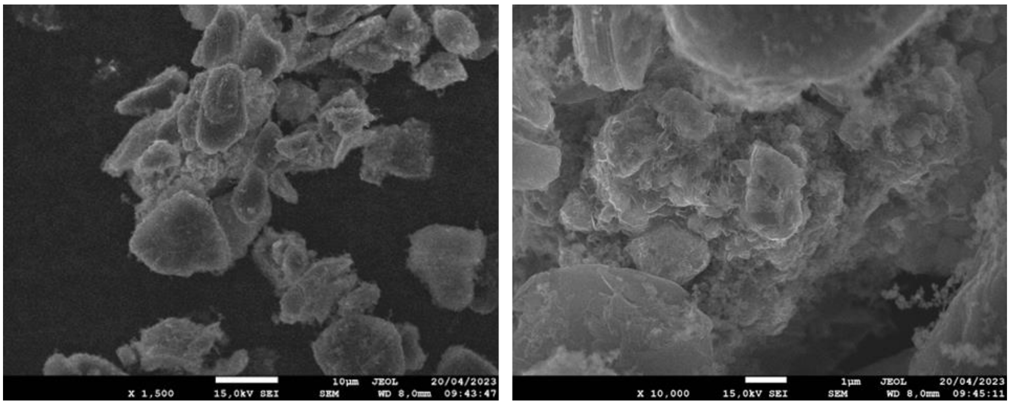

Figure 25. SEM images for PRE02 precursors.

PRE01 is mainly composed by Li_2CO_3, with impurities of LiF (&).

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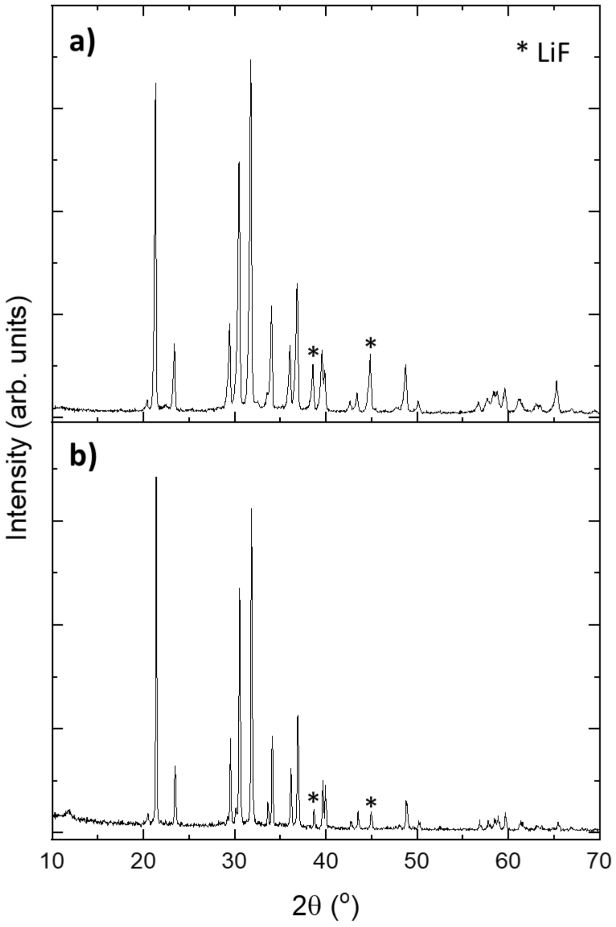

Figure 26. XRD for PRE01 precursors.

Table 11. Chemical composition of PRE01 by AA.

% (w/w)	PRE01 from BM01	PRE01 from BM03
Li	17.29	17.44
F	0.85	0.61
P	0.09	0.06

Mineralogical composition calculated from the chemical composition of PRE01 is shown in .

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Table 12. Mineralogical composition calculated for PRE01 precursors by AA.

	PRE01 from BM01	**PRE01 from BM03**
Li_2CO_3	90.59%	91.98%
LiF	1.15%	0.83%
Li_3PO_4	0.31%	0.23%

Figure 27. Li_2CO_3 photography.

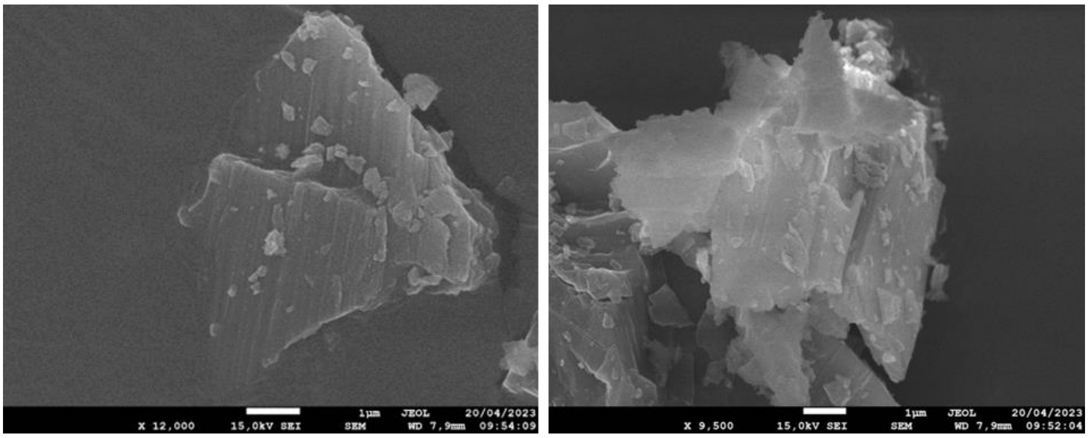

Figure 28. SEM images for PRE01 precursors.

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Table 13. Chemical composition of PRE02 by AA.

% (w/w)	PRE02 from BM01	PRE02 from BM03
Li	1.21	0.59
Ni	12.58	15.94
Co	4.31	4.99
Mn	3.98	4.68
Al	3.50	2.15
Fe	0.01	0.04
Cu	0.50	2.47

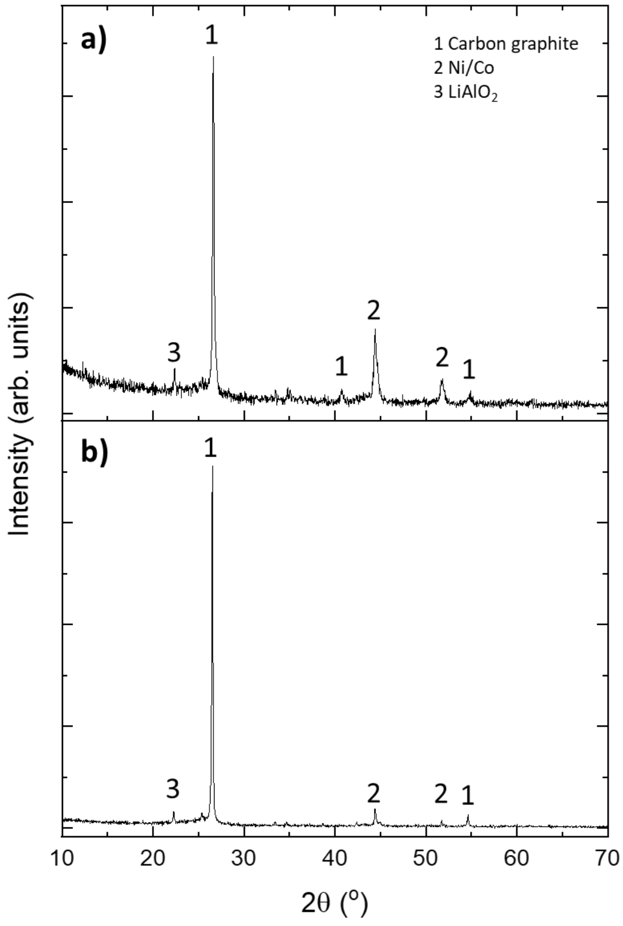

Figure 297. XRD for PRE02 precursors from (a) BM01, and (b) BM03.

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PRE02 is mainly composed by Ni, Co, Mn and Al, with still some content of Li (). The mineralogy () is mainly composed by graphite, and shows that some metals (Ni and Co) have been formed during the carbothermic reduction. As can be appreciated in , the compositions of PRE02 samples show lower amount of Li than the initial black mass, indicating that Li was successfully recovered.

The leaching experiments of PRE02 to recover Ni, Co and Mn was carried out. In this sense, PRE02 precursors were subjected to malic acid leaching, leading to PRE02_2 solids. Chemical composition is shown in . As can be appreciated, metal content has significantly been reduced.

Table 14. Chemical composition of PRE02_2 by AA.

% (w/w)	PRE02_2 from BM01	PRE02_2 from BM03
Li	0.08	0.08
Ni	2.54	3.19
Co	0.92	0.86
Mn	0.05	0.05
Fe	<0.01	<0.01
Cu	2.25	2.15

Subsequently, the leached solution obtained was precipitated to recover Ni, Mn and Co oxalates. The precursor obtained (PRE03_2) was characterized by XRD and AA. XRD patterns shown that Ni, Mn, Co oxalates was obtained ().

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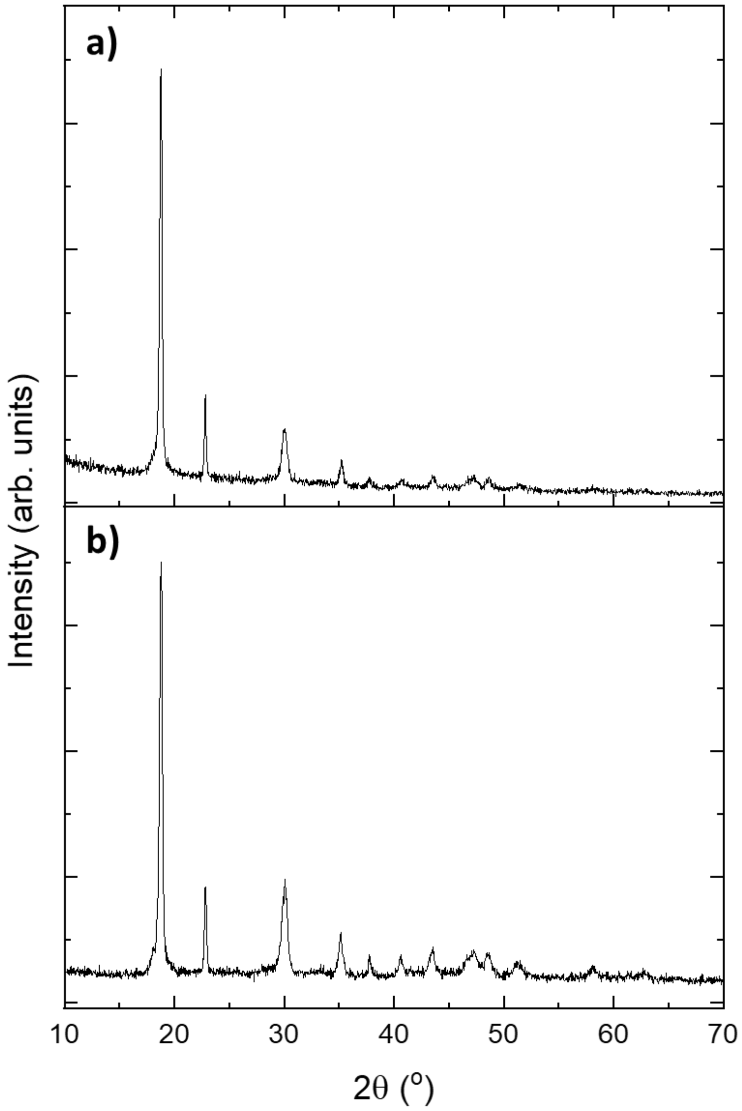

Figure 30. Ni, Mn, Co oxalates from (a) BM01 and (b) BM03 BMs.

Table 15. Chemical composition of oxalates obtained.

% (w/w)	**PRE03_2 from BM01**	**PRE03_2 from BM03**
Li	0.11	0.08
Ni	17.91	17.44
Co	5.71	5.48
Mn	4.59	6.11

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Cu	0.03	0.01
Fe	0.004	0.004

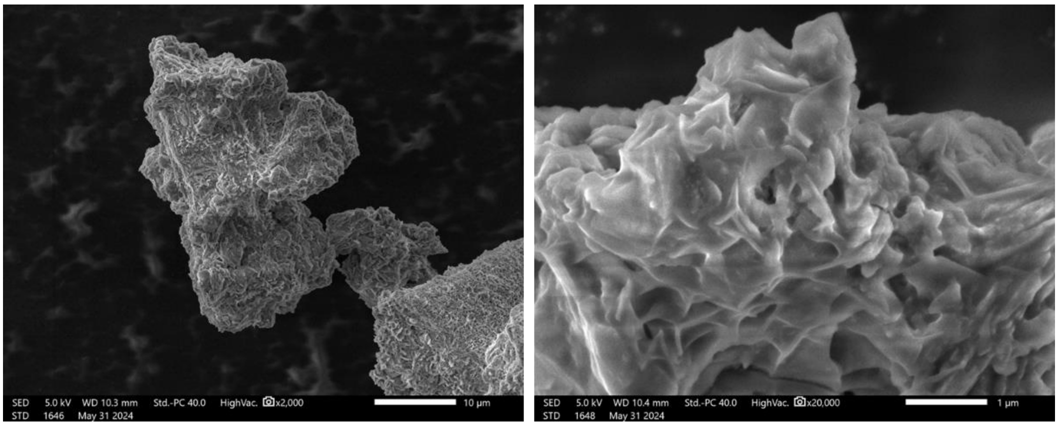

Figure 31. SEM images for the PRE03_2 samples.

As previously described, the final obtained solid was acidic leached using hydrochloric acid with a 10 M concentration. Then, the final metals mixture was subjected to liquid-liquid extraction process as-previously described.

After that, re-extraction step was carried out as previously described, and the obtained solids was characterized by XRD () and AAS ().

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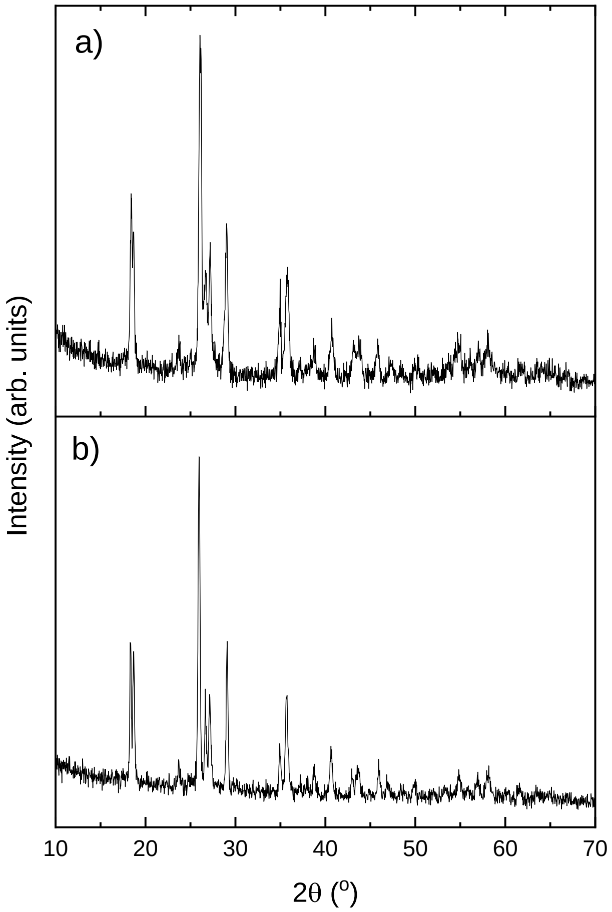

Figure 32. XRD for PRE04_2 from (a) BM01, and (b) BM03.

Table 16. Chemical composition for PRE04_2 solids.

% (w/w)	PRE04_2 from BM01	PRE04_2 from BM03
Li	<0.01	0.01
Ni	1.46	0.79
Co	20.38	17.68
Mn	9.58	5.98
Cu	0.99	7.81
Fe	<0.01	<0.01

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After cobalt separation, the obtained solution (which mainly contain Ni and Mn) was evaporated until a greenish solid was reached. The chemical composition for the solid was calculates from AA measurements after digestion of the powder. As can be appreciated in , only small amounts of Co were detected.

Final solid was also characterized by XRD (see), where some diffraction maxima which can be indexed to Ni/Mn-oxalate as well as nickel chloride were found.

Table 17. Chemical composition of oxalates/chlorides after Co extraction obtained.

% (w/w)	**PRE05_2 from BM01**	**PRE05_2 from BM03**
Li	0.14	0.10
Ni	25.63	22.22
Co	0.65	0.56
Mn	4.55	5.37
Cu	0.01	0.006
Fe	0.01	0.03

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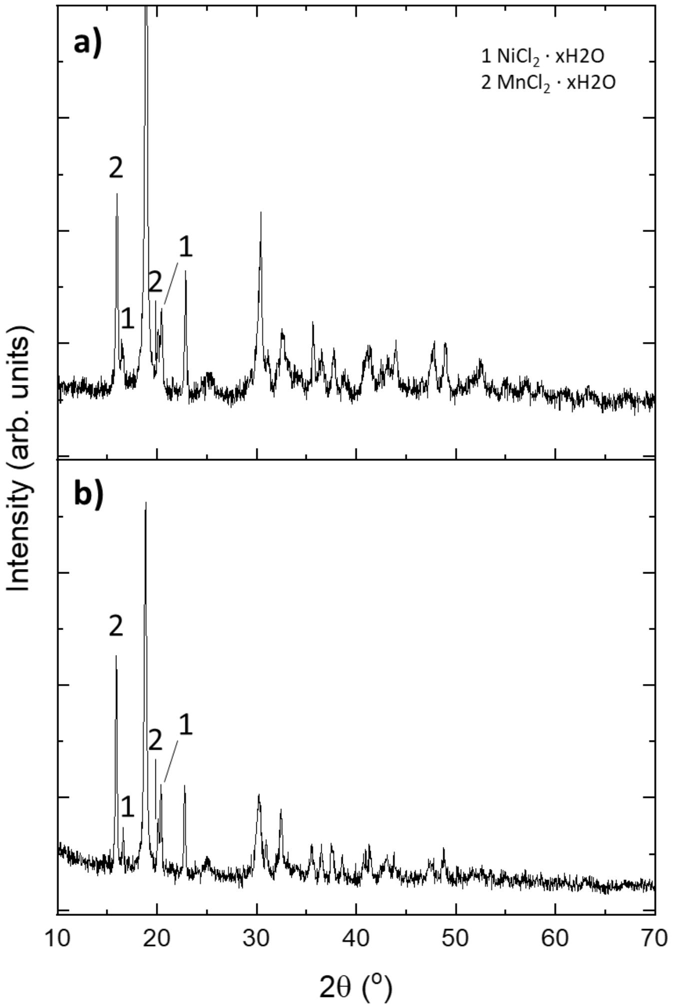

Figure 33. XRD patterns for PRE05_2 samples from (a) BM01, and (b) BM03.

As an example, shows SEM micrograph for the solid obtained where non-regular shape was observed.

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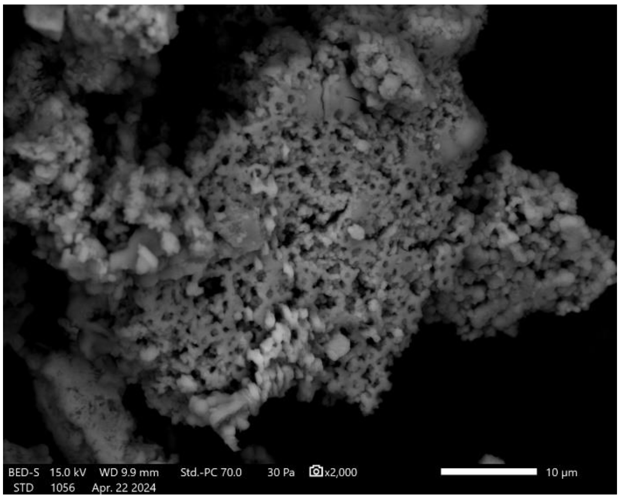
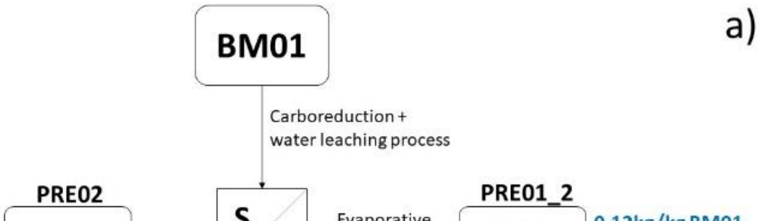


Figure 34. SEM micrograph for the PRE05_2 from BM01 sample.

In summary, diagram for the pyro-hydrometallurgical process for each black mass is shown in . The obtained amount for each precursor obtained is also exhibit per black mass kilogram in it. Kg/kg BM (blue), the recovery of each metal (green), mineralogical phases (dark grey) for each step are exhibit in the . As can be appreciated, after the carbothermic reduction reaction and water leaching, non-soluble residues with high metals content were obtained. Li was recovered as Li_2CO_3 after evaporative crystallization. 0.09 kg/kg BM01 and 0.11 kg/kg BM03 were obtained. However, after the malic acid leaching, metals content was significantly reduced. In this sense, 0.76 and 0.63 kg per kg BM were obtained. After the malic acid leaching, oxalic acid was added in order to obtain PRE03_2 solids, which were principally metals oxalates. The obtained precursors contain a significant amount of Ni, Mn, Co metals while the calculated amounts of monovalent and trivalent metals (such as Li, Al) were despicable. For the investigated black masses, 0.58 kg and 0.50 kg were obtained per kg BM01 and BM03, respectively. In order to carry out the cobalt separation, liquid-liquid extraction process was investigated. After that, two different precursors were obtained then (i.e. PRE04_2, and PRE05_2). 0.10 kg/kg BM and 0.09 kg/kg BM as well as 0.32 kg/kg BM and 0.23 kg/kg BM were obtained from BM01 and BM03, respectively. Finally, summarizes the obtained results for each black mass.



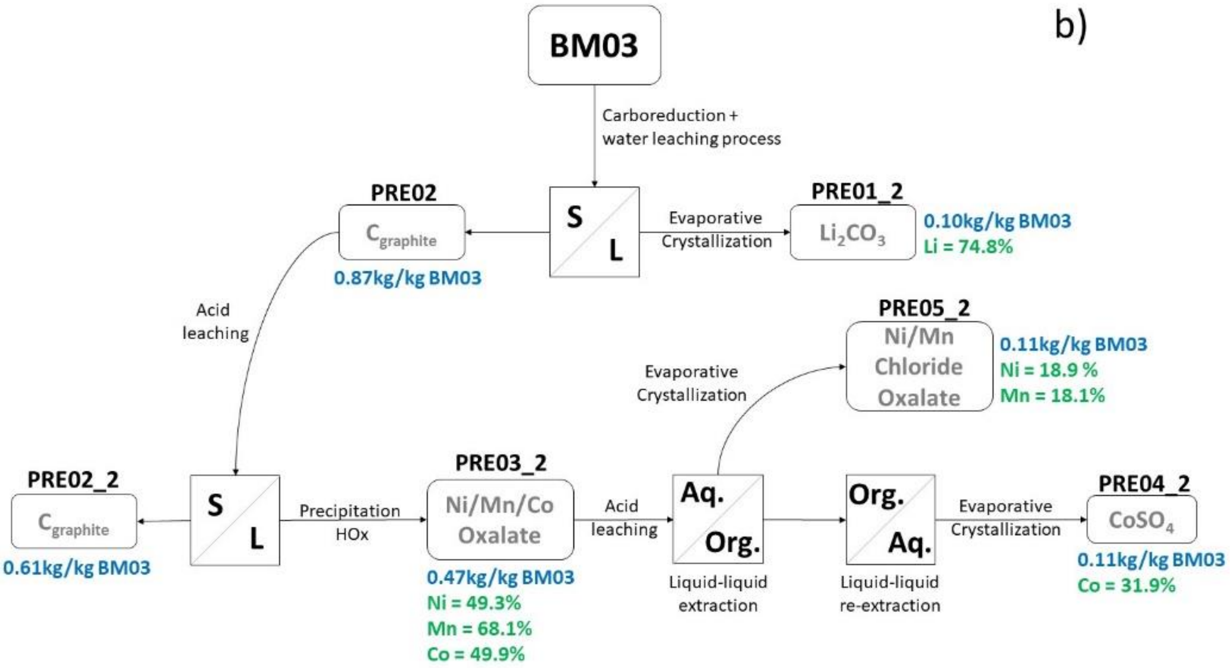


Figure 35. Pyro-hydrometallurgical process diagram for (a) BM01, and (b) BM03.

Table 18. Comparative results obtained for each black mass.

	Mineralogical phase	BM01		BM03	
		kg/kgBM	Recovery (%)	kg/kgBM	Recovery (%)
$C_{graphite}$	Impurified $C_{graphite}$	1.11	-	0.87	-
$C_{graphite}$	Purified $C_{graphite}$	1.03	-	0.61	-
Li	Li_2CO_3	0.12	69.1	0.10	74.8
Ni	Ni,Mn,Co oxalate	0.53	73.01	0.47	49.3
Mn			59.1		68.1
Co			67.9		49.9
Co	$CoSO_4$	0.09	50.9	0.11	31.9
Ni	Ni,Mn oxalate/chloride	0.33	75.3	0.11	18.9
Mn			39.2		18.1
Co			5.5		1.5

4. Cathode direct recycling processes at lab-scale

4.1 Re-lithiation and electrochemical re-lithiation of cathodes

Due to the capacity degradation associated with lithium loss in spent LIBs, recent direct recycling processes have mainly focused on recovering this lost lithium through re-lithiation, since traditional recycling destroys the original structure of LIB materials, resulting in recycled products that, cannot be directly used to make new batteries[i]. Thus, there is an urgent need to develop efficient recycling technologies. CARTIF has investigated two different methods: **hydrothermal** and **electrochemical** re-lithiation.

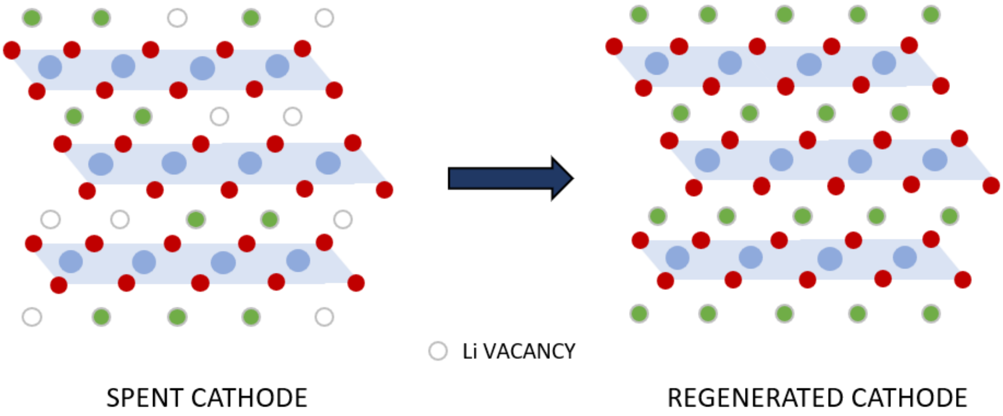
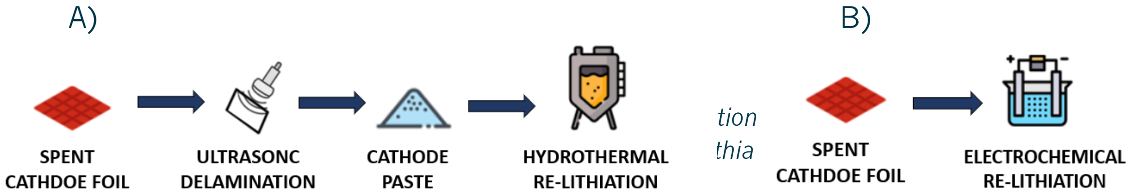


Figure 43. Schematic of the direct regeneration of cathode material.

For the electrochemical re-lithiation technique, cathode sheets obtained from manual dismantling (ST3.2.3) described in Deliverable D3.2, were used. For hydrothermal re-lithiation, cathode active material (CAM) in its solid form obtained from ultrasonication delamination (ST3.2.3) described in Deliverable D3.2, was used.



4.1.1 Hydrothermal re-lithiation

Hydrothermal re-lithiation is a promising method for direct recycling spent lithium-ion batteries (LIBs). This process involves treating spent battery materials with a solution containing an excess lithium source, allowing the added lithium to integrate into the structures of the spent cathodes[ii]. It is a highly controlled process, and key parameters, which must be precisely controlled and adjusted during the process, are temperature, pressure and reaction time. Those conditions are crucial and must be carefully adjusted to achieve the re-lithiation of CAM.

The following section outlines the detailed procedure and experimental setup used for hydrothermal re-lithiation, as well as the characterization of the re-lithiated materials.

- **Hydrothermal re-lithiation experimental setup**

Figure 45 shows the experimental setup for the direct regeneration test. In the hydrothermal re-lithiation process, a concentration of powder cathode obtained from the ultrasonic delamination process, is added to a high-pressure reactor containing a hydroxide lithium solution (LiOH), and then it is heated to the desired temperature. The temperature and pressure are maintained throughout the reaction duration. After the reaction time elapsed, the reactor content is filtered to separate the solid CAM from the liquid phase. First, the washed solid CAM is dried in an oven and then the dried material is annealed in a muffle furnace to enhance crystallinity and ensure thorough re-lithiation.

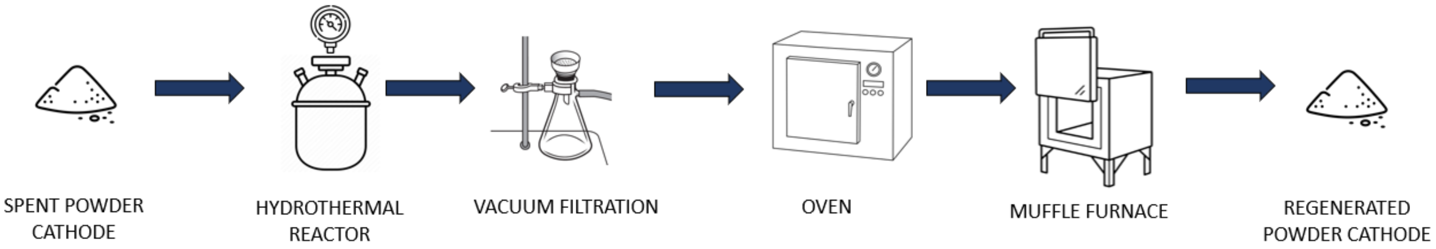


Figure 45. Hydrothermal re-lithiation experiment setup.

In order to achieve the optimal conditions of the hydrothermal process, a 3x2x2 full factorial design was carried out, to identify which variables (temperature, reaction time and lithium solution concentration) and combinations of variables have a significant effect on re-lithiation. The total number of combinations or tests that were carried out was 12 (Table 19).

Table 19. Experimental design for hydrothermal re-lithiation.

Test	LiOH concentration (M)	Temperature (°C)	Reaction time (hours)
1	4	160	2
2	4	160	1
3	4	220	2
4	4	220	1
5	2	160	2
6	2	160	1
7	2	220	2

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8	2	220	1
9	0.5	160	2
10	0.5	160	1
11	0.5	220	2
12	0.5	220	1

- **Hydrothermal Re-lithiation Procedure**

The reactor was loaded with the spent cathode powder at 50 g/L with a LiOH solution (Figure 46). The pressure can vary according to the process and the phase of the materials involved, although in this case it was fixed by the temperature (at 160ºC → P ≈ 5.5 bar and at 220ºC → P ≈ 21.5 bar). Once the re-lithiation process in the reactor is completed, the re-lithiated cathode material was filtered and washed with deionized water to remove any LiOH residue and then dried at 90°C for 24h (Figure 47). The dried cathode material was annealed in a muffle furnace at 850°C for 4h to reconstruct the material's crystallinity and enhance the restoration of its original structure (Figure 48).

Figure 46. Hydrothermal re-lithiation beginning.

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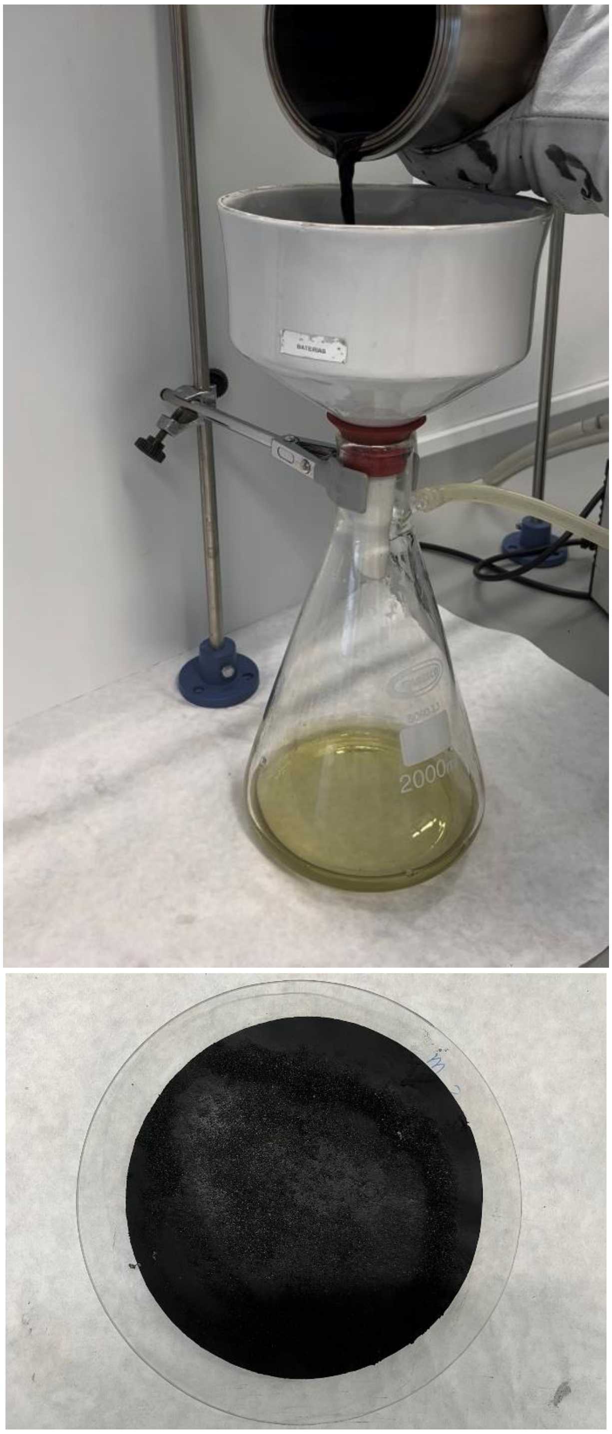

Figure 47. Filtered cathode material after hydrothermal re-lithiation.

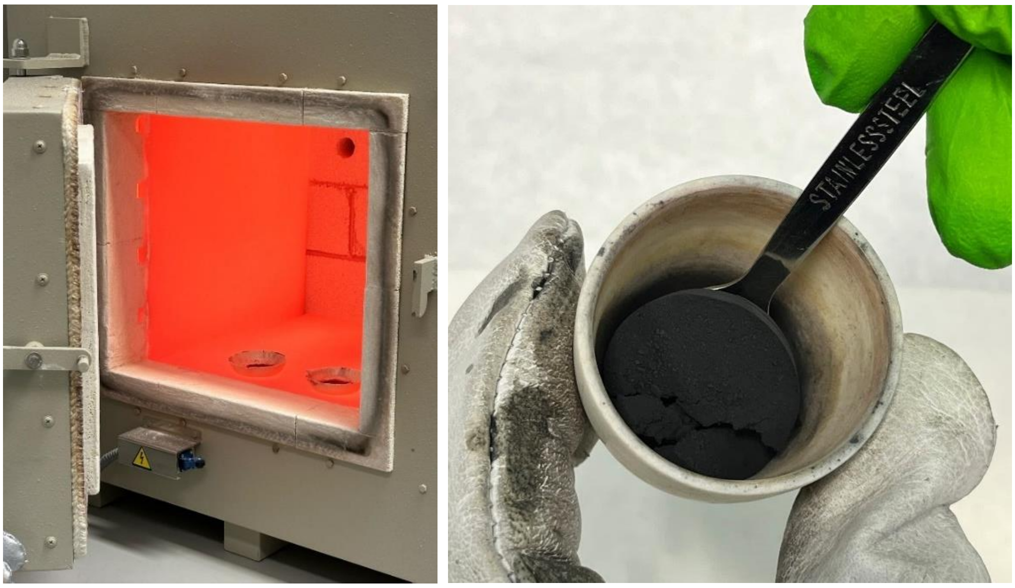

Figure 48. Cathode material annealing.

At the end of each experiment, four samples were obtained: the initial LiOH solution, the filtered solution, the solid after drying in oven, and the solid after annealing in muffle furnace (Figure 49). All samples were analysed by Inductively coupled plasma mass spectrometry (ICP-MS) to quantify the metal content in both the solid fraction and the filtrate post solid-liquid separation. These sample results enabled the evaluation of lithium recovery efficiency in the cathode powder.

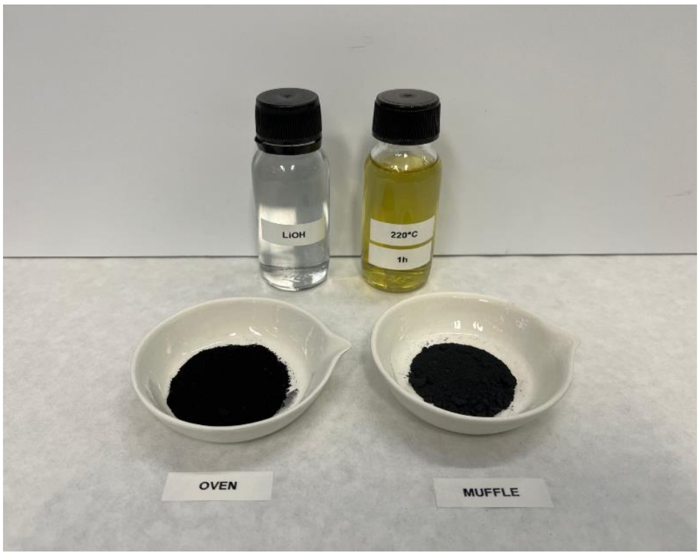

Figure 49. Samples obtained after a hydrothermal re-lithiation experiment.

- **Results and Discussion**

After hydrothermal re-lithiation, the Li composition of the regenerated cathode materials was measured by ICP-MS. To compare the results of experimental design and calculate the efficiency of the hydrothermal re-lithiation, it was necessary to know the baseline metal content of the initial cathode powder. All results are summarized in Table 20.

Table 20. Composition of the degraded and regenerated cathode materials.

	Li/(Ni+Mn+Co)
Degraded CAM	0.928
Test 1	1.046
Test 2	1.103
Test 3	0.908
Test 4	0.936
Test 5	0.924
Test 6	0.938
Test 7	0.951
Test 8	0.962
Test 9	0.886
Test 10	0.862
Test 11	0.877
Test 12	0.838

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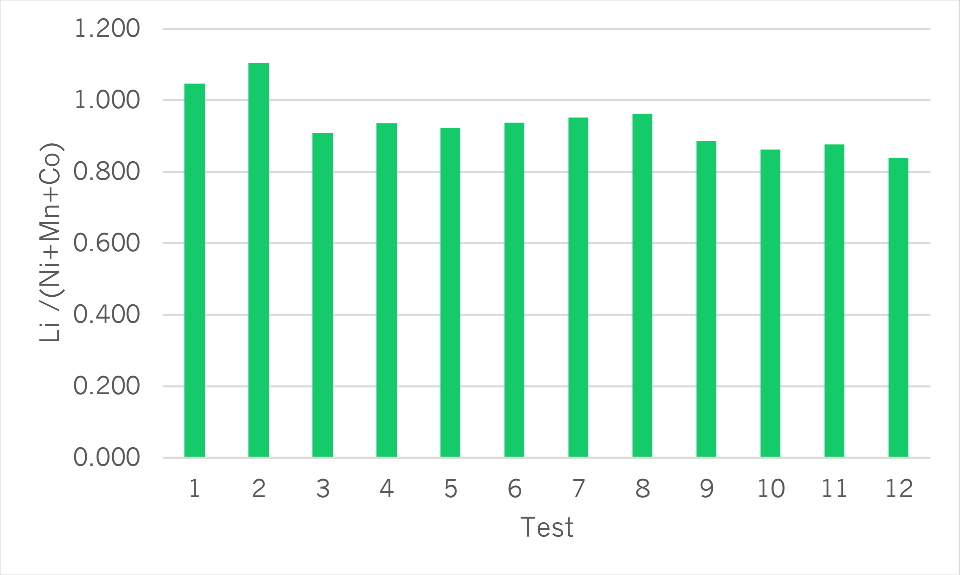

Figure 50. Li composition of the regenerated cathode materials.

The Li concentration of degraded CAM was 0.928, which is not perfect stoichiometry. Figure 50 shows that for practically all hydrothermal treatment test the Li concentration of regenerated CAM has improved with respect to degraded one. In TEST 1, 2 and 8, the Li stoichiometry increased to 1.046, 1.103 and 0.962, respectively. Based on these results, it is important to continue investigating how other factors could influence the hydrothermal re-lithiation process.

The cathode material before and after hydrothermal re-lithiation was characterized to observe morphological and microstructural changes. Figure 51 (a,b) shows the SEM images, and Figure 51 (c,d) presents the elemental composition of the surfaces analysed by energy dispersive X-ray spectroscopy (EDS). Characterization was performed using an acceleration voltage of 20 kV and a working distance of 10 mm.

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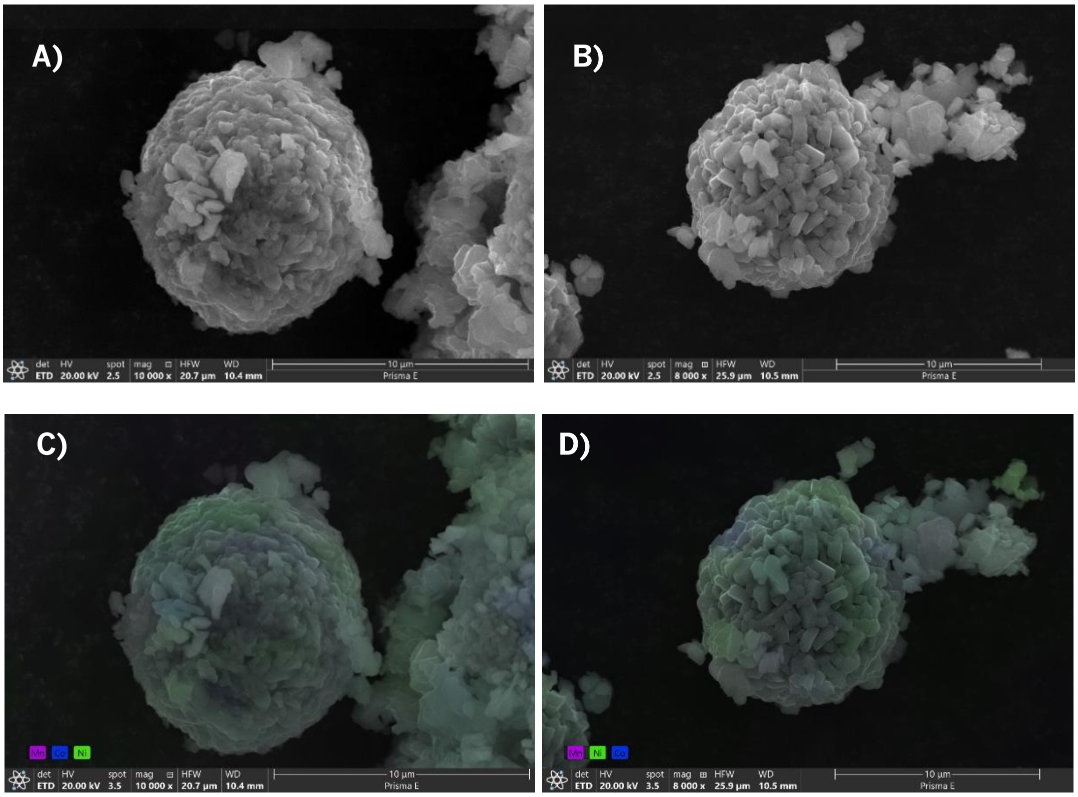

Figure 51. SEM images of the cathode active material a) Degraded b) Regenerated. EDS imagens of the cathode active material c) Degraded d) Regenerated.

SEM image of the degraded and regenerated CAM showed that its morphology consists of spherical particles. Figure 51B shows an important difference between the degraded and regenerated cathode material: before the hydrothermal process, the particles did not have a crystalline structure, while the cathode material after the regeneration process has been able to recover this structure. EDS imagens indicated that the material is composed of nickel (green), manganese (purple), and cobalt (blue), which are characteristic components of an NMC battery, which a predominance of the green colour, since it is an NMC622 battery.

4.1.2 Electrochemical re-lithiation

Electrochemical re-lithiation is another technique for restoring lithium content in CAM through a direct recycling process. In this method, lithium-deficient cathode material is brought into contact with a solution containing lithium ions in an electrochemical cell (Figure 52). This cell is formed by immersing a working electrode (WE), a counter electrode (CE), and a reference electrode (RE) in the lithium ion solution.

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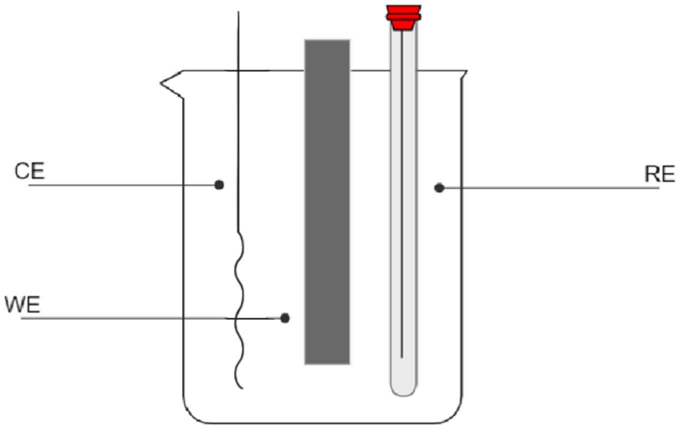

Figure 52. Electrochemical cell

In this process, the lithium-deficient cathode material (Li_xNMCO_2) undergoes a re-lithiation reaction by incorporating lithium ions (Li^+) from the solution, leading to the formation of a fully lithiated cathode material (Li_2NMCO_2). The redox reactions occurring at the CE and the WE during the re-lithiation of the Li_xNMCO_2 foil are shown below[iii].

$$\text{CE: } 4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad (1)$$

$$\text{WE: } Li_xNMCO_2 + (1\text{-}x)\, Li^+ + (1\text{-}x)\, e^- \rightarrow Li_2NMCO_2 \quad (2)$$

These redox reactions drive the re-lithiation process, effectively restoring the lithium content in the cathode material and demonstrating a promising approach for recycling lithium-ion batteries. This method can enhance the efficiency and sustainability of battery recycling, contributing to the circular economy by reducing the need for new raw materials and minimizing waste.

- **Electrochemical re-lithiation experimental setup**

An electrochemical device was set up for regeneration of NMC materials. It includes a working electrode, reference electrode and a counter electrode.

In the Figure 53, the spent cathode foil used in experimentation is shown.

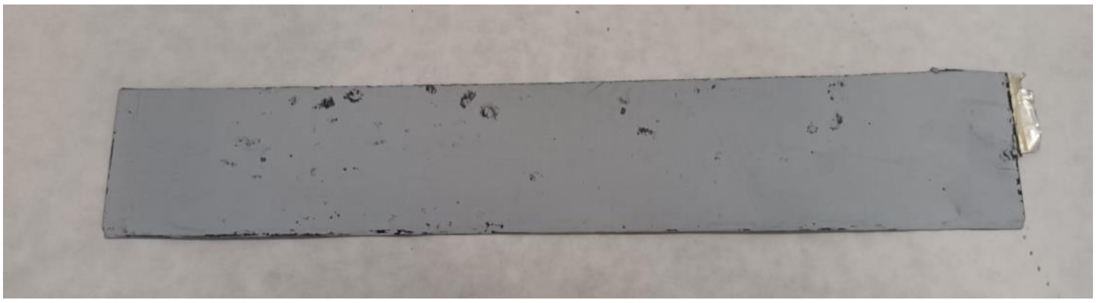

Figure 53. Spent cathode foil used in experimentation.

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Electrochemical measurements were carried out using a potentiostat-galvanostat OrigaFlex (Figure 54). During the experiment, solution samples were collected to monitor the variation in the concentration of Li^+ ions using ICP analysis.

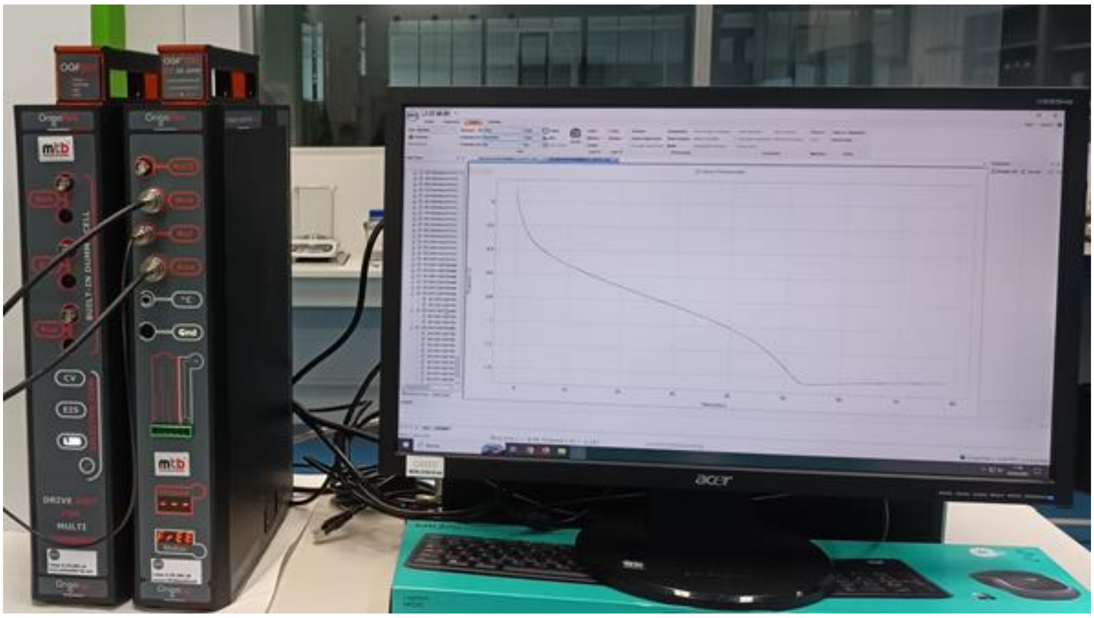

Figure 54. Potentiostat-galvanostat OrigaFlex

- **Electrochemical Re-lithiation Procedure and results**

Parameters such as the source and concentration of the lithium-ion solution, temperature and stirring, among others were varied to optimize the electrochemical process.

The results achieved in the experimental design and the optimal conditions of the process cannot be include in this report because this process is being analysed internally whether it is patentable and could harm the exploitation of the results.

- **Material characterization**

To characterize the surface of the CAM with high-resolution images, a scanning electron microscopy (SEM-EDS) analysis was performed. Figure 55a shows the CAM surface after the electrochemical re-lithiation process. It was characterized by SEM with an acceleration voltage of 20 kV and a working distance of 10 mm. The elemental composition of the surface was analysed by energy dispersive X-ray spectroscopy (EDS), as shown in Figure 55b.

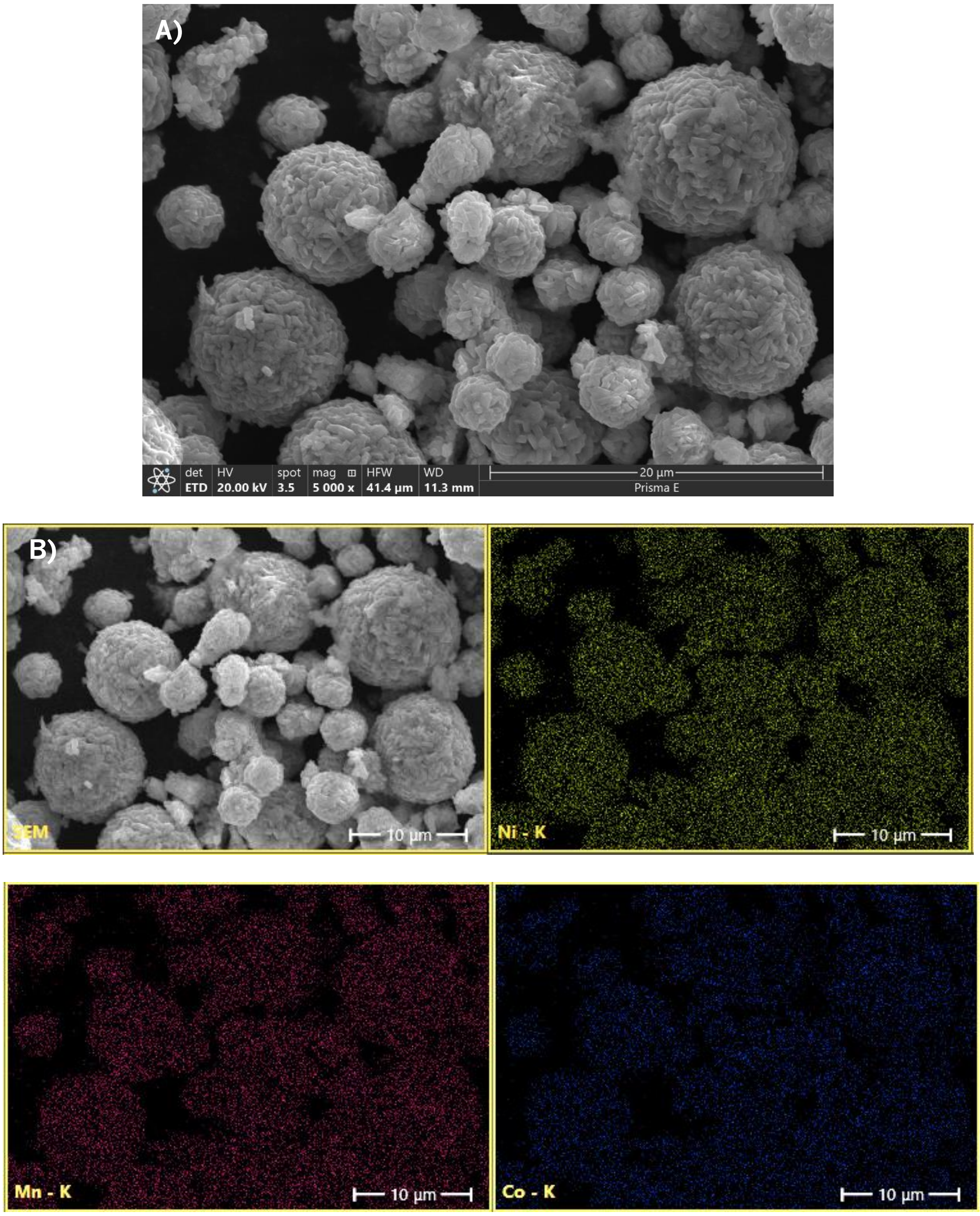

Figure 55. Cathode active material powder after electrochemical re-lithiation process a) SEM image b) Element map by EDS.

The SEM image of the CAM showed that its morphology consists of spherical particles. The elemental map indicated that the material is composed of nickel (yellow), manganese (red), and cobalt (blue), which are characteristic components of an NMC battery.

4.2 NADES leaching of cathodes

EURECAT has proposed a direct recycling process based on NADES to recover Li, Co, Mn and Ni. The recovery yields obtained are higher than the EC targets set by 2028. The effect of a pretreatment to remove the aluminium foil has been studied. A NADES based on choline-chloride, ascorbic acid and lactic acid has been selected among other options based on NADES. The process has been optimised based on temperature, bulk density, and scale. Lithium phosphate and Ni-Co-Mn oxalate had been obtained as precursors. The results have been compared with the use of citric acid which is another known green solvent.

4.2.1 Cathode pre-treatment

Cathodes from dismantled cells were used in NADES studies. At small scale the cathodes were cut to small coupons of 1x1 cms. The exterior of the cathode was discarded because there was no cathodic material at the rim. Some of these coupons were digested and used to determine the chemical composition of the cathode. However, at higher scale studies, whole cathodes were used.

During the extraction experiments, it was noticed that aluminum was co-extracted when using NADES and it was interfering in the purification step. The same happened using citric acid instead of NADES. Therefore, a pretreatment step was added to dissolve the binder between the aluminum foil and the cathodic material, recovering the aluminum foil as a solid metal before the extraction stage. In the case of NADES experiments a process similar to the one described in D3.2 was used, using diluted citric acid and ultrasounds to remove the aluminum layer. The degree of metals extracted in the diluted citric acid was determined and the remaining cathode material was used for NADES extraction to verify that the system did not interfere with the extraction.

Table 19. Metal recovery on the pretreatment and extraction stages using diluted citric acid and NADES.

	Li	Al	Mn	Co	Ni
	%	**%**	**%**	**%**	**%**
Pretreatment	11.6	18.5	9.1	10.1	9.9
Extraction	73.1	3.0	65.4	70.8	68.7

Diluted citric acid was capable of extracting almost 10% of lithium, nickel, cobalt and manganese in solution. Also, approximately 18% of aluminum was extracted. This drawback can be addressed simply by reducing the contact time. Another option could be to use the diluted citric acid as the water fraction in the NADES preparation, to avoid the metal loss or to recover the metals using oxalic acid as described in the following sections. The final extraction is lower than usual, mostly due to the loss of some cathodic material that remained attached to the aluminum foil. This part can be improved as it has already demonstrated by CARTIF at deliverable D3.2. using a specially designed setup and sonotrode. The experiments of this section used a commercial lab ultrasound system that is not as accurate as the one used by CARTIF in D3.2.

For the citric acid case, the separation is even much simpler since in this case concentrated citric acid was used, but at ambient temperature to avoid aluminium extraction. Then the aluminium foil was removed, and the remaining solid and solution were heated to start the extraction stage. In this sense, the nickel, cobalt or manganese that could be extracted by the use of citric acid was already in the extracting solution.

The metal recovery during pretreatment and during extraction are presented in the following table:

Table 20. Metal recovery on the pretreatment and extraction stages using concentrated citric acid.

	Li	Al	Mn	Co	Ni
	%	%	%	%	%
Pretreatment	20.88	23.20	16.16	15.73	16.93
Extraction	82.53	23.22	73.34	73.88	75.31

The amount of metals extracted during the pretreatment at 25C in this case is not problematic because the same solution is used for the extraction. The 23% of aluminium extracted is lower than the values obtained without pretreatment (52%) and can be improved simply by using lower temperatures or a shorter reaction time. The extraction was performed using a whole cathode, and the extraction yield was not far from the ones obtained in the upscaling studies, giving that the aluminium detachment was done by hand and some cathodic material was still attached to the foil. All these small drawbacks can be easily solved, leaving only the advantages of the pretreatment.

4.2.2 Extraction of metals

4.2.2.1 Study of NADES as extractants

Different NADES were studied to evaluate their effect on metal recovery. The NADES tested consisted on the combination of four different compounds (choline chloride, citric acid, lactic acid and ascorbic acid), being choline chloride always present in the mixtures studied (). For the sake of comparison, all experiments were made at the same temperature, bulk density, reaction time and volume.

Table 21. Screening of NADES used to evaluate their effect con metal recovery, where C1 is compound 1, C2 is compound 2 and C3 is compound 3.

Code	C1	C2	C3
ChCl-CA	Choline chloride	Citric acid	-
ChCl-LA	Choline chloride	Lactic acid	-
ChCl-AA	Choline chloride	Ascorbic acid	-
ChCl-CA-LA	Choline chloride	Citric acid	Lactic acid
ChCl-CA-AA	Choline chloride	Citric acid	Ascorbic acid
ChCl-LA-AA	Choline chloride	Lactic acid	Ascorbic acid

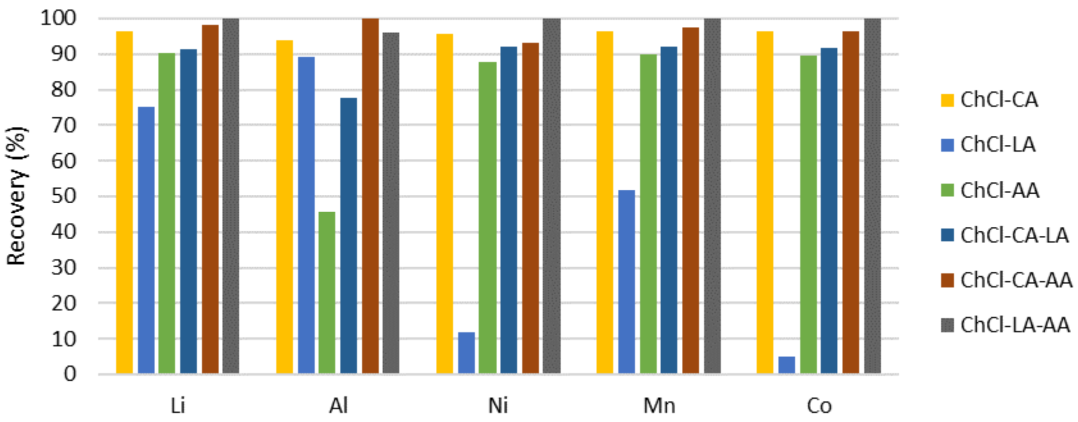

Figure 36. Recovery of metals using NADES.

In general, the use of NADES was effective to recover metals from cathodes (). Focusing on the main metals (Li, Ni, Mn, Co), all NADES tested allowed recoveries over 87%, except the mixture of choline chloride and lactic acid, with recoveries below 75%. Nevertheless, when ascorbic acid was added to the mixture of choline chloride and lactic acid, the highest recoveries were observed, achieving the complete extraction of Li, Ni, Mn and Co.

Overall, ChCl-LA-AA consistently demonstrated the highest extraction efficiencies across all tested metals, making it the most effective solvent. While other solvents like ChCl-CA and ChCl-CA-AA also had a good performance, ChCl-LA-AA stood out for its superior efficiency across the board. The performance of the NADES varied with the type of metal, but ChCl-LA-AA proved to be the best candidate for efficient metal extraction applications due to its consistent high recovery yield.

4.2.2.2 Comparison between NADES and other green solvents

The extraction of metals is a critical process in various industries, and traditionally, organic acids have been widely used for this purpose. This study primarily focused on the potential and advantages of NADES for metal extraction. Therefore, to validate their efficiency, a comparison with organic acids was conducted. Specifically, three different organic acids—citric acid, lactic acid, and ascorbic acid—were evaluated. The results of these evaluations were compared to the best-performing NADES identified in the previous section, which is the combination of choline chloride, lactic acid and ascorbic acid. In this case, the same conditions than NADES were used. Results are shown in .

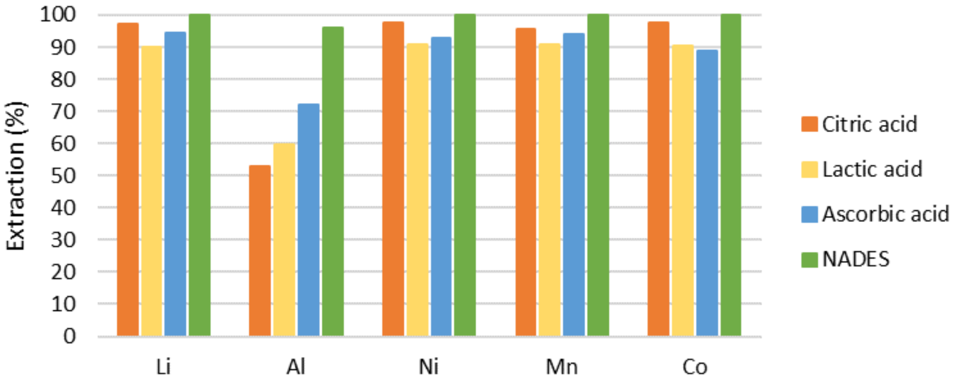

Figure 37. Comparison of the extraction of metals using NADES and organic acids.

Across all tested metals, NADES consistently exhibited superior or near-superior extraction efficiencies, highlighting their overall effectiveness. Among the organic acid tested, citric acid resulted the most effective one, but slightly less efficient than ChCl:LA:AA (NADES). In particular, lactic and ascorbic acids recovered around 90-94% of Li, Ni, Mn and Co, whereas citric acid recovered more than 95% of these metals at the same conditions. In the case of aluminium, the recovery using organic acids was less than 72% while 96% of it were recovered using ChCl:LA:AA.

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Overall, NADES consistently outperformed or matched the performance of the traditional organic acids across all metals tested. This underscored the significant potential and advantages of using NADES in metal extraction processes, demonstrating their effectiveness as a more efficient and possibly greener alternative to conventional organic acids.

4.2.2.3 Optimization to improve the recovery of metals

The extraction process was optimized, varying the operational conditions like solid-liquid ratio and temperature, not to increase the recovery yield that already was maximal but to make the process more economic, reducing energy and reagents intake. In this case, the optimization was done using the ChCl:LA:AA NADES (). Reaction time and volume was the same in all tests.

Table 22. Conditions tested to optimize NADES extraction.

Number	Solid-liquid ratio	Temperature (°C)
1	LOW	80
2	MID	25
3	HIGH	80
4	HIGH	80

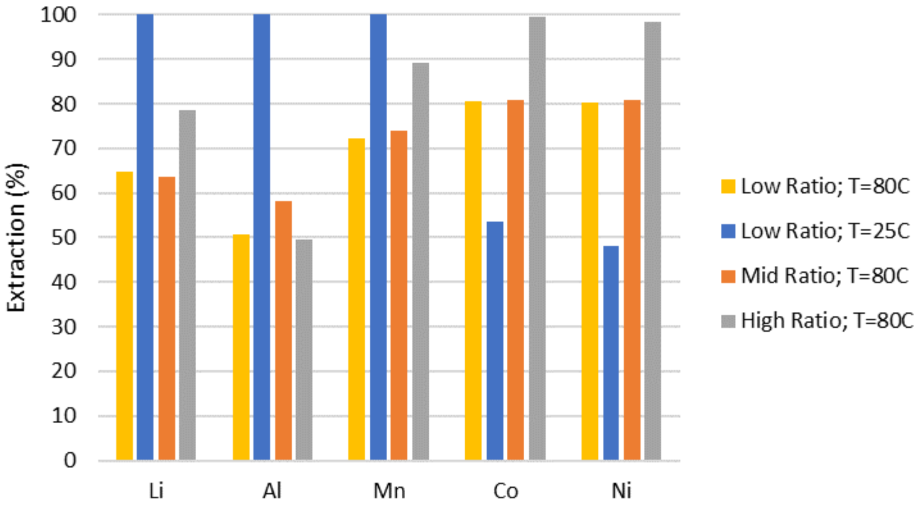

Figure 38. Optimization of metal recovery using NADES extractant.

Results are shown in . The recovery of lithium, aluminium and manganese improved when the temperature of the process was reduced from 80°C to 25°C.

However, the reduction of temperature implied worse recoveries of cobalt and nickel. Moreover, during the extraction at 25°C the samples became more viscous which in fact could prevent further work at higher solid-liquid ratios. Although working at 25°C allows a more selective extraction for Li, Al and Mn, considering the importance of Co and Ni in Li-ion recycling, the best option was considered to be to keep the temperature at 80°C during extraction.

Regarding the variation of solid-liquid ratio, it seemed that increasing the ratio improved the recovery of metals. However, the improvement of metal recovery also produced a dramatic increase on the viscosity, which hindered the operability and scalability. Therefore, thinking on the scalability of the process low ratios at 80ºC were selected for the metal extraction.

Once the best conditions were found, they were applied to citric acid recovery to compare the extraction with ChCl:LA:AA at the same conditions.

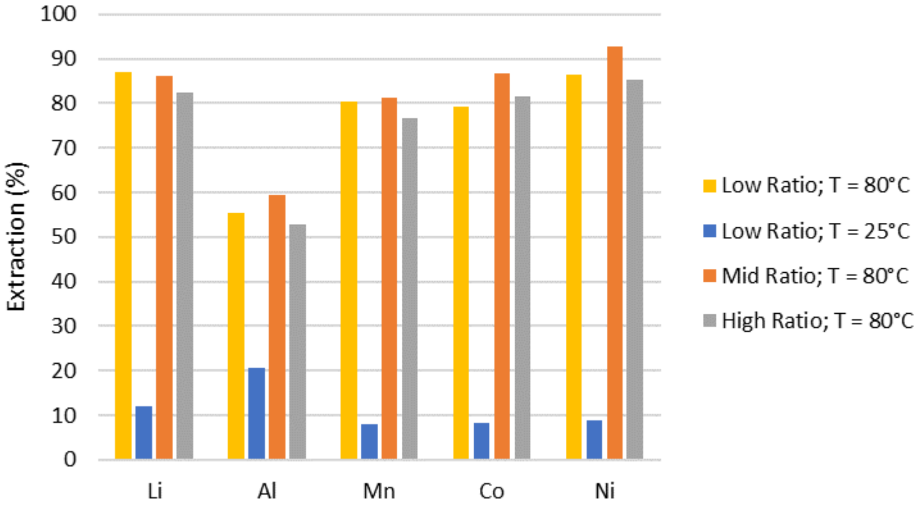

Figure 39. Citric acid extraction optimised as a function of solid/liquid ratio and temperature.

In this case the temperature proved to be a critical factor on metal recovery using citric acid. This temperature factor was used in the pretreatment stage explained before, to separate the aluminium foil with a reduced aluminium extraction (from ~55% to 23%). On the other hand, increasing the ratio almost not hampered the metal recovery and the viscosity was kept low, allowing then higher ratios in the case of citric acid.

Then, summarizing the NADES had still the highest recovery yield, but citric acid was able to work at higher solid/liquid ratios.

4.2.2.4 Scale-up for metal extraction

Previous experiments at laboratory scale demonstrated the viability of metal recovery using NADES. However, the technology was scale-up to corroborate their efficiency at higher scale. For this reason, experiments to extract metals from cathodes using 2L of extractant were tested. The assays were performed in a discontinuous stirred tank reactor ().

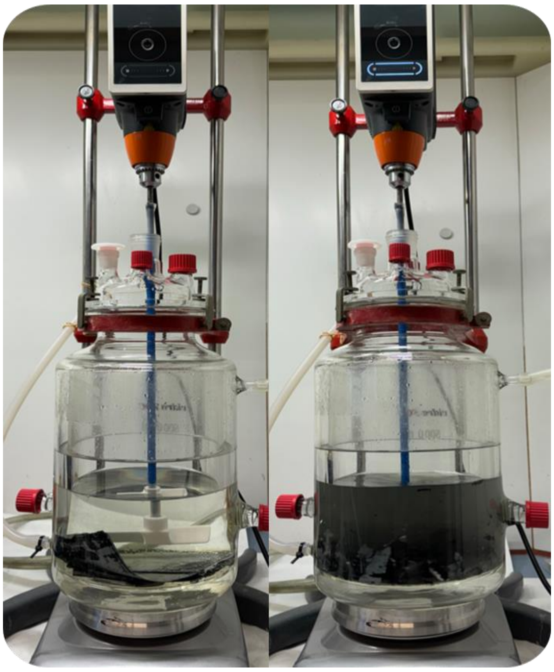

Figure 40. Scaling up of the extraction process using a stirred tank reactor: initial state (left) and after 4 hours of operation (right).

In the experiments, the lab scale conditions of temperature, solid/liquid ratio and reaction time were replicated. The extractant used was the NADES based on choline chloride, lactic acid and ascorbic acid. Results are shown in .

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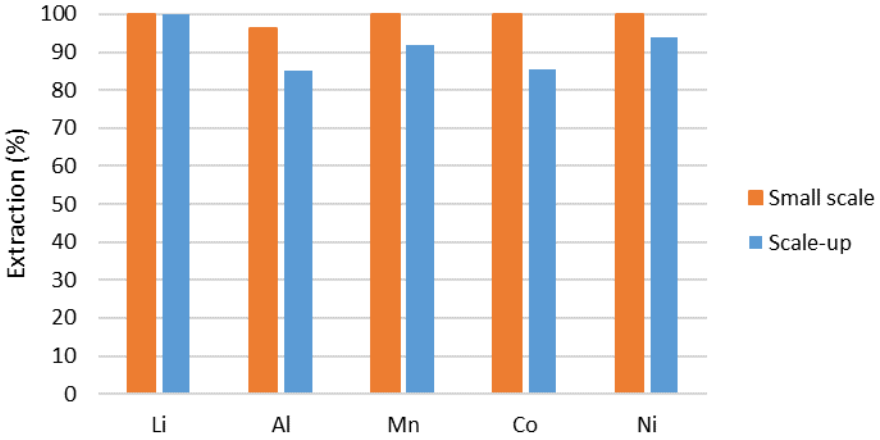

Figure 41. Extraction of metals using a stirred tank reactor compared to small-scale extraction, performed at the same solid-liquid ratio and temperature.

Despite the scale-up of the technology resulting in a reduction in the amount of recovered metals, the extraction process remained efficient, achieving recovery rates of 100% for lithium, 94% for nickel, 92% for manganese, and 85% for aluminium and cobalt. These differences can be attributed to variations in the technologies employed: small-scale extractions utilized orbital stirring due to the small volume (20 mL), whereas the scale-up process employed mechanical agitation. On the other hand, at lab scale cathodes were cut to coupons of 1x1cms, and the exterior of the cathode was discarded due to the lack of cathodic material in some parts. For the upscaling, whole cathodes were used, and therefore the chemical composition of the cathode could be overestimated because not all the cathode is covered in cathodic material as can be seen in the next picture.

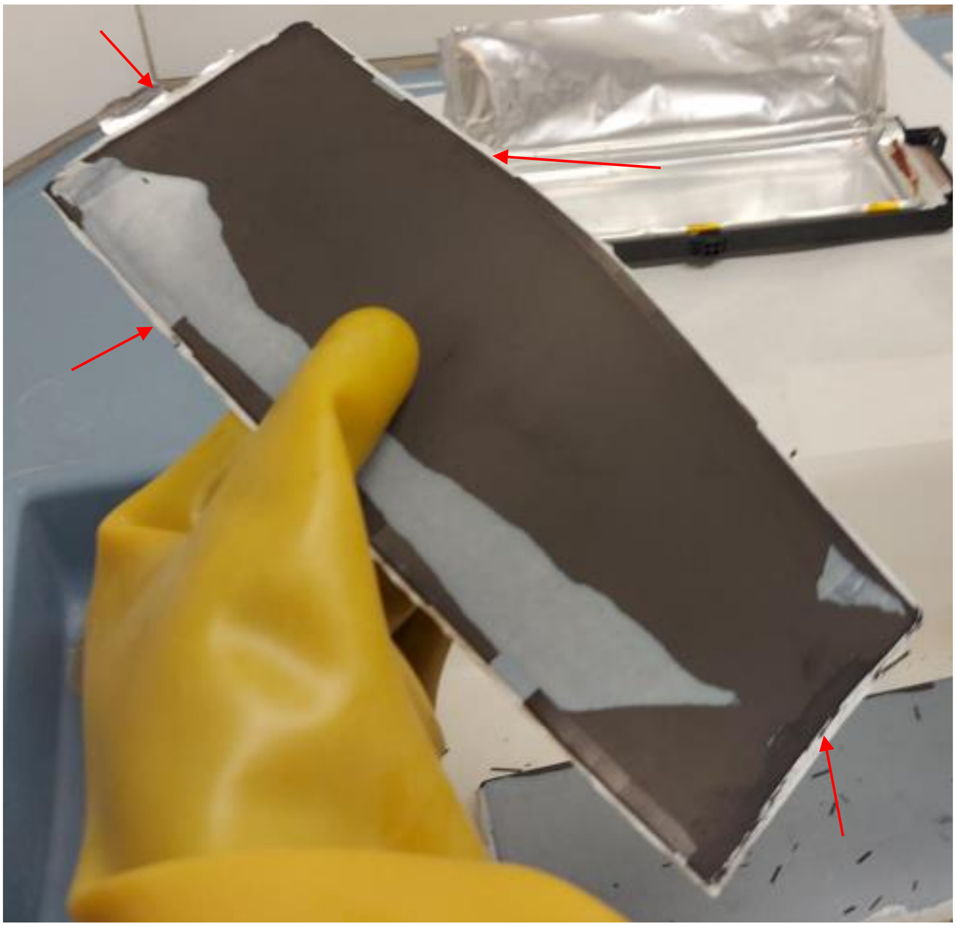

Figure 42. Picture of a cathode. The red arrows signal the external parts of the cathode without cathodic material, specially at the top were there is the aluminium tab.

In conclusion, the assay demonstrated the viability of performing the extraction process at a larger scale, following a methodology more akin to industrial applications.

To corroborate the efficiency of NADES extraction at a higher scale-up, citric acid 1.5M at the same operational conditions was tested at this scale to compare with NADES extraction. Results are shown in .

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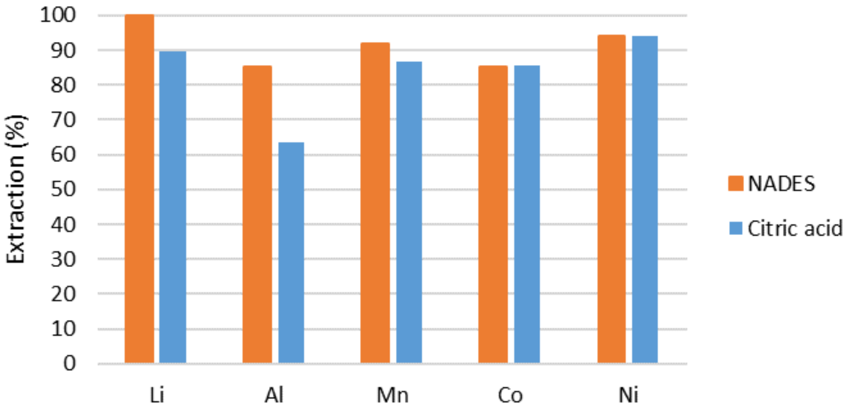

Figure 43. Metal extraction using a stirred tank reactor.

Overall, citric acid was found to be less efficient than NADES for metal recovery, consistent with results observed at small scale. Specifically, NADES recovered 5% more manganese, 11% more lithium, and 22% more aluminium compared to citric acid, while both extractants achieved comparable recovery rates for cobalt and nickel. These findings confirm that NADES, composed of choline chloride, lactic acid, and ascorbic acid, is more effective than citric acid for metal recovery. These scalability studies were just a proof of concept. The next step would be to optimise the extraction process to achieve the same recovery yields obtained in lab scale.

4.2.3 Precipitation processes

The joint precipitation of nickel, manganese and cobalt was proposed as a fast and effective method of obtaining usable material as a precursor to make cathodic material. The following figure shows how the complete process would look like, from the extraction of the metals to the lithium phosphate synthesis, passing through the intermediate precipitation of the joint metals. ().

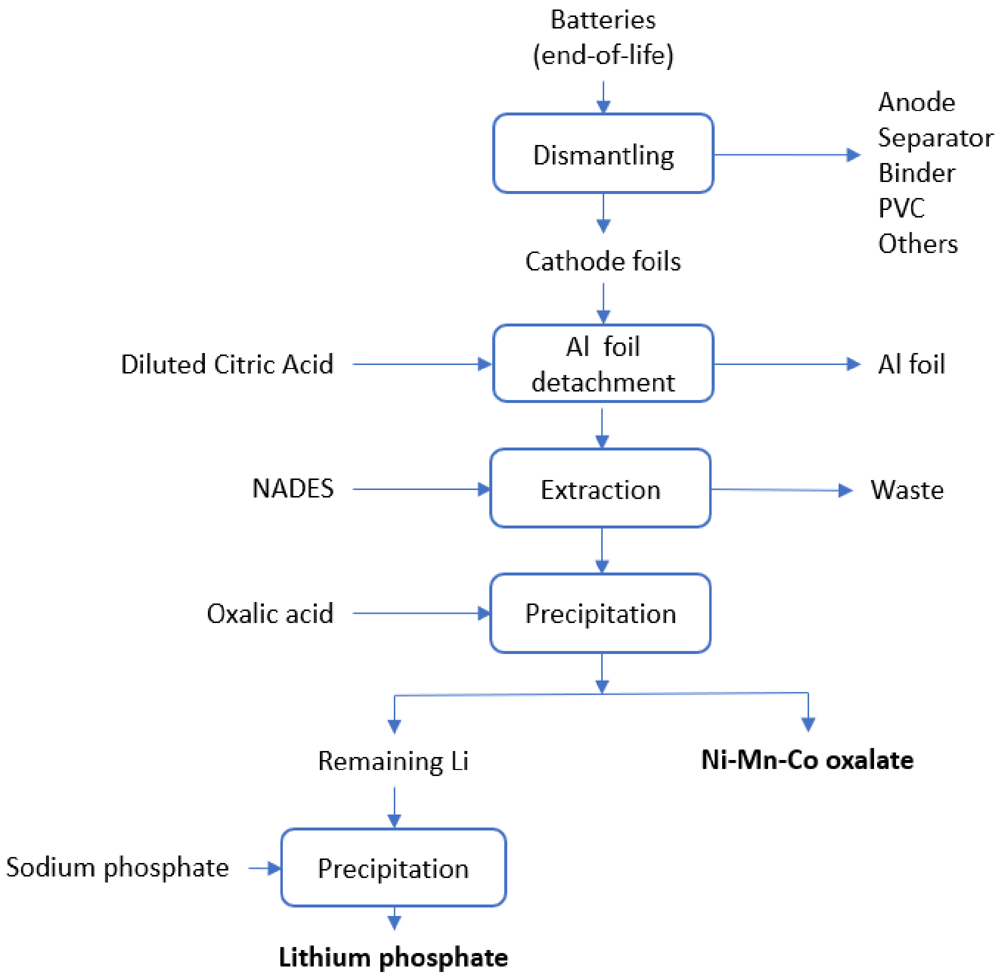

Figure 44. Complete route to extract metals from batteries by the recovery of Ni-Mn-Co as a mixed oxalate in precipitation process.

In this scheme, there would be a pretreatment stage where the battery would be dismantled to obtain the different modules and from there the cells. Each cell would be dismantled in turn to obtain the cathode foils, on which the hydrometallurgical process would be directly applied. This process has the advantage that the metals of interest are much more concentrated than in the black mass, and there are fewer metals that can interfere. Its automation and industrialization are more complex, but there is on-going research on the field as reported in deliverable D3.2. In order to avoid aluminium in solution, the cathode foils were pretreated using diluted citric acid, to detach the aluminium foil. The selected NADES was then used for cathode direct extraction, recovering most of the metals of interest with yields close to 100%. The extraction also left a residue mainly composed of organic compounds used in the cathode synthesis. Note that this extraction method avoids the conventional pretreatment using N-methyl-pyrrolidone (NMP) and subsequent calcination.

Therefore reduces the energy consumption and high economic and environmental impact reagents such as NMP.

Once in solution, the joint precipitation route proposes adding oxalic acid to precipitate the combined oxalate of nickel, cobalt, and manganese. A clean lithium stream would remain in solution, which could be recovered in the form of lithium phosphate. This is a precursor used in $LiFePO4$ battery chemistries. The precipitated oxalate could be calcined to obtain the corresponding metal oxide, or be used as a precursor itself, depending on the synthesis route for the cathode mixed oxide. The solid-state route, using oxides as precursors, will continue mixing lithium hydroxide with the recovered metal oxides. Depending on the chemistry desired, the mixture can be adjusted by adding additional nickel, manganese, and cobalt oxides. The mixture is then milled, calcined, and sintered. A lithium, nickel, manganese, and cobalt oxide (Li-NMC) of the selected chemistry will be obtained, ready to be used in the manufacture of new cathodes. Besides the Li-NMC oxide, lithium phosphate is also obtained as a product in this scheme. The obtained phosphate could also be used as a lithium source, for lithium iron phosphate cathodes. Lithium iron phosphate batteries have also an important market, that is increasing every year.

The laboratory-level study has focused on the oxalate production stage, as it is the most critical step. It should be noted that the proposed process allows closing the loop from battery waste to new Li-NMC oxides for cathode manufacturing, but several viable business models, including selling NMC oxalate as is, would be possible. In this project, the key extraction and precipitation stages have been developed. Specifically, the joint precipitation of nickel, cobalt, and manganese has been studied, given that the mixture of these metals after proper treatment is used as a precursor for preparing the cathodic material used in manufacturing new cathodes in lithium-ion batteries. As in the extraction, the precipitation with oxalic acid was tested using NADES and citric acid extracts to compare the effectiveness of the method using the same experimental conditions ().

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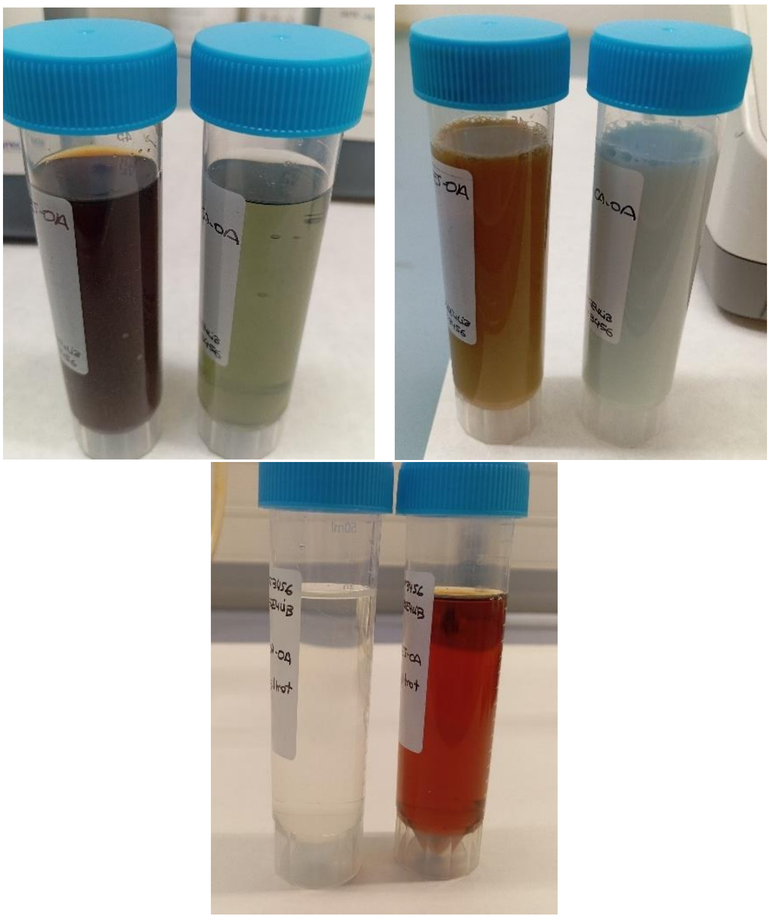

Figure 45. NADES (brown samples) and citric acid (grey samples) at three stages: initial solution, during precipitate formation, and post-filtration, shown from left to right, respectively.

When oxalic acid is added to the extract, the concentration of all metals, with the exception of lithium, is significantly reduced, implying that they have precipitated. This is corroborated by the data shown in , which shows the amount of each metal that has precipitated in the two cases studied with respect to the initial amount of metals in the extract.

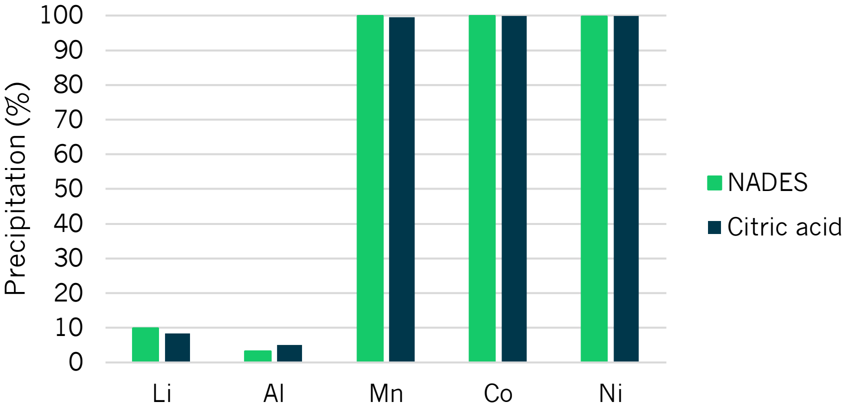

Figure 46. Precipitation of metals using oxalic acid.

Precipitation from the NADES extractant (containing choline chloride, lactic acid and ascorbic acid) was as effective as precipitation from citric acid, thus validating that NADES could be used to recover metals from cathodes which can be then precipitated as it occurred with traditional organic acids such as citric acid (see).

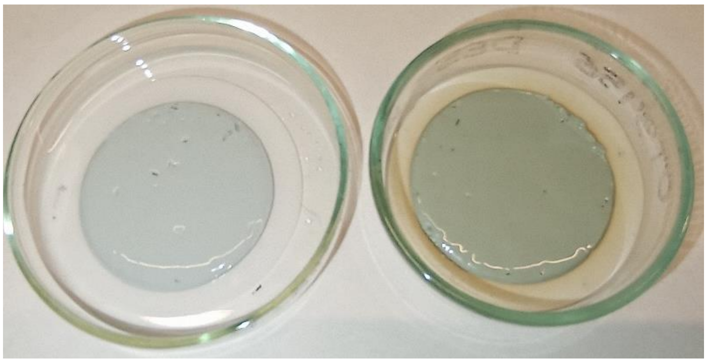

Figure 47. Precipitates formed after the addition of oxalic acid, using citric acid (left) and NADES (right) as the solvent.

Lithium in solution was recovered as lithium phosphate adding sodium phosphate to the solution, increasing the pH and evaporating part of the volume, to concentrate the lithium phosphate beyond the solubility limit. The result of the lithium recovery yield for the NADES route is 58% of the initial concentration in solution, with a purity of 94%. Manganese and aluminium are the main impurities. Regarding the citric acid route the recovery of lithium was slightly higher 62% of the initial concentration in solution, in this case the purity of lithium was 73%, which was low due to a high intake of aluminium during the precipitation (26%). This aluminium intake will be solved during the aluminium foil separation using ultrasounds.

Pictures of the lithium phosphate both from NADES and citric acid route are shared in the following picture:

Figure 48. Lithium phosphate from NADES (left) and citric acid (right).

Finally, the recovery yield using NADES and using citric acid were compared at the different stages and in total:

Table 23. NADES metal recovery yields

Stage	Li (%)	Mn(%)	Co(%)	Ni (%)
Pretreatment to detach aluminium foil				
Extraction	100	100	100	100
Oxalate precipitation	9.8	99.9	100	99.7
Phosphate precipitation	58	-	-	-
TOTAL	53	99.9	100	99.7

Table 24. Citric acid metal recovery yields.

Stage	Li (%)	Mn(%)	Co(%)	Ni (%)
Pretreatment + Extraction	97.2	95.6	97.4	97.6
Oxalate precipitation	8.3	99.5	99.9	99.9
Phosphate precipitation	62	-	-	-
TOTAL	56	95.1	97.3	97.5

In the NADES pretreatment stage, we can consider that the diluted citric acid is used in the NADES synthesis, or that the metals are recovered using the same oxalate precipitation process, already proven successful with higher concentrations of citric acid. Metal oxalate solubilities are low for nickel, cobalt and manganese. So, the metals extracted by diluted citric acid in the pretreatment stage were considered to be recovered in one way or another. As for the citric acid the pretreatment stage and extraction stage are combined in a way that no metal is lost.

During the extraction stage excellent recovery rates were proven at lab scale. At the upscaling step, it was proven that the upscaling was feasible, and it is considered that the recovery yields could be achieved optimising the process.

Once more using the NADES we obtain higher recoveries of Co, Mn and Ni than using citric acid. Regarding lithium phosphate the recovery is slightly lower, but the purity is much higher. Anyhow in both cases the results are higher than the targets set in the last EC battery directive for lithium, nickel, and cobalt recoveries (Li:50%, Ni:90%, Co:90%). These results are based on the lab scale experiments. To obtain the same results at a higher scale more efforts are required.

5. Conclusions

To evaluate recycling solutions for black mass at lab scale two different black masses were investigated. For it, two different approaches were assessed: i) hydrometallurgical process and ii) combined pyro-hydrometallurgical process. Black masses investigated were previously treated by thermo-mechanical pre-treatment process, or an electrohydraulic fragmentation process. Microstructural characterization of the black masses reveals particles agglomerated in both cases. However, mineralogical composition for the black mass that was thermo-mechanical treated shows a decomposition of the spinel phase typical of NMC622 cathodes, with the presence of metal oxides, and lithium carbonate. However, the black mass that was treated by electrohydraulic fragmentation reveals the spinel phase.

For both black masses investigated some precursors were obtained. Nevertheless, due to the possibility to selective recover of Li_2CO_3 by the pyro-hydrometallurgical process, this method has been chosen for the subsequent studies.

In general, the best results were obtained using the black mass that was thermo-mechanical treated (i.e. BM01). However, optimization conditions for each step are ongoing.

As detailed on the previous sub-sections, several recycled materials obtained from different processes, have been tested. These samples have been classified in terms of their chemical nature, as it is one of the most important factors which determines the chemical behaviour, in other words, the complexity or facility of working with them to prepare suitable liquid precursor mixtures for FSP technology.

After all tests carried out, a general procedure has been defined which includes the different stages to take into account for working with recycled materials on their transformation into precursor mixtures ().

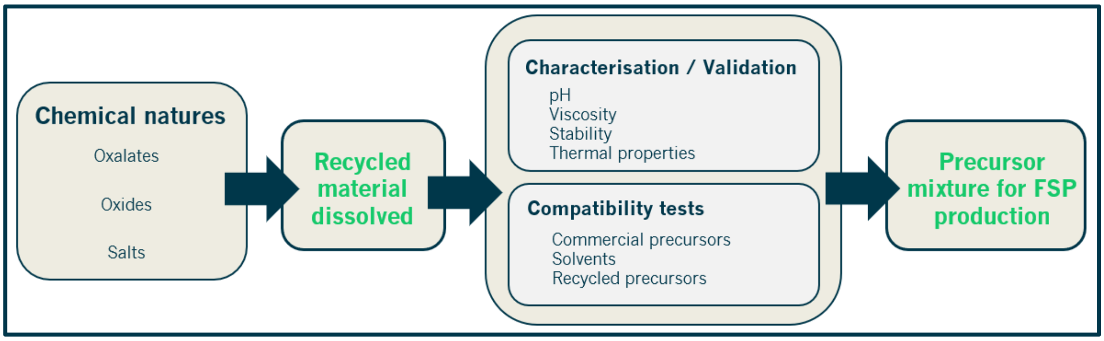

Figure 49. Procedure to transform recycled materials into optimum precursor mixtures.

Additionally, several conclusions have been extracted:

- **Metal, metal oxides, and graphite.** This powder sent by CSIC required a pre-thermal treatment to remove the graphite, in order to avoid any possible interference during the formation of cathode nanoparticles, as well as, reducing the presence of impurities on the final material. On the other hand, once the material was cleaned, hard digestion conditions were needed to transform the powder into a homogeneous solution. Nevertheless, due to the presence of different chemical natures on the powder, digestion tests resulted in inhomogeneous solutions.

As the resulting digestion solution is acid, in some cases, it is needed an intermediate step of neutralization.

- **Metal oxides.** The cathode powder received from CARTIF was completely dissolved in an acid media. The homogeneous digestion liquid was mixed in different solvents, studying its compatibility and viability to get a suitable precursor mixture for the FSP equipment. In that sense, a preliminary precursor mixture was achieved with the desired cations present on it.
- **Metal carbonates** are often used for precursor mixture, and as shown on the tests, a liquid precursor can be achieved. Nevertheless, it is possible also to carry out an intermediate transformation of the salt into nitrate, which is a more easily-handle material.
  In this case, a liquid recycled lithium precursor was obtained, and with it, a preliminary precursor mixture was prepared and validated.
- **Metal oxalates.** As this kind of materials decompose to oxides with low temperature, a thermal treatment was avoided. A specific digestion procedure was defined to get a homogeneous liquid solution without missing any interesting element on the process. The compatibility tests carried out after ended in good way, as some alcoholic media were compatible with the liquid sample.

Considering all the conclusions listed above, several of the recycled materials received with different chemical nature, have been validated to prepare precursor mixtures for the FSP technology.

An efficient direct recycling process has been developed to regenerate degraded cathode foil and powder materials from spent lithium-ion batteries. Through hydrothermal re-lithiation, the lithium stoichiometry was restored to different levels depending on the conditions. It is important to continue investigating how other factors can influence the hydrothermal re-lithiation process to achieve the best result for scaling up. SEM images showed that the cathode material after the hydrothermal process recovered its crystalline form. The electrochemical re-lithiation process was controlled by a diffusion mechanism influenced by the concentration of Li^+ ions, temperature, and stirring. The re-lithiation products showed crystal structures and chemical compositions of Ni, Mn, and Co similar to standard NMC 622 materials.

On the other hand, a direct cathode recycling process based on NADES has been developed. Citric acid has been selected as a similar process to compare with, since citric acid is also considered a green solvent. The process based on NADES has a higher metal recovery than the one using citric acid, confirming the huge potential of NADES in the metal recovery industry. The only drawback of the use of NADES is its increase in viscosity when using high solid liquid ratios, especially when compared to the citric one. The final metal recovery of lithium, cobalt and nickel using NADES, has been calculated taking into account the recovery yield at each step of the process, being 53% for lithium, 100% for cobalt, and 99.7% for nickel. The recovery of manganese has been also high, 99.9%. The recovery of lithium, cobalt and nickel, is higher than the targets set by the last EC battery directive (>90%, >90%, >50%).

After evaluating the results obtained, two of the main objectives of WP3 has been achieved, Recovery of valuable materials from spent LIBs and materials re-using: validate valorized materials to batt value chain. The materials obtained were oxalates of Ni/Co/Mn, oxalates of Ni/Co, $CoSO_4$ and lithium salts, Li_2CO_3 and Li_3PO_4. The use of these products as precursors for cathode active materials will be collected in deliverable D3.6. Report on validation of recovered materials re-use on new cells.

Moreover, the actual results will be used to scale-up some of the technologies studied, that will be developed during WP4.

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[i] https://doi.org/10.1021/acs.est.3c01369
[ii] https://doi.org/10.1016/j.egyr.2023.05.264
[iii] https://doi.org/10.1002/adsu.201900088

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