

Deliverable D4.2

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



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

WP4 - Scaling and validation of feasible technologies

D4.2 - Development, testing and validation of recycling solutions for cathode and black mass

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List of Abbreviations

ACRONYMS	DESCRIPTION
BM	Black mass
AA	Atomic absorption
ACC	ACCUREC
FRA	FRAUNHOFER
TRL	Technology Readiness Level

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1. Executive summary

This deliverable collects the main results obtained during the development of pilot scale test for recycling black mass technologies and cathode direct recycling technologies carried out in T4.3.

The technology scaled for black mass recycling consists of a combined pyro+hydrometallurgical treatment is based on perform a pyrometallurgical step to recover lithium from black mass. Once the lithium is recovered, the solid obtained were leached with malic acid + O₃, 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 carried out from the residue of lithium recovery.

2. Introduction

After the development of the recycling solutions for black mass and the recycling solutions for cathode direct recycling at lab scale, the best conditions obtained in this phase were then scale-up to TRL 5-6 and demonstrated in the facilities of CSIC, LUR and CARTIF.

Regarding the recycling of black mass, CSIC scale-up the combined pyro-hydrometallurgical technology, to recover in the first step lithium and after the different treatments, such as, leaching, precipitation and liquid-liquid extraction, recovering Co, Ni and Mn. The precursors obtained were the starting point to synthetize cathode active materials.

3. Recycling solutions for black mass at pilot scale

3.1 Black mass comparison

During lab-scale tests 3 black masses (BM) were received, one from ACC (BM01), and two from FRA (BM02 & BM03). To perform the pilot-scale tests more quantity were required, and another 3 BMs were received, two from ACC (BM04 & BM05) and one from FRA (BM06). Chemical composition, determined by atomic absorption (AA) and total carbon content, determined by combustion, of all BMs are collected in Table 1 and Table 2.

Table 1. Chemical composition of BMs used at the lab scale determined by AA.

wt. %	BM01	BM02	BM03
Li	3.6	3.22	2.75
Ni	11.3	16.70	16.58
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

Table 2. Chemical composition of BMs used at pilot-scale determined by AA.

wt. %	BM04	BM05	BM06
Li	3.0	3.2	1.15
Ni	9.5	14.8	12.54
Co	5.6	3.6	2.80
Mn	3.3	3.9	3.21
Fe	0.02	0.02	0.05
Cu	2.49	0.35	2.53
C _{total}	53.9	53.1	40.5

Figure 1 shows the XRD patterns for the different black masses investigated. In the case of BM04, carbon, graphite, and metal oxide phases were detected in the XRD measurements. For the BM05 sample, lithium carbonate, graphite carbon, lithium aluminate (LiAlO_2), and metal were detected. Finally, the XRD pattern for the BM06 shows carbon, graphite, and $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) phases.

As can be appreciated, the chemical as well as mineralogical composition of the BM04 to BM06 black masses are slightly different, which leads to modifying the general scheme. It should be noted that in the case of BM05, a previous hydrolysis step in order to recover Li_2CO_3 is needed.

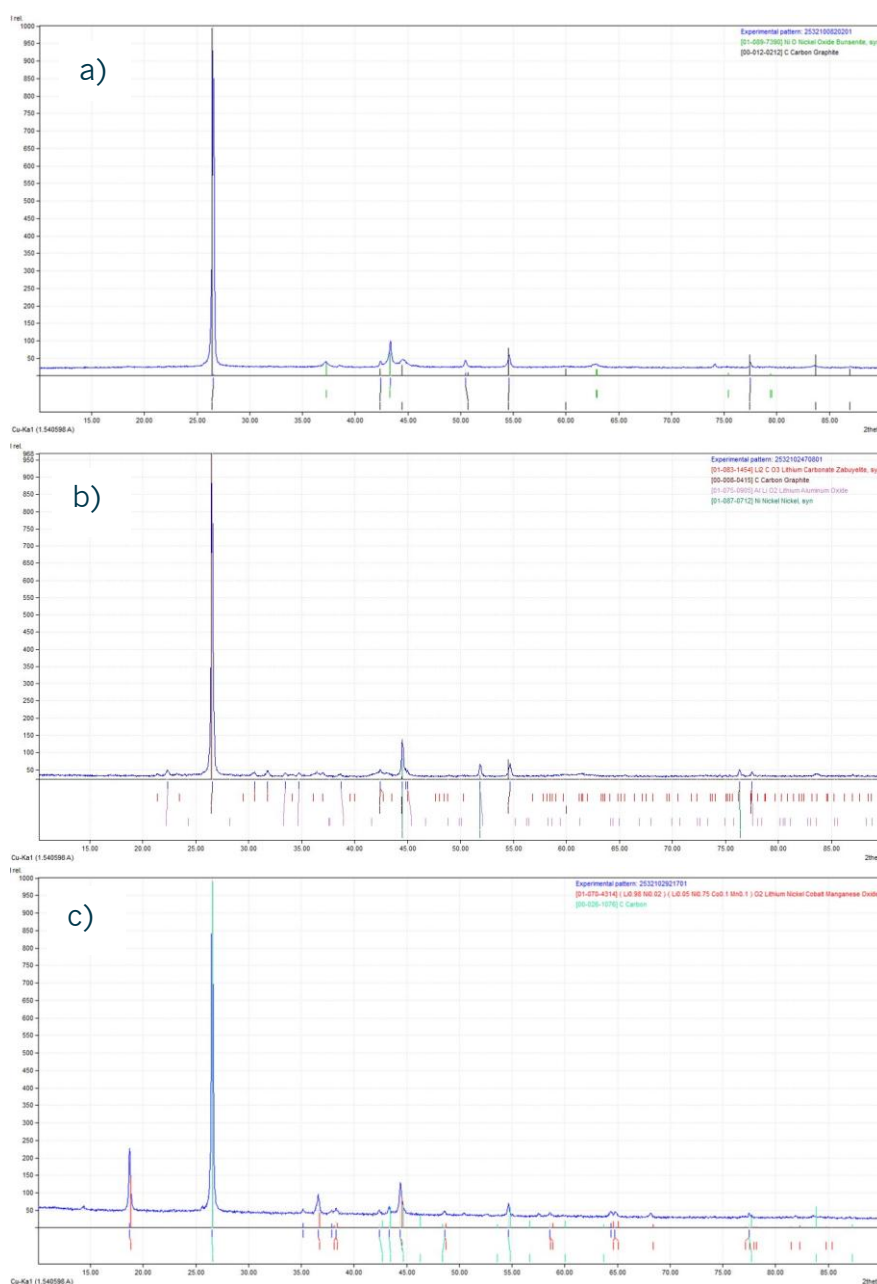


Figure 1. XRD for the BMs used in the pilot scale test a) BM04, b) BM05, c) BM06.

3.2 Combined pyro-hydrometallurgical process at pilot scale

According to the results obtained in lab-scale tests, the best process turned out to be the combination of a pyrometallurgical process, based on a carbo-reduction step, followed by a hydrometallurgical process, to recover Li, Ni, Co, and Mn. The process employed, summarized in Figure 2, remains equal to the use during the laboratory tests, changing the equipment used to increase the quantity processed per batch. The pilot tests were carried out using 5 kg batches.

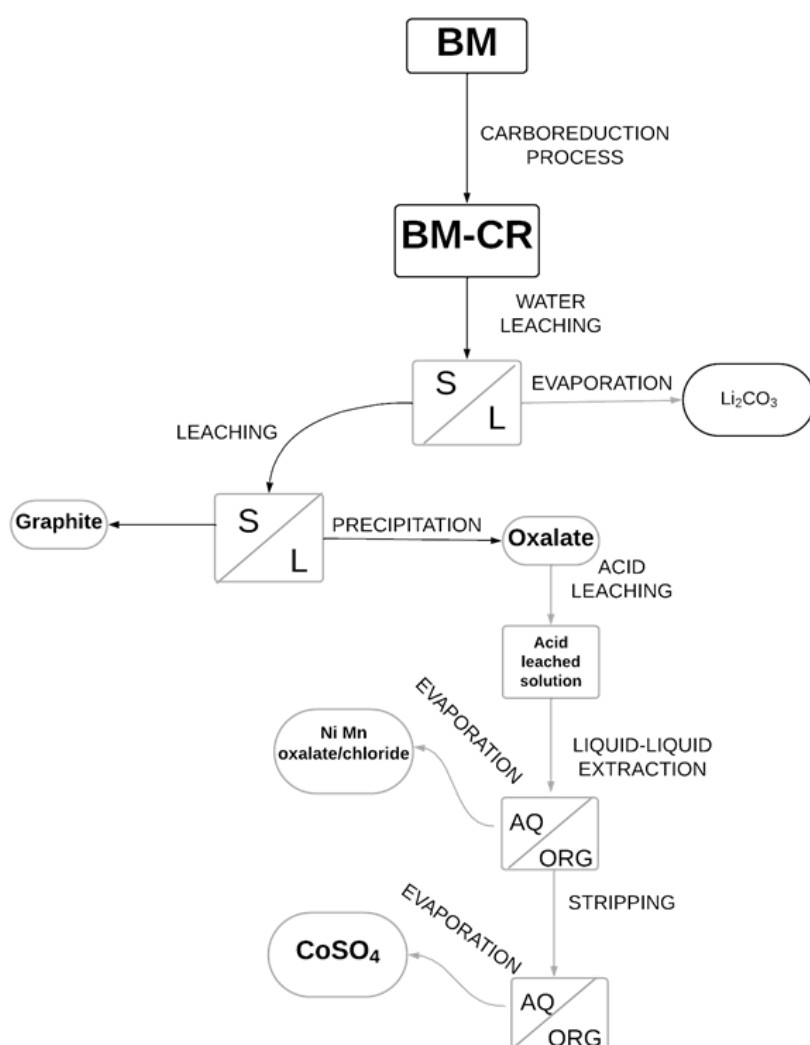


Figure 2. Process diagram for the pyro-hydrometallurgical process.

3.2.1 Equipment

The carboreduction process was carried out in an AFI-02 induction furnace containing an N₂ atmosphere (Figure 3). For leaching, both water leaching and acid leaching, a jacketed glass reactor vessel with 10L of capacity was used (Figure 4). After water leaching, Li₂CO₃ (PRE01) was obtained using a rotavapor (Figure 5). After acid leaching, PRE03 (metal oxalates) were obtained using the jacketed reactor shown in Figure 6. Liquid-liquid extraction for the separation of Co was performed in the jacketed funnels (Figure 7), and the evaporative crystallization to obtain PRE04 and PRE05 were carried out in a rotavapor (Figure 8).



Figure 3. Furnace used for the carboreduction process.



Figure 4. Glass reactor used in the leaching steps.

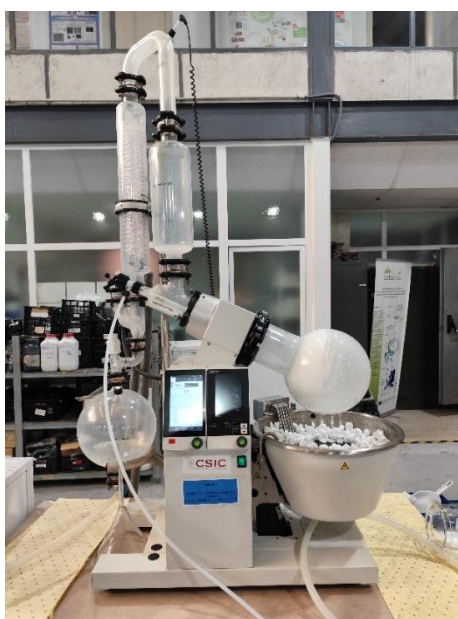


Figure 5. Rotavapor used in evaporative crystallization to obtain PRE01 (Li₂CO₃)



Figure 6 Precipitation reactor (obtention of PRE03, Co+Ni+Mn oxalate)



Figure 7. Liquid-liquid extraction funnels

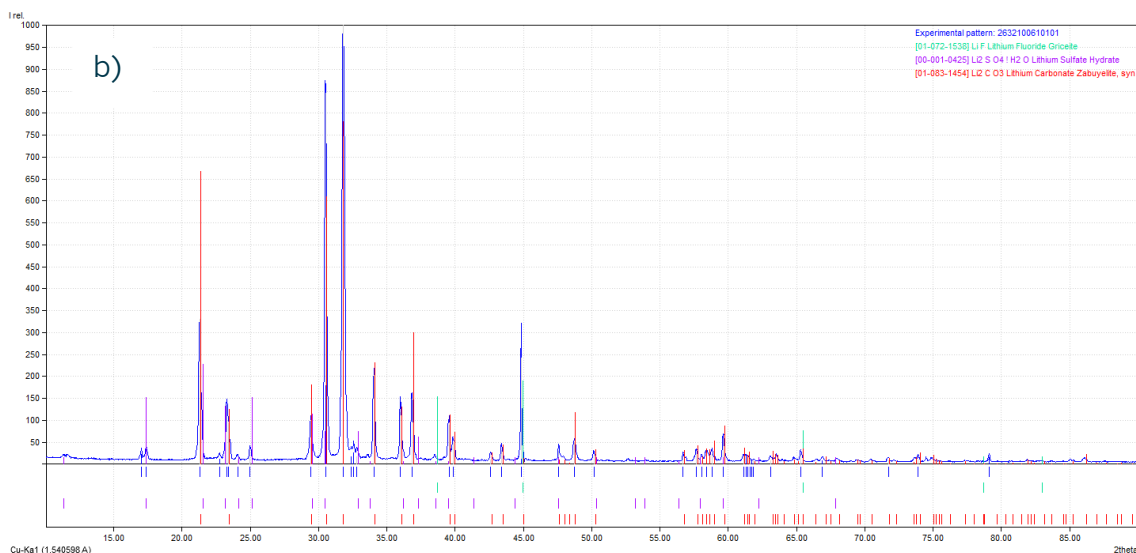
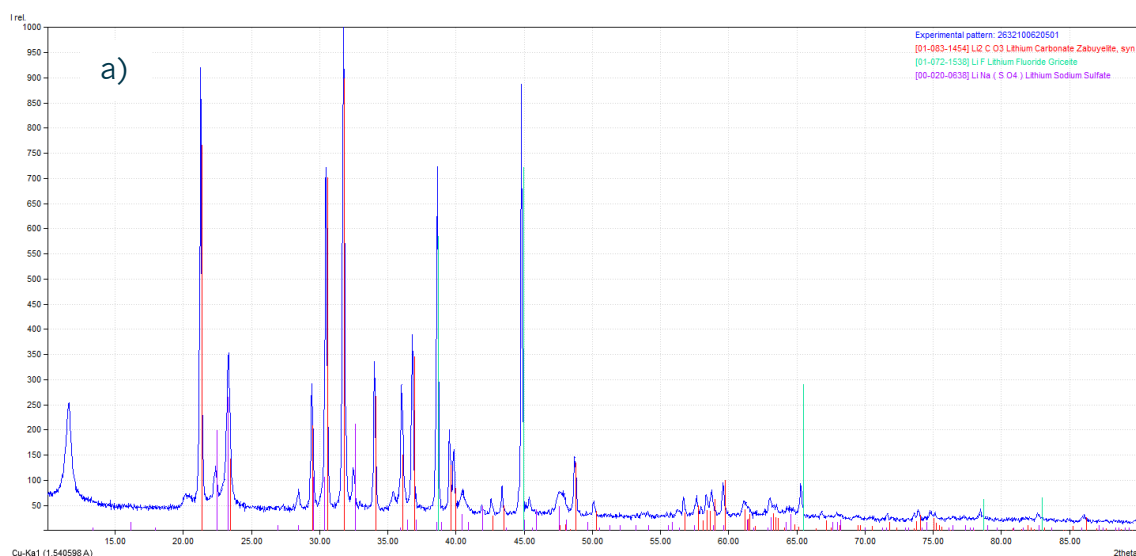


Figure 8. Rotavapor used in evaporative crystallization to obtain PRE04 and PRE05 (Ni+Mn oxalate and CoSO_4).

3.2.2 Pilot test results

The first step consists of a carbothermal reduction reaction to recover lithium from the black mass.

Figure 9 and Table 3 exhibit the XRD patterns and the calculated chemical composition for each lithium carbonate obtained from the black masses studied.



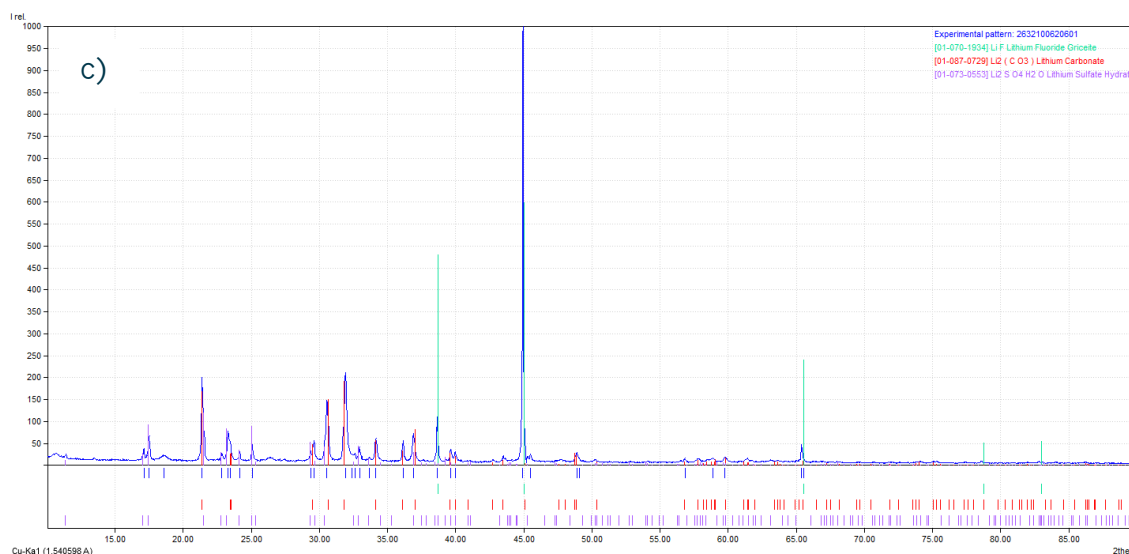


Figure 9. XRD of PRE01 from a) BM04, b) BM05, c) BM06.

Table 3. Chemical composition of Li_2CO_3 obtained after pyrometallurgical step+water leaching.

wt. %	BM04	BM05	BM06
Li_2CO_3	74.48	93.93	93.60
LiF	25.02	5.81	6.1
Li_3PO_4	0.50	0.27	0.3

The next steps consist of acid leaching, followed by selective precipitation of Ni, Mn, and Co as their corresponding oxalates.

XRD measurements (Figure 10) demonstrate that Ni/Mn/Co oxalates were obtained as expected in all cases, independently of the starting black mass.

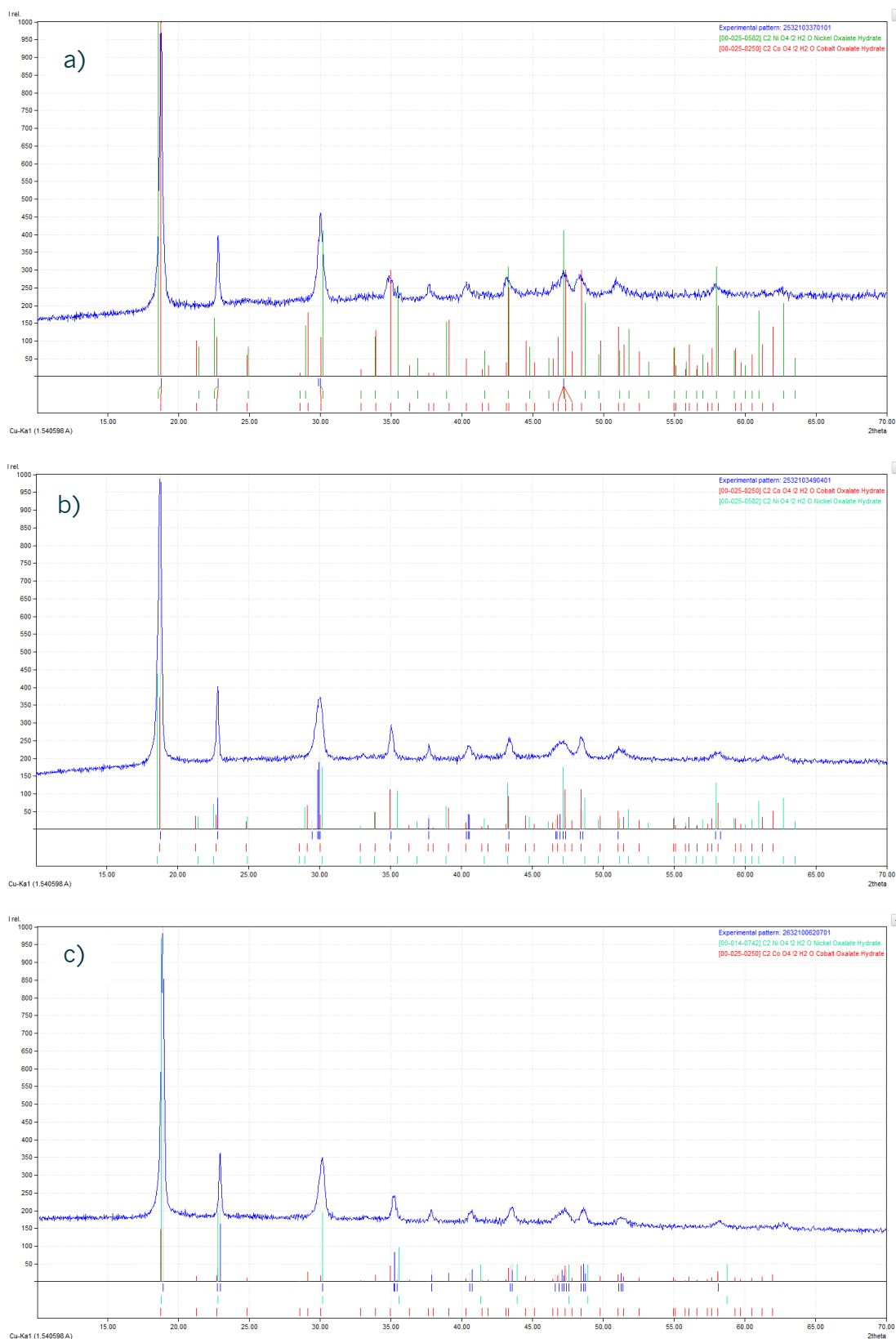


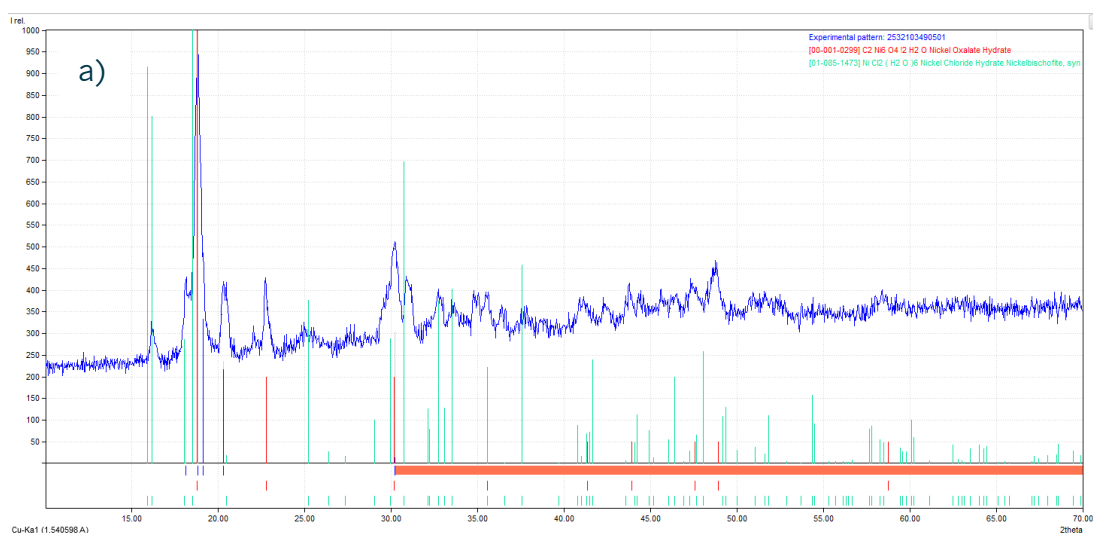
Figure 10. XRD of PRE03 from a) BM04, b) BM05, c) BM06.

The chemical composition of the recovered oxalate precursors obtained for each black mass is shown in Table 4. The calculated chemical composition for the precursors obtained through the scale-up test of the oxalates is similar to the obtained at lab-scale.

Table 4. Chemical composition of oxalates obtained.

wt. %	BM04	BM05	BM06
Li	0.12	0.16	0.14
Ni	14.11	17.01	17.45
Mn	8.97	6.72	6.53
Co	4.6	3.94	5.01
Cu	1.19	-	0.01
Fe	-	-	0.09

To recover Co, these oxalates were acid-leached with 10 M HCl to obtain a metal-concentrate solution. Each solution was subjected to a liquid-liquid extraction process using the synthesized DES, which is selective for Co separation. After this step, the aqueous phase was evaporated until a Ni, Mn precursor solid was obtained. A mixture of nickel/manganese chloride and oxalate was found in all cases, as exhibited in Figure 14.



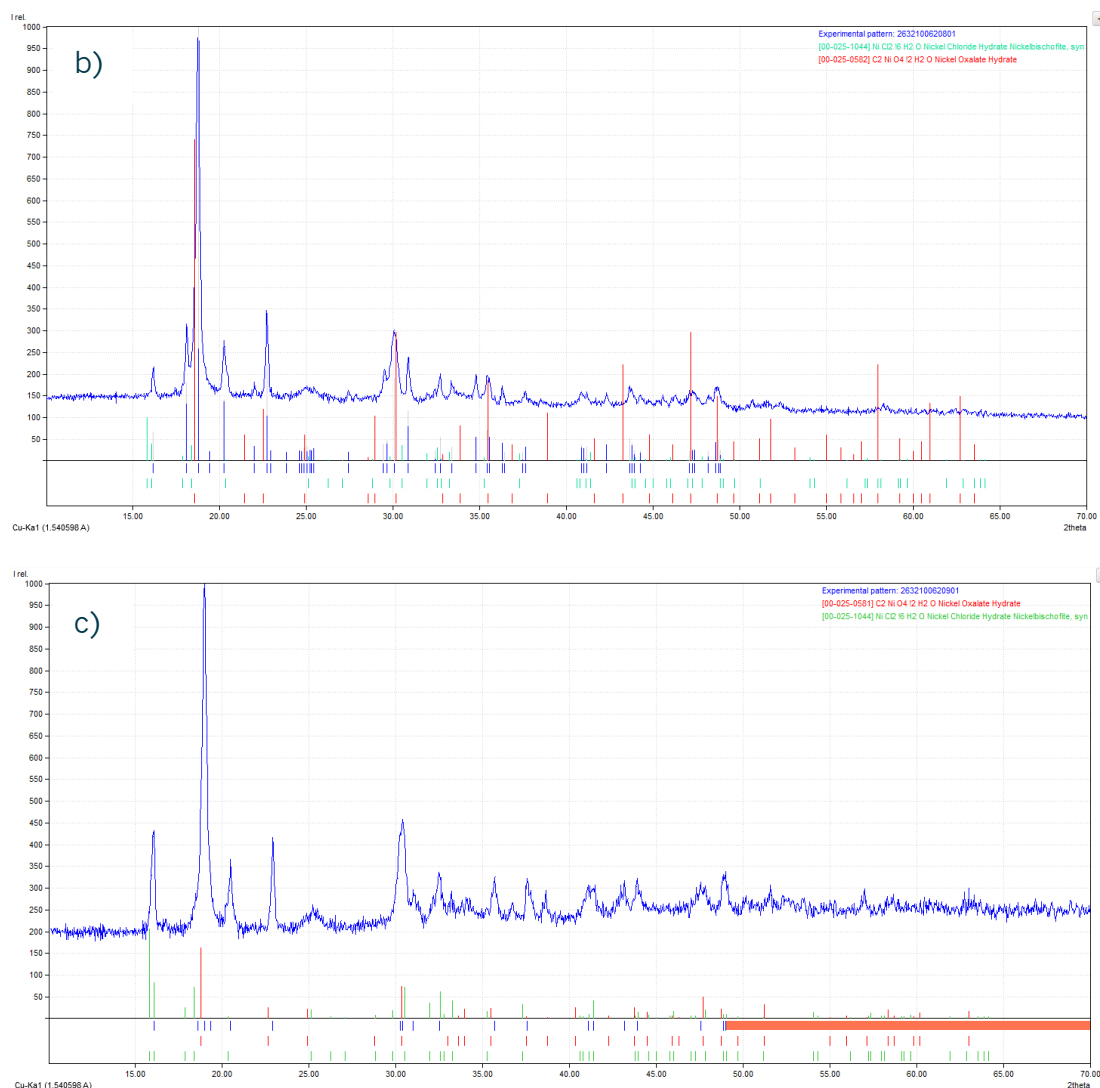


Figure 11. XRD of PRE05 from a) BM04, b) BM05, c) BM06.

Table 5 shows the chemical composition for each recovered precursor.

Table 5. Chemical composition of PRE05 obtained.

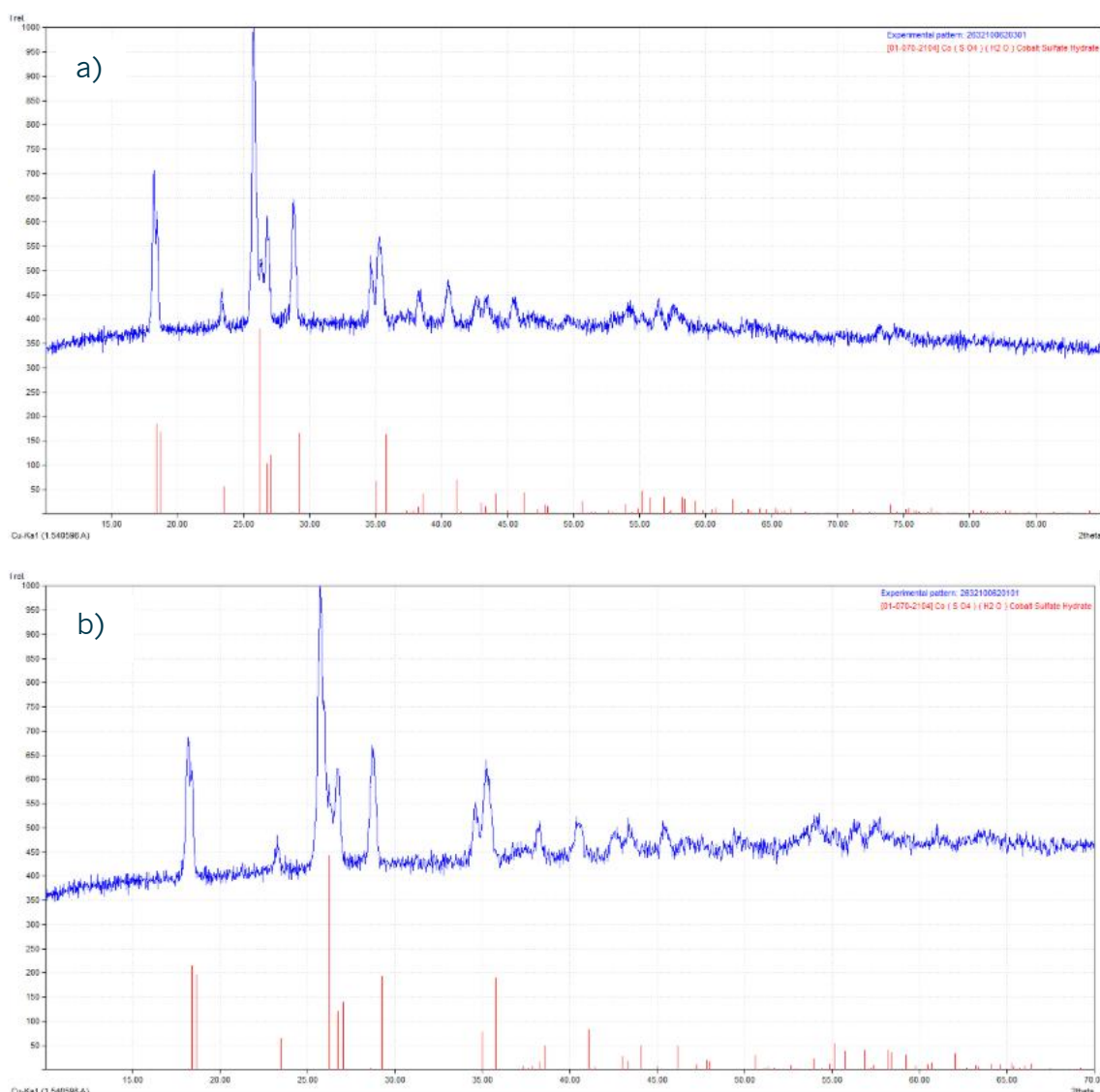
wt. %	BM04	BM05	BM06
Li	0.14	0,20	0.19
Ni	23.86	22.90	23.41
Mn	8.06	6.22	5.59
Co	0.39	0.31	0.33
Cu	0.21	-	-
Fe	-	0.002	0.11

In this case, the chemical composition of the precursors is again similar to that obtained through lab-scale tests.

The final steps consist of stripping the Co-loaded DES, followed by evaporative crystallization to obtain the corresponding Co precursors. XRD patterns show the formation of cobalt sulphate (see **Error! No se encuentra el origen de la referencia.**). As previously mentioned, the chemical composition (

Figure 12. XRD of PRE04 from a) BM04, b) BM05, c) BM06.

Table 6) is also very similar to that of the precursors obtained through lab-scale tests.



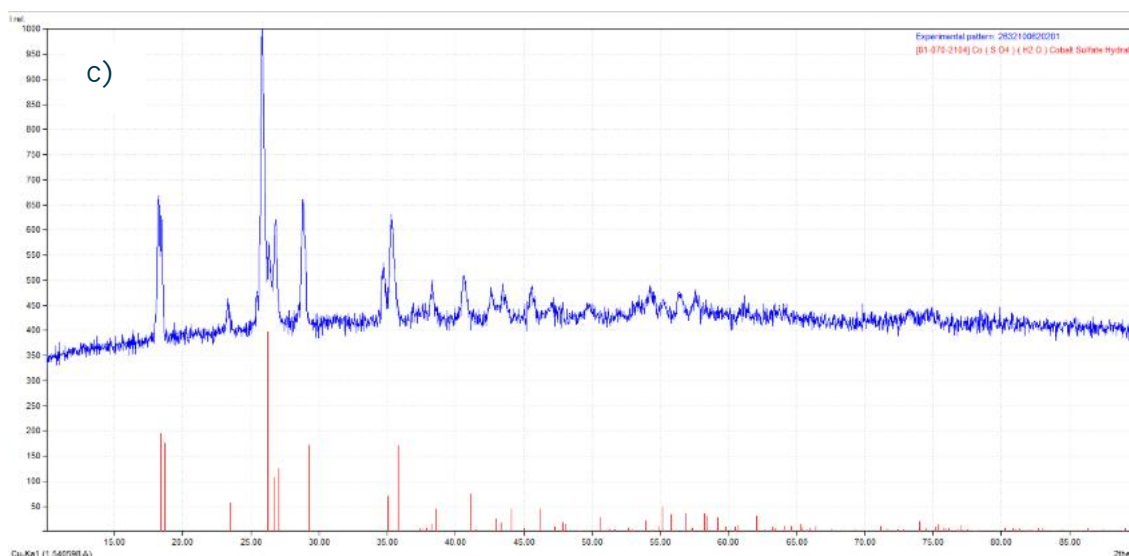


Figure 12. XRD of PRE04 from a) BM04, b) BM05, c) BM06.

Table 6. Chemical composition of PRE04 obtained.

wt. %	BM04	BM05	BM06
Li	0.002	0.002	-
Ni	0.38	0.49	1.59
Mn	12.90	12.90	11.93
Co	20.39	21.55	18.48
Cu	2.08	0.004	0.02
Fe	-	-	-

Table 8 summarizes a comparison between the product quantity obtained in the lab-scale and in the pilot scale for both dismantling processes. There are no major differences between the lab and pilot scale, except in the case of lithium carbonate for the Fraunhofer black mass in the pilot scale, but this is due to the lithium concentration in BM06 being lower than in BM03, not because of the change of scale in the process.

Table 7. Products obtained in pilot scale.

Element	Precursor	BM04		BM05		BM06	
		kg/kg BM	Rec. (%)	kg/kg BM	Rec. (%)	kg/kg BM	Rec. (%)
Li	Li ₂ CO ₃	0.025	72.9	0.17	97.7	0.02	83.5
Ni	Ni, Mn, Co oxalate	0.26	59.9	0.49	68.2	0.37	53.6
Mn			66.5		75.6		56.2
Co			44.5		81.1		79.1
Co	CoSO ₄	0.06	45.8	0.09	83.7	0.07	59.6
Ni	Ni, Mn oxalate/chloride	0.11	45.2	0.33	61.3	0.23	44.3
Mn			26.7		46.7		29.7
Co			1.7		4.2		3.2

4. Recycling solutions for cathode direct recycling at pilot scale

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 batteries¹. Thus, there is an urgent need to develop efficient recycling technologies.

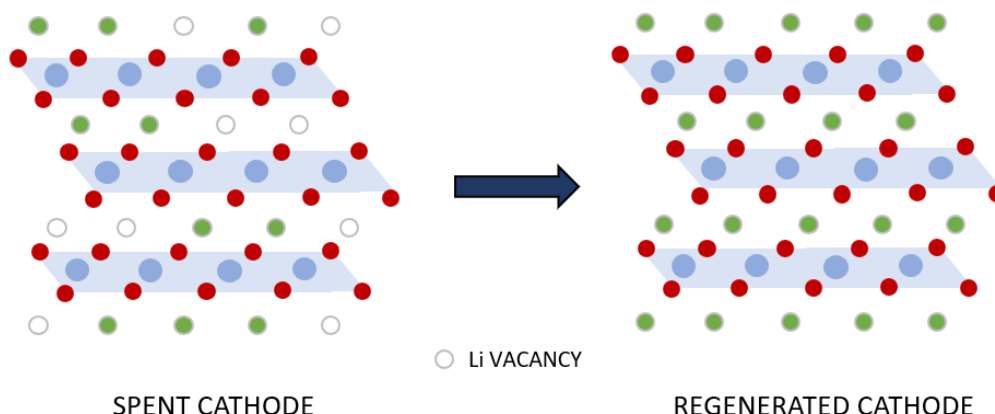


Figure 13. Schematic of the direct regeneration of cathode material.

4.1. Hydrothermal re-lithiation of cathodes

For hydrothermal re-lithiation, cathode active material (CAM) in its solid form obtained from ultrasonication delamination (ST4.2.3) was used.

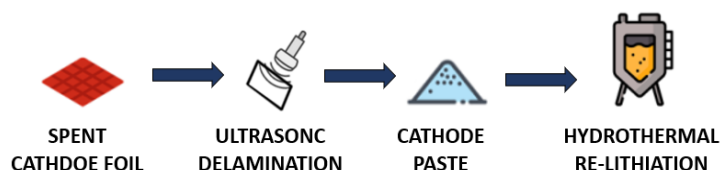


Figure 14. Previous cathode pretreatment: Ultrasonic delamination for Hydrothermal Relithiation

4.1.1. Hydrothermal re-lithiation at pilot scale

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 cathodesⁱⁱ. 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 15 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 2L 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.

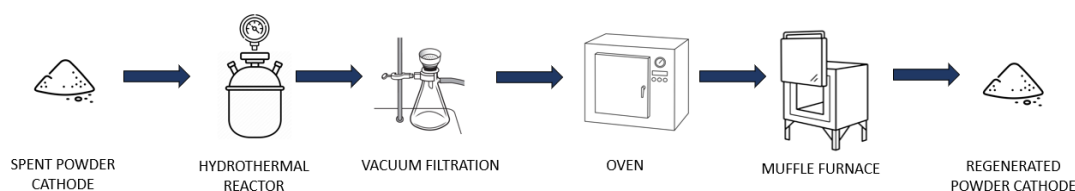


Figure 15. Hydrothermal re-lithiation experiment setup.

Based on results of D3.3, the scale up process was carried out. The total number of tests that were carried out was 8 (Table 8).

Table 8. Experimental design for hydrothermal re-lithiation.

Test	LiOH concentration (M)	Temperature (°C)	Reaction time (hours)
1	2	160	1
2	2	160	2
3	2	220	1
4	2	220	2
5	4	160	1
6	4	160	2
7	4	220	1
8	4	220	2

- **Hydrothermal Re-lithiation Procedure**

The reactor was loaded with the spent cathode powder at 50 g/L with a LiOH solution (Figure 16). 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 160°C → $P \approx 5.5$ bar and at 220°C → $P \approx 21.5$ 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. The dried cathode material was annealed in a muffle furnace to reconstruct the material's crystallinity and enhance the restoration of its original structure (Figure 17).

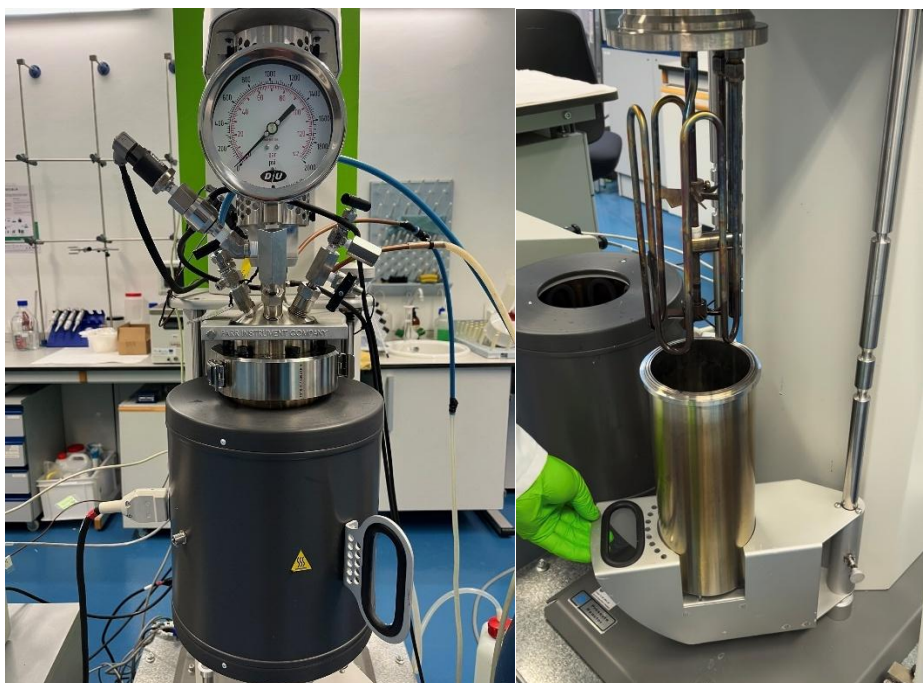
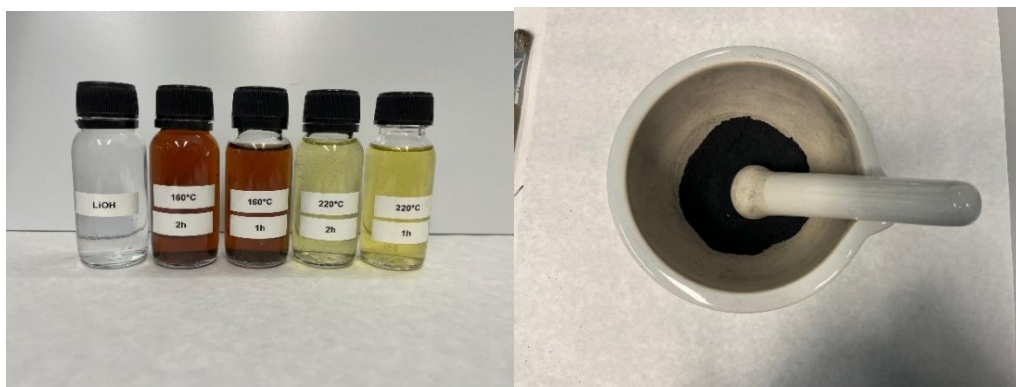


Figure 16. Reactor of 2L used during hydrothermal re-lithiation scaling process



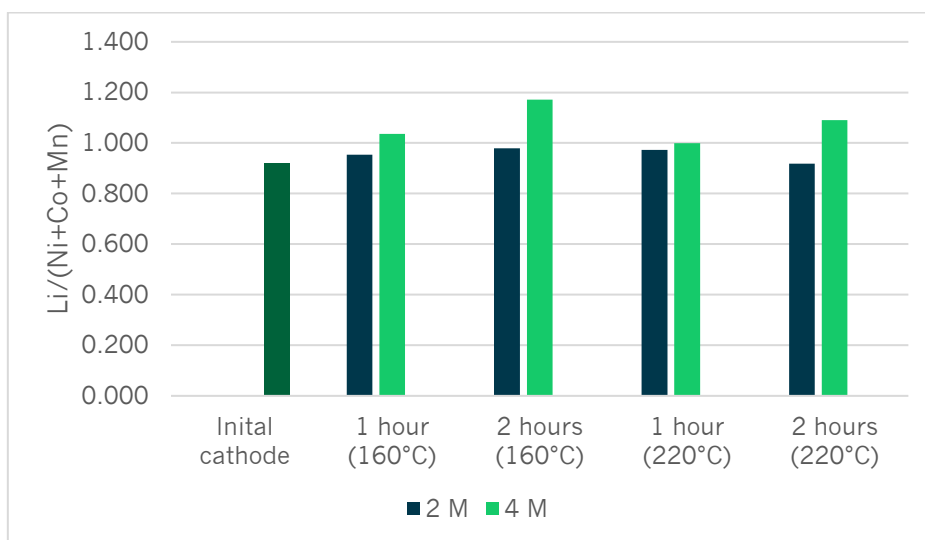
Figure 17. Cathode material annealing.

At the end of each experiment, three samples were obtained: the initial LiOH solution, the filtered solution and the solid after annealing in muffle furnace (Figure 18). 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 18. Samples obtained after a hydrothermal re-lithiation experiment.*

• Results and Discussion

After hydrothermal re-lithiation, the $\text{Li}/(\text{Ni}+\text{Mn}+\text{Co})$ ratio 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 (Figure 19).

*Figure 19. $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$ stoichiometric ratio for regenerated cathode materials.*

XRD was also used to analyse the regenerated CAM. The I_{003}/I_{104} peak intensity ratio was calculated, as it reflects the level of cation mixing. It is generally accepted that Ni^{2+} can occupy the Li^+ sites, and such Li–Ni disorder can lead to capacity loss. When $I_{003}/I_{104} > 1.2$, the electrochemical performance is typically improvedⁱⁱⁱ. The XRD patterns of regenerated NCM622 particles with $I_{003}/I_{104} > 1.2$ are shown in Figure 20, along with their corresponding I_{003}/I_{104} values.

The effect of LiOH concentration, temperature, and reaction time on the structural properties of regenerated NCM622 was evaluated using the I_{003}/I_{104} ratio and the $Li/(Ni+Co+Mn)$ ratio. At 2 M LiOH, increasing the reaction time from 1 to 2 h at 160 °C significantly improved the I_{003}/I_{104} ratio (from 1.19 to 1.48), indicating enhanced cation ordering, with a $Li/(Ni+Co+Mn)$ ratio close to unity (0.98). In contrast, at 220 °C, prolonged reaction time led to a decrease in both ratios, suggesting structural degradation or lithium loss.

At 4 M LiOH, the highest I_{003}/I_{104} value (1.54) was obtained at 160 °C for 1 h. Extending the reaction time to 2 h caused a sharp deterioration in structural ordering ($I_{003}/I_{104} = 1.06$), despite a substantial increase in lithium content. At 220 °C, intermediate I_{003}/I_{104} values (~ 1.3) were observed, with $Li/(Ni+Co+Mn)$ ratios near or above unity.

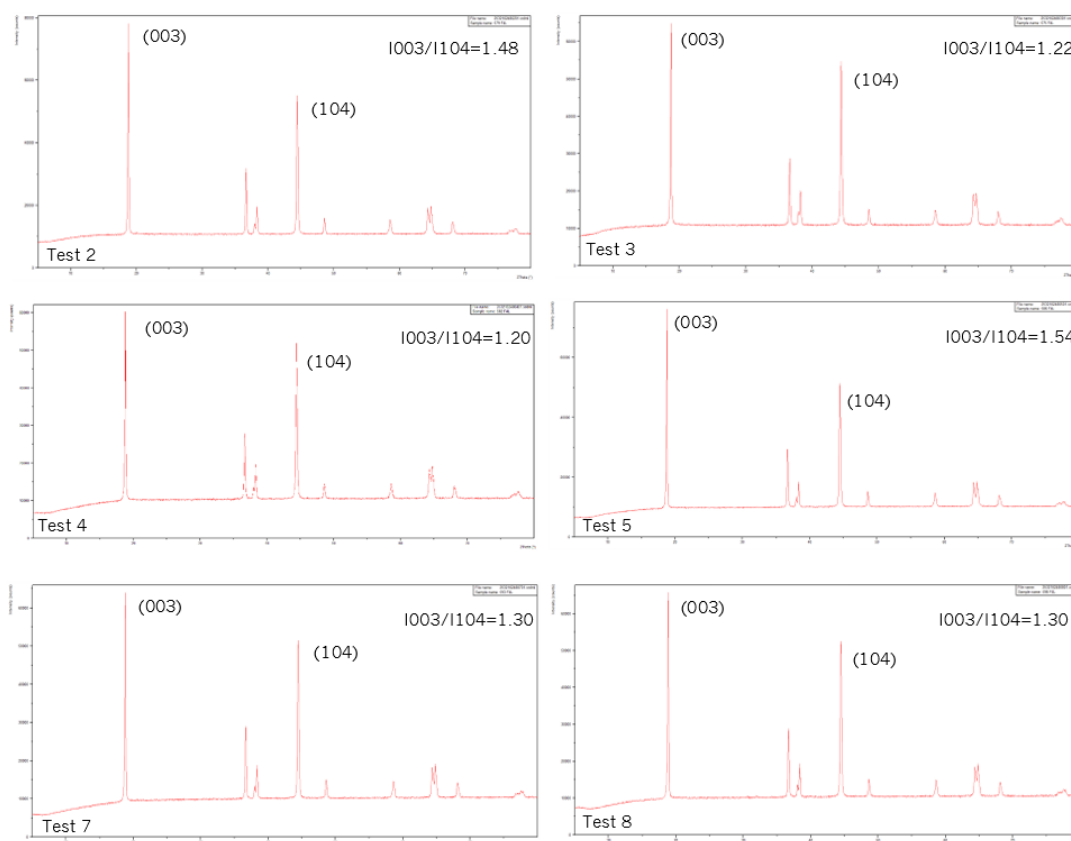


Figure 20. XRD patterns for tests 2, 3, 4, 5, 7 and 8.

The cathode material before and after hydrothermal re-lithiation was characterized to observe morphological and microstructural changes. Figure 21 (A, B) shows the SEM images, and Figure 21 (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.

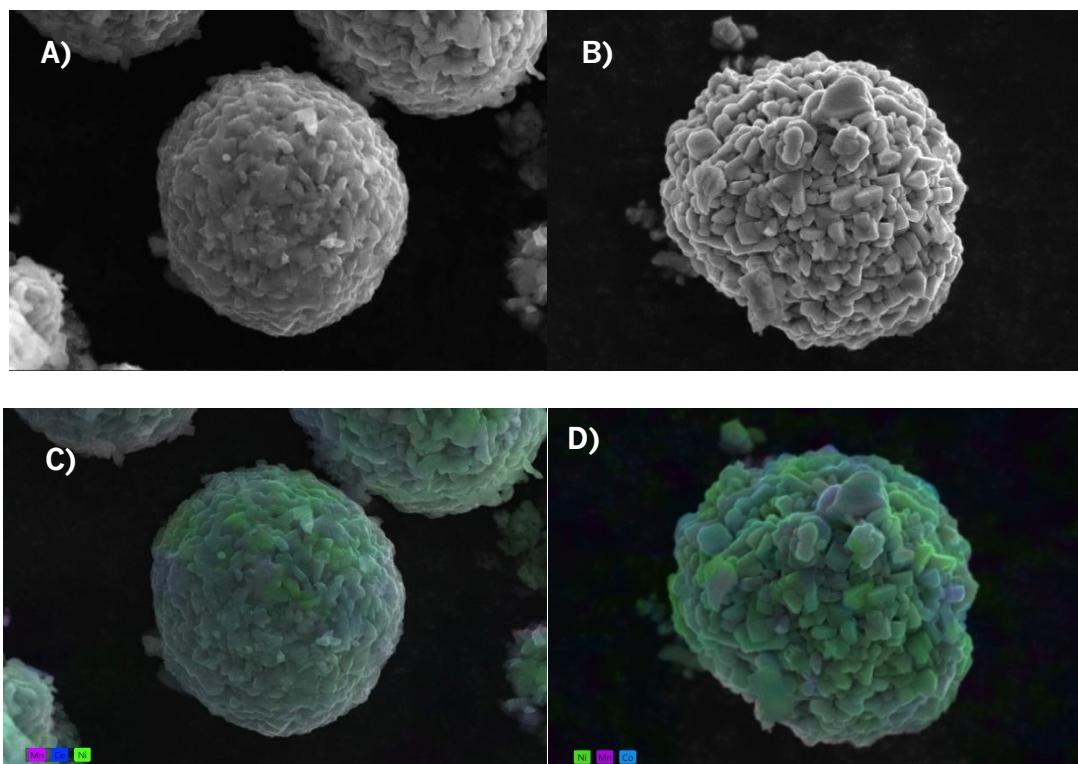


Figure 21. SEM images of the cathode active material A) Degraded B) Regenerated. EDS images of the cathode active material C) Degraded D) Regenerated.

SEM image of the degraded and regenerated CAM showed that its morphology consists of spherical particles. Figure 21 (A and B) shows an important difference between the degraded and regenerated cathode material: before the hydrothermal process, the particles show relatively smooth and featureless particles, with no clearly defined surface features, suggesting a loss of structural order and poor crystallinity. In contrast, the cathode material after the regeneration process exhibits a rough and highly textured surface with well-defined grain-like features, indicating the restoration of a more ordered crystalline structure. This morphological change confirms the effectiveness of the regeneration process in reconstructing the material. EDS images 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.

4.2. Electrochemical re-lithiation of cathodes

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. This cell is formed by immersing a working electrode (WE), a counter electrode (CE), and a reference electrode (RE) in the lithium-ion solution.

For the electrochemical re-lithiation process, cathode foils obtained from manual dismantling (ST3.2.3) described in Deliverable D3.2, were used.

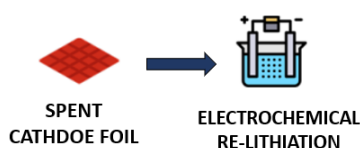


Figure 22. Previous cathode pre-treatment: Non-delamination for Electrochemical Re-lithiation recycling.

4.2.1. Electrochemical re-lithiation at pilot scale

- **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 23, the entire spent cathode foil used in scaling experimentation and the half-spent cathode foil used in lab experimentation are shown.

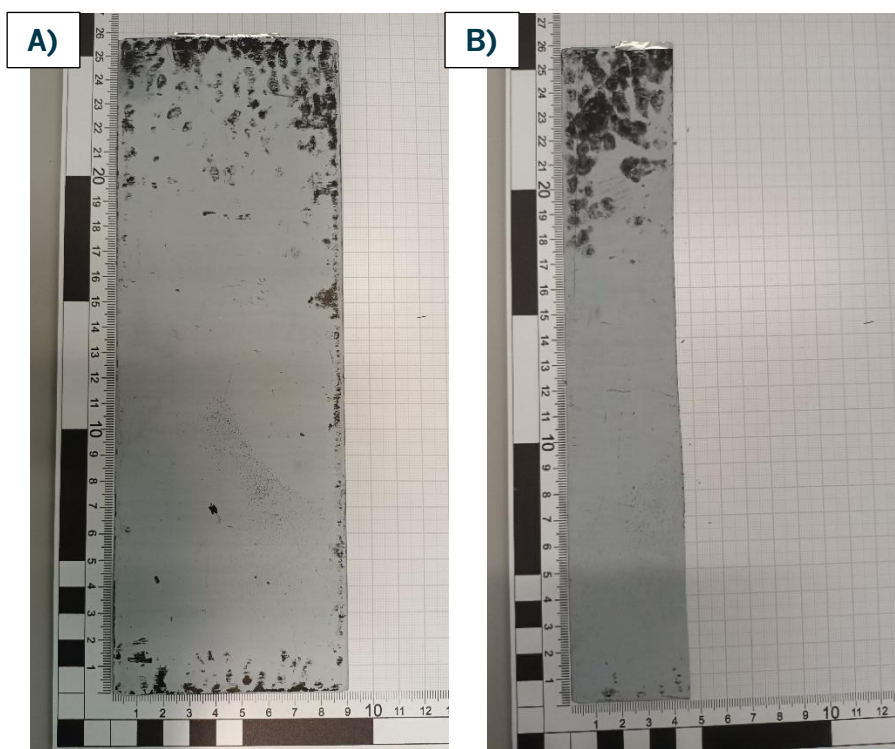


Figure 23. A) Entire spent cathode foil B) Half spent cathode foil

Electrochemical measurements were carried out using a potentiostat-galvanostat OrigaFlex (Figure 24). During the experiment, solution samples were collected to monitor the variation in the concentration of Li^+ ions using ICP analysis.

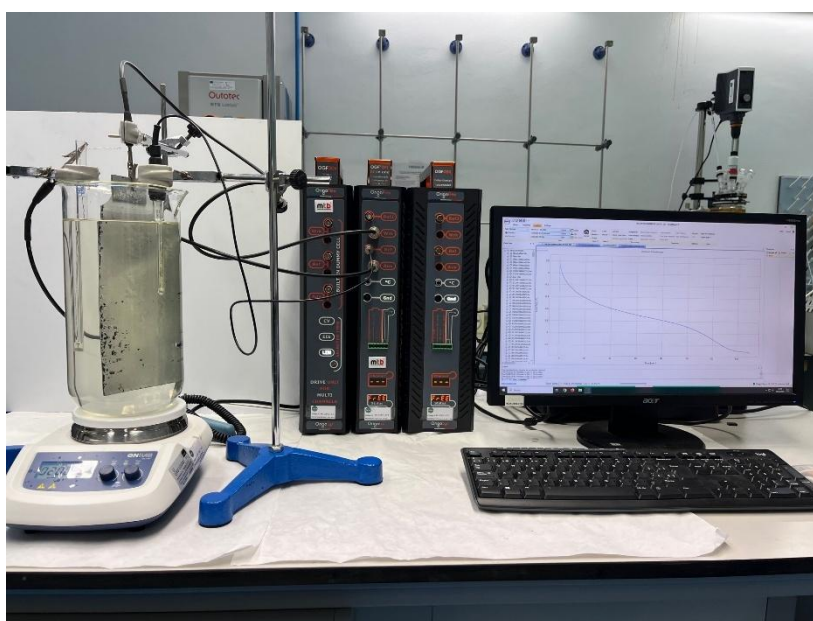


Figure 24. Electrochemical cell and potentiostat-galvanostat OrigaFlex

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

The process was previously optimized at lab scale (D3.3). With the parameters such as source and concentration of lithium-ion solution, temperature and stirring, among others, the process was validated at pilot scale.

The electrochemical re-lithiation was performed in a dedicated electrochemical cell developed for lithium-ion battery recycling applications and protected under the Spanish utility model “Electrochemical cell for recycling lithium-ion batteries” (Ref.1621-U-CELDA).

The first set of experiments focused on combining electrochemical re-lithiation with subsequent thermal treatment in a muffle furnace to promote delamination of the aluminium current collector cathode coating and recover the cathode active material (CAM). Initial tests were performed with individual cathode foil, followed by experiments with multiple foils simultaneously. After electrochemical re-lithiation, the cathode foils were thermally treated at different temperatures, for periods of 2 to 4 hours.

Thermal treatment at 600 °C was determined to be the most suitable condition for separating the CAM from the aluminium current collector. At this temperature, the CAM could be separated relatively easily. On the other hand, treatments at lower temperature were not effective for delamination: the cathode foils remained practically unchanged, or the aluminium foil remained too ductile, making mechanical separation difficult. Treatments at higher temperatures, facilitated thermal processing but resulted in a decrease in the lithium content of the recovered CAM.

The influence of muffle furnace temperature on the $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$ molar ratio was evaluated using ICP analysis for CAM powder re-lithiated and for the relithiated foil. The results are shown in Table 3. It showed a clear decrease in lithium content with increasing thermal treatment temperature. For the re-lithiated CAM treated as a powder, the $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$ ratio decreased from 0.949 at 600 °C to 0.891 at 700 °C and 0.723 at 800 °C. A similar trend was observed when the entire re-lithiated cathode foil was treated: the ratio decreased from 0.936 at 600 °C to 0.919 at 700 °C and 0.828 at 800 °C. These results indicate that high temperature treatment promotes lithium loss from the active material.

Table 9. Results of Li/(Ni+Co+Mn) molar ratio with different temperatures

SAMPLE	MUFFLE CONDITIONS		ICP ANALYSIS
	T (°C)	T(h)	Li/(Ni+Co+Mn)
Initial CAM	-----	-----	0.912
Relithiated CAM powder	-----	-----	0.969
Relithiated CAM powder	600	4	0.949
Relithiated CAM powder	700	4	0.891
Relithiated CAM powder	800	4	0.723
Relithiated foil	600	4	0.936
Relithiated foil	700	4	0.919
Relithiated foil	800	4	0.828

Comparing the two treatment approaches, slightly higher Li/(Ni+Co+Mn) ratios were obtained when the relithiated CAM was first separated from the aluminium current collector and then thermally treated, rather than treating the entire relithiated cathode foil directly. But the results confirmed that 600°C is the most favourable thermal treatment temperature.

SEM analysis was carried out in order to evaluate the morphology of the relithiated CAM after the muffle treatment. Two types of samples are compared in the Figure 25. On one hand, the relithiated CAM powder and on the other hand, the CAM recovered from relithiated cathode foils. Both after thermal treatment at 600°C. Characterization was performed using an acceleration voltage of 20 kV and a working distance of 10.9 mm.

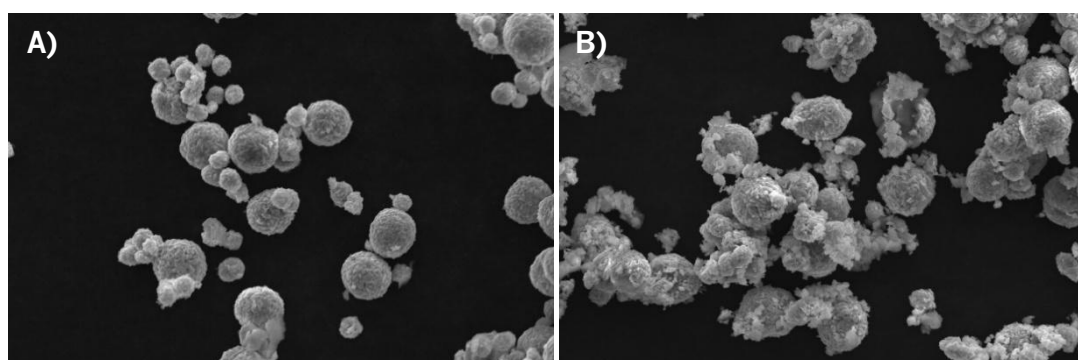


Figure 25. A) Relithiated CAM powder after annealing at 600°C. B) CAM recovered from relithiated cathode foil after annealing at 600°C.

The SEM image of the relithiated CAM powder shows a cleaner and more homogeneous morphology. The spherical CAM particles appear more clearly defined and less agglomerated, with fewer fine residues or fragmented material between particles. The rounded morphology of the CAM is largely preserved after the thermal treatment.

The SEM image of the CAM recovered from the relithiated foil shows a more heterogeneous appearance. Although spherical CAM particles are still visible, the sample contains a higher amount of agglomerated material, fine fragments and irregular particle clusters. This less clean morphology is likely related to the previous attachment of the active material to the aluminium current collector and the subsequent thermal delamination and sieving step used to recover the CAM.

On the other hand, as part of the scale-up assessment, the electrochemical relithiation process was applied to two cathode foils simultaneously under the selected operating conditions, previously optimized at lab scale: 1M Li_2SO_4 , 60 °C, and solution stirring. The aim of this test was to evaluate whether the process could be extended from individual cathode foil to the simultaneous treatment of more than one foil. After electrochemical relithiation, the relithiated cathode foils were thermally treated in a muffle furnace at 600 °C for 2 h. This temperature was previously selected, as it enabled efficient separation of the CAM from the aluminium current collector while limiting lithium loss. After the thermal treatment, the CAM was separated from the aluminium current collector using a 45 µm sieve.

ICP analysis was carried out on the CAM obtained from the original cathode foils and on the CAM recovered after the combined treatment (electrochemical relithiation, thermal treatment and sieving). The $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$ ratio was used as the main indicator to evaluate the efficiency of the treatment.

Table 4. Results of $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$ molar ratio to two cathode foils simultaneously

Sample		$\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$
1	Initial CAM	0.914
	Relithiated foils	0.939
2	Initial CAM	0.916
	Relithiated foils	0.979
3	Initial CAM	0.937
	Relithiated foils	0.968

4	Initial CAM	0.951
	Relithiated foils	0.957
5	Initial CAM	0.934
	Relithiated foils	0.943

The results showed an increase in the Li/(Ni+Co+Mn) ratio for all the analysed samples after the complete treatment sequence.

These results confirm that the simultaneous treatment of two cathode foils is technically feasible. The increase in the Li/(Ni+Co+Mn) ratio in all analysed samples indicates that lithium enrichment was achieved and maintained after the full process sequence.

Overall, this test represents a relevant step towards process scale-up, demonstrating that the selected electrochemical conditions can be successfully applied to more than one cathode foil at the same time.

The cathode material before and after electrochemical re-lithiation and annealing (Figure 26) was characterized to observe morphological and microstructural changes. The elemental composition of the surface was analysed by energy dispersive X-ray spectroscopy (EDS). Characterization was performed using an acceleration voltage of 15 kV and a working distance of 10 mm.

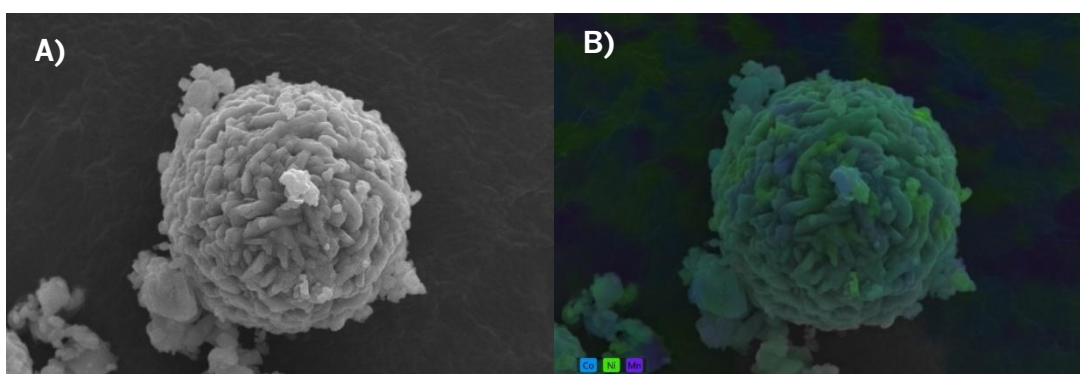


Figure 26. CAM powder after electrochemical re-lithiation and annealing process. A) SEM image B) Element map by EDS.

The SEM image of the CAM after annealing process showed that its morphology consists of spherical particles. The element map indicated that the material is composed of cobalt (blue), manganese (purple) and nickel (green), which are characteristic components of an NMC battery.

4.3. Recycling precursor mixtures for Flame Spray Pyrolysis productions (LUREDERRA)

One of the strategies for using recycled materials obtained from black mass is the preparation of optimum metal precursors suitable for the Flame Spray Pyrolysis equipment (FSP). Within this technology, nano-scaled active materials could be produced for later get cathodes.

LUREDERRA has worked with recycled materials from CSIC and CARTIF, in which the processing level and the recycling procedure followed were different. Along WP3 specific routes were defined to transform them into liquid recycled precursors and then, prepare the optimum liquid precursor mixtures. A clear scheme of this procedure is shown on the following figure.

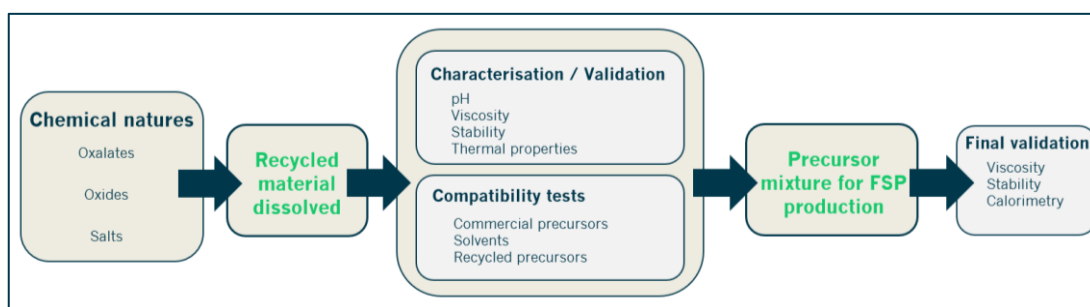


Figure 27. General scheme.

The feasibility of those materials was studied at laboratory scale during WP3 activities. Detailed information of all tests is included on D3.3. As a summary, main conclusions extracted are compiled on the following table (Table 10).

Table 10. Overview of the transformation procedure to transform recycled materials into optimum precursor mixtures.

RECYCLED MATERIAL	METAL COMPOSITION	DESCRIPTION OF THE ROUTE FOLLOWED AND RESULT OBTAINED
Mixture of metal, metal oxides and graphite powder (CSIC)	Carbon, cobalt, nickel, manganese, and other impurities such as aluminium, iron and copper.	Firstly, a thermal treatment was required for the removal of graphite. Then, hard digestion conclusions 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.
Metal oxides (CARTIF)	Nickel, manganese, cobalt, lithium mainly.	The powder was directly dissolved in an acid media. The homogeneous digestion liquid was mixed with different solvents and a suitable precursor mixture for the FSP equipment was achieved including some pH adjustment.
Metal carbonates (CSIC)	Lithium	A liquid precursor was achieved directly from the carbonate, with the presence of an inorganic acid. Additionally, an intermediate salt was obtained from the carbonate to get a more-easily handled material. In both cases, a suitable recycled precursor mixture was obtained.
Metal oxalates (CSIC)	Nickel, Cobalt Manganese,	A specific digestion procedure was defined and followed to get a homogeneous liquid solution without missing any interesting element on the process. The compatibility tests carried out after with different alcoholic media ended in good way, and a suitable recycled precursor was achieved.
Sulphates (CSIC)	Cobalt	This material can be used directly as a cobalt precursor for enriching other precursor mixtures prepared with low quantity of this metal. It is compatible with an alcoholic media, after a pre-solution into water.

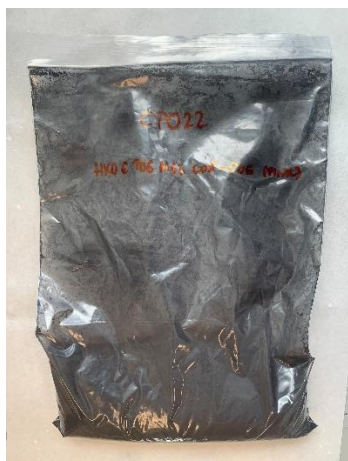
Analysing the results obtained and detailed on the above table, the recycled materials selected and used for the up-scaling were:

- Mixed metal oxides from CARTIF
- Lithium carbonate from CSIC
- Mixed oxalates from CSIC

In line with the project and as agreed with other partners, LUREDERRA has been focused on two main active material compositions: LiNMC622 and LiNMC811.

4.3.1. Up-scaled LiNMC622 recycled precursor mixture.

For this LiNMC622 composition, it was decided to use recycled material from CARTIF, as it contained a similar metal ratio, so less modifications and steps would be required.



Element	% (w/w)
Ni	39.873
Mn	8.709
Co	6.546
Li	6.957
Al	0.206
Fe	0.000

Figure X. Recycled cathode powder from CARTIF and elemental analysis.

The procedure followed was similar to the one previously defined (Table 10) but adapting it to a higher scale, which means basically using more quantity of recycled materials and high-capacity equipment. First of all, an acid digestion was carried out to transform the recycled material into a liquid stable precursor.



Figure 28. Acid digestion of recycled material from CARTIF.

The acid digestion successfully transformed the solid material into a liquid recycled precursor. Then, to prepare the corresponding precursor mixture for the combustion of the FSP, a stage for finetuning the physico-chemical properties was required. First of all, the lithium content was adjusted (including some extra lithium to compensate the lithium loss during combustion) with

recycled lithium carbonate from CSIC. Additionally, other parameters such as concentration, calorimetry, viscosity and pH, were optimised.

Along WP3, the most promising production parameters were defined. Those conditions required a low temperature of combustion, low viscosity of the precursor mixture and a specific extra lithium content. Following these instructions, the recycled precursor mixture LiNMC622 was designed and validated.

Table 11. Characterisation of recycled precursor mixture.

	Recycled liquid precursor mixture LiNMC622	
Calorimetry	415 cal/g	
Viscosity	1,59 cP	
pH	3,5	
Stability	Good	

4.3.2. Up-scaled LiNMC811 recycled precursor mixture.

On the other hand, for this composition LiNMC811, LUREDERRA has worked with up-scaled recycled materials from CSIC, specifically, a mixed oxalate of Ni, Mn and Co and lithium carbonate.

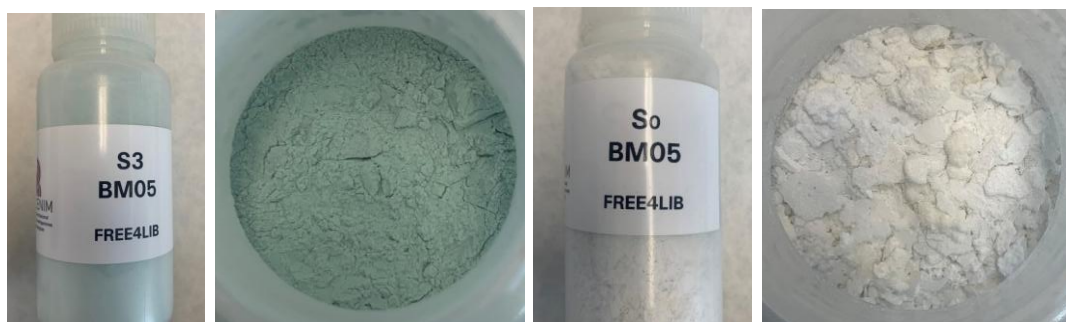


Figure 29. Recycled mixed oxalate of Ni, Mn and Co, materials from CSIC.

In the same way as mentioned before, the procedure already defined for this nature of material (oxalates) was adapted to a bigger scale. In that sense, the first stage consisted of an acid digestion. Some technical parameters like timings and concentrations were modified until getting a transparent liquid solution.



Figure 30. Evolution of the recycled powder during the acid digestion, and final solution.

This stage performed successfully and all the recycled powder was completely transformed into liquid. Next stage was to prepare the liquid precursor mixture. In that sense and taking into account the initial composition of the mixed oxalate, the metal ratio was adjusted looking for the desired LiNMC811 composition. These adjustments were done both with recycled precursors (lithium carbonate from CSIC) and other commercial ones.



Figure 31. Liquid precursor mixture for LiNMC811.

In order to get an optimum precursor mixture for the FSP, several requirements concerning the physicochemical properties should be achieved: good stability, low calorimetry and viscosity values; and neutral pH. This last measurement was too low that an adjustment was required. In that sense, several tests were done in a small-scale, until getting the right pH value.

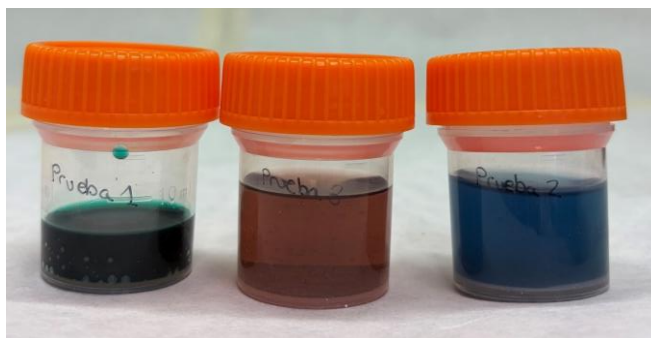


Figure 32. pH adjustment of the recycled precursor mixture.

Finally, the resulting recycled precursor mixture was completely characterised and validated for later production on the FSP. All physico-chemical properties are gathered on the following table.

Table 12. Characterisation of recycled precursor mixture.

	Recycled liquid precursor mixture LiNMC811	
Calorimetry	289 cal/g	
Viscosity	1,29 cP	
pH	3,7	
Stability	Good	

5. Conclusions

CSIC demonstrated the viability of pyro-hydrometallurgical process developed at lab scale in batches of 5 kg, obtaining precursor feasible for the synthesis of cathode active materials by different routes. Table 13 shows the precursors obtained per batch.

Table 13. Products obtained in pilot scale.

Element	Precursor	BM04	BM05	BM06
		kg/batch	kg/batch	kg/batch
Li	Li_2CO_3	0.13	0.85	0.25
Ni	Ni, Mn, Co oxalate	1.30	2.45	1.85
Mn				
Co				
Co	CoSO_4	0.30	0.45	0.35
Ni	Ni, Mn oxalate/chloride	0.55	1.65	1.15
Mn				
Co				

CARTIF has demonstrated the technical feasibility of efficient direct recycling processes (hydrothermal and electrochemical) to regenerate degraded cathode foil and powder materials from spent lithium-ion batteries, preserving the characteristic NMC composition and spherical particle morphology.

The results of hydrothermal re-lithiation process confirmed that lithium solution concentration, temperature and reaction time strongly influence in the structural recovery of the cathode material. The best results were achieved when the conditions were moderated, specially at 160°C. In this case, improved Li/(Ni+Co+Mn) ratios and favourable XRD indicators were observed. This re-lithiation preserved the spherical NMC622 morphology transforming the degraded smooth surface into a rougher, like a grain structure, indicating a material reconstruction and confirming the presence of Ni, Co and Mn. On the other hand, when the conditions were more severe (higher temperatures and longer reaction times), it negatively affected to the structural quality of the regenerated material.

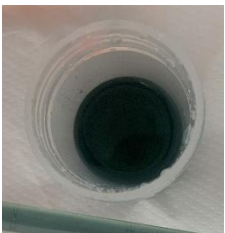
The electrochemical process also proved to be effective in restoring the lithium content in the cathode foils. The selected conditions in WP3, were successfully applied at pilot scale, treating simultaneously several cathode foils. After electrochemical process, thermal treatment at 600°C was the most suitable condition to separate CAM from current collector. The regenerated CAM was compared with commercial NMC622, and it was observed that the regenerated CAM also preserved the main NMC622 layer crystalline phase with no secondary phases detected. However, the lower I003/I104 ratio compared with commercial NMC622 indicates higher Li/Ni cation mixing and lower structural ordering.

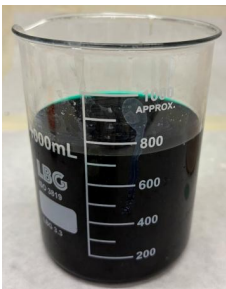
In general, both technologies demonstrated potential for direct cathode recycling at pilot scale.

LUREDERRA has validated the feasibility of preparing optimum precursor mixtures for FSP productions from recycled materials. Recycled materials from different natures can be transformed into liquid precursors with desired physico-chemical properties. Additionally, they can be mixed with other recycled materials as well as commercial ones to prepare a suitable precursor mixture. The synthesis of active materials through FSP requires specific conditions, like low temperature combustion. In that sense, recycled precursor mixtures had been successfully adapted to these conditions, achieving low calorimetry values.

On the other hand, both recycled materials used on the up-scaling required an acid digestion, conducting to a very low pH of the resulting liquid precursor. An extra adjustment was required looking for a neutral value. After several tests, the optimisation was achieved without any inconvenient in terms of precipitates.

Table 14. Summary.

SOLID RECYCLED PRECURSOR	LIQUID RECYCLED PRECURSOR	PRECURSOR MIXTURES	PHYSICO-CHEMICAL CHARACT.
Metal oxides (CARTIF) Li, Ni, Mn, Co 	2713 cal/g 1.62 cP 	Li adjustment with commercial precursor	NMC622 Calorimetry: 415 cal/g Viscosity: 1.59 cP 

Metal oxalate (CSiC) Ni, Co, Mn 	2854 cal/g 1.42 cP 	Adjustment with recycled and commercial precursor	NMC811 Calorimetry: 289 cal/g Viscosity: 1.29 cP 
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Further activities with these recycled precursor mixtures, including the FSP productions and the resulting materials are included and detailed on *Deliverable 4.4. Evaluation report on up-scaled active materials from recycled precursors.*

ⁱ Dobó, Z., Dinh, T., & Kulcsár, T. (2023). A review on recycling of spent lithium-ion batteries. *Energy Reports*, 9, 6362–6395.

ⁱⁱⁱ Song, H., Zhang, Z., Zhang, L., Dong, W., Ding, Y., Wang, Z., Wang, H., Deng, H., & Cheng, Q. (2023). Recycling of lithium ion battery cathodes by targeted regeneration. *Ionics*, 29(9), 3543–3547. <https://doi.org/10.1007/s11581-023-05134-4>