detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

LI-ION BATTERY RECYCLING AT PILOT SCALE: DEMONSTRATING THE RESYNTHESIS ROUTE ALSO FOR NMC-LFP MIXED BLACK MASS

Francesca Pagnanelli [1,2,*], Pietro Altimari [1], Pier Giorgio Schiavi [1], Ludovica D'Annibale [1], Alyssa Mancini [1], Marco Colasanti [1], Emanuela Moscardini [2], Lorenzo Toro [2], Ludovica Baldassari [2] and Luigi Toro [2]

[1] *Department of Chemistry, "Sapienza" University of Rome, p.le A. Moro 5, 00185 Rome, Italy*
[2] *Eco Recycling s.r.l., via F. Siacci, 4, 00197 Rome, Italy*

Article Info:
Received:
23 April 2024
Revised:
20 June 2024
Accepted:
12 July 2024
Available online:
17 September 2024

Keywords:
Li-ion batteries
Recycling
Pilot plant
Re-synthesis
NMC precursors
LFP

ABSTRACT

The hydrometallurgical recycling of end-of-life Li-ion batteries constitutes a sustainable path for the integral recovery of battery components. However, the heterogeneity of electrode materials constitutes a limitation for process optimization that must provide robust and flexible strategies. In this work, the preliminary results obtained as part of the demonstration activities of the LIFE DRONE project are reported with particular attention to the possibility of integrating the recycling process based on the resynthesis of NMC (Nickel Manganese Cobalt) cathodes with the treatment of mixed black mass also containing LFP (Lithium Ferrous Phosphate) electrodic powders. The experimental results obtained highlight the possibility of leaching NMC black mass in the absence of hydrogen peroxide when NMC-LFP mixtures are used with almost quantitative extraction yields of metals. In particular, working without H2O2 at 60°C for 3 h the following yields of extraction were obtained: 89% for Ni, 69% for Mn, 89% for Co, 91% for Li, 90% for Fe, 100% for P, 56% for Al and 32% for Cu. Furthermore, the experimental data showed that by varying the pH of the leach liquor, it is possible to separate selectively iron phosphate by quantitative precipitation (100% for Fe, 100% for P and 60% for Al) before proceeding with NMC resynthesis.

1. INTRODUCTION

The recycling of Li-ion batteries constitutes a fundamental step in the green transition process, both for the recovery of material resources (secondary raw materials) and for preventing the release of toxic metals into the environment. Recent updates to European regulations include Li-ion batteries as a new target type for which specific recycling rate requirements must be ensured (EU Regulation 2023/1542). The new Regulation opens the way to hydrometallurgical processes with significantly lower environmental impacts than conventional pyrometallurgical ones (Domingues et al., 2023). Nevertheless, hydrometallurgical processes still present various challenges in terms of safety and economic sustainability, leaving the door open for technical innovations that can simplify the recycling process. However, this need clashes with the structural and chemical complexity of Li-ion batteries

The automotive and electronics markets are predominantly characterized by NMC (Nickel Manganese Cobalt) batteries, which feature cathodes in the form of lithium transition metal oxides, such as nickel, manganese, and cobalt with various stoichiometries, while heavy-duty vehicles and stationary storage systems are characterized by Li-ion batteries with lithium iron phosphate (LFP) cathod active materials. However, this classification is vague as materials such as LFP can also be mixed within NMC batteries to increase thermal stability and therefore battery safety. There are several technical challenges in recycling Li-ion batteries.

The safe opening of Li-ion batteries requires measures to prevent explosion due to the presence of flammable solvents in the electrolytes. Furthermore, the evolution of cathodic material compositions, such as transition metal oxides, has led to materials entering the market (and thus into waste streams to be fed into recycling plants) with highly variable contents of nickel, manganese, and cobalt. The original recycling approach relied on downstream procedures typical of hydrometallurgy (chemical precipitation and solvent extraction) to remove metallic impurities (aluminium, iron, copper) and to separate manganese and

* Corresponding author:
Francesca Pagnanelli
email: francesca.pagnanelli@uniroma1.it

https://doi.org/10.31025/2611-4135/2024.19412

nickel from cobalt, which was the target metal of an initial generation of Li-ion batteries predominantly based on Li-CoO_2 (Pagnanelli et al., 2016; Abo Atia et al., 2019). The limited availability and high price of cobalt have driven the evolution of oxide chemistry towards stoichiometries with lower cobalt content, and therefore recycling processes cannot avoid recovering all the different types of metals present in batteries (nickel, manganese, cobalt, and lithium). The approach of recovering metal salts separately (via solvent extraction) incurs significant investment and operating costs that compromise the economic sustainability of the recycling process, whose potential is limited by end-of-life battery collection. An alternative and simpler approach from the downstream operations perspective is re-synthesis, in which the metals present in the purified leachate, free from metallic impurities, are directly recovered by producing mixed precursors (generally hydroxides) with metal stoichiometry that can be adjusted and corrected by adding salts (Schiavi et al., 2021).

Further complications arise from the lack of automated sorting systems for Li-ion batteries based on their chemistry (e.g., NMC and LFP) and the mixing of different cathode materials within the same batteries or in electric vehicle battery packs (such as various stoichiometries of NMC or NMC-LFP). This requires additional flexibility in hydrometallurgical processes to handle mixed cathodic materials. In the literature, studies on LFP batteries are mainly focused on direct recycling processes (without cathode dissolution) due to the low intrinsic value of these materials (Wang et al., 2022; Xu et al., 2024). However, for mixtures of NMC-LFP materials, the direct recycling strategy would necessitate a preliminary separation of the different cathodic materials, which has not yet been achieved. This implies that, to treat mixed NMC-LFP black masses, it will be necessary to dissolve both materials for their recovery.

Some hydrometallurgical recycling works of LFP batteries have been reported in the literature, typically utilizing an acid (sulfuric acid) to obtain phosphates, iron, and lithium in solution (Zheng et al., 2016). To keep iron in solution, it's necessary to prevent its oxidation, as it would otherwise precipitate as iron phosphate (Gerold et al., 2022). Alternatively, it is possible to work in the presence of an oxidizing agent (in the case of iron, hydrogen peroxide can be used), promoting the selective dissolution of lithium and recovering $FePO_4$ in the solid phase along with graphite (Li et al., 2017).

Recent works are addressing the problem of treating this mixture of black mass proposing a selective leaching of other metals except Fe, and then performing an additional leaching of the solid residue to recover Fe (Song et al., 2023).

In this general context, this work reports the first results at pilot scale of cathodic resynthesis from NMC black mass and also the results of simultaneous leaching of NMC-LFP black mass under the transferability activity foreseen in the LIFE DRONE project (LIFE DRONE project) for the extension to other types of wastes of the developed process route of NMC re-synthesis. The process in comparison with previously reported consider the simultaneous extraction of all metals and the following selective recovery of graphite, NMC precursors, $FePO_4$ and Li_2CO_3.

2. MATERIALS AND METHODS

2.1 Integrated process for recycling of Li-ion batteries and production of NMC cathodes

The process under validation at pilot scale within the activities of the LIFE DRONE project, includes the shredding of end of life (EoL) Li-ion batteries and the separation of the black mass from other recyclable fractions (steel, aluminium and copper), then the hydrometallurgical section for black mass dissolution and precursors resynthesis (as NMC hydroxides), and finally the production of lithiated mixed oxides as cathodic materials for new batteries. In Figure 1 the overall diagram of the integrated process is reported.

2.1.1 Main process operations at pilot scale

The integrated process for cathodic material production from black mass through resynthesis route was performed at pilot scale in different operative sections (Figure 2).

Dismantling of Li-ion batteries have been performed using the pilot plant designed and constructed during the LIBAT project (LIFE LIBAT project) dedicated to the recycling of Li(0) primary batteries. The process includes a cryo-mechanical crushing, dry separation (sieving and magnetic) and final bath in water (Pagnanelli et al., 2023). The cryo-mechanical section (400 kg/day potentiality) included a cryogenic pretreatment performed on the batteries in order to prevent explosions and control flame formation during crushing. Thermally stabilized batteries (−80°C for 45 min using a N_2 liquid shower in a cabinet) were then crushed in a hammer mill with 10 mm under-sieve. Crushed material was sieved (1 mm) and the over-sieve was separated by magnetic separation using a magnetic over-belt placed above the sieving belt. After this treatment, three

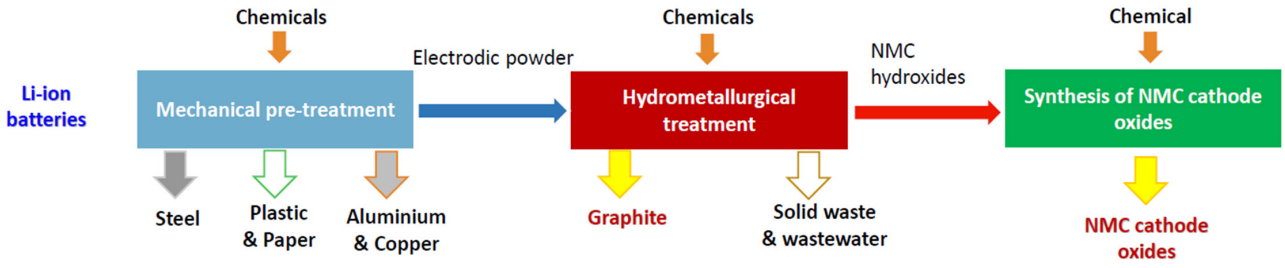

FIGURE 1: Schematic representation of the different sections of the recycling process.

FIGURE 2: Sections of the pilot plants: the cryo-mechanical section (a), the hydrometallurgical section for resynthesis (b), and the cathodic material production section (c).

fractions were collected: fine powder made up of electrode materials, a coarse magnetic fraction made up of external steel cases, and a non-magnetic coarse fraction made of large fragments of collectors and separators of plastic and papers. Copper and aluminium fragments from undersieve fraction and non magnetic oversieve fraction are separated by eddy currents.

The sequence of operations in the hydrometallurgical section was reported in Figure 3.

Black mass (30 kg per batch) was leached by using H_2SO_4 (18%ww, provided by Soave & Fontana) and adding 30%v H_2O_2 solution (provided by Soave & Fontana), with 1:10 kg/L solid to liquid ratio for 3 h under mechanical stirring at 60°C. Leach liquor was separated by filtration, purified with pH increase by NaOH (30%ww provided by Soave & Fontana) and then recovered by filtration. Pre-purified leach liquor was then corrected by metal (Ni, Mn, Co) sulphate (provided by Soave & Fontana) addition for obtaining the target stoichiometry (NMC111) and then used for mixed oxide precursor precipitation adapting a previous recipe (Schiavi et al., 2021): solution was added with NH_4OH (25%ww provided by Soave & Fontana) and NaOH (30%ww provided by Soave & Fontana) for pH correction (11), then kept under mechanical stirring at 60°C for 8 hours, periodically injecting N_2 in the reactor. Precursors were filtered and washed by water, dried in an oven at 100°C overnight, mixed with 10% stoichiometric excess of Li_2CO_3 (recovered from LIBAT process (Pagnanelli et al., 2023)) and thermally treated in a muffle with a two-stage ramp: 5 hours at 450°C and then 10 hours at 950°C.

2.2 Characterization of black mass and cathodic materials from pilot scale

NMC black mass was provided by S.E.Val. by performing cryo-mechanical treatment of EoL Li-ion batteries of NMC type according to the optimized process route developed in the LIBAT project (Pagnanelli et al., 2023), while LFP black mass is made up of cathode scraps furnished by FAAM. Cathodic materials are those obtained by pilot plant according to previously described route (Section 2.1.1).

The characterization of the incoming black mass and produced cathodic materials was performed by mineralization. The mineralizations were carried out by weighing 0.100 g of solid; these were placed in a 50 mL flask into which 4 mL of hydrochloric acid (VWR Chemicals, 37%ww), 4 mL of nitric acid (VWR Chemicals, 65%ww) were added, and 2 mL of hydrogen peroxide solution (Sigma Aldrich, 30%ww). The sample was subjected to magnetic stirring at a temperature of approximately 100°C for 3 hours. The mineralization operation just described was carried out 3 times in order to have 3 replicates for the chemical characterization of the sample. After 3 hours, the flasks are allowed to cool and brought to volume, to carry out the various dilutions starting from 1:10, 1:100, 1:1000; 1:5000. Finally, these dilutions are analyzed with the Inductively Coupled Plasma – Optical Emission Spectrophotometer, ICP-OES (Perkin Elmer, optical emission spectrometer Avio 220 Max) from which the different concentrations of the metals of interest are obtained.

Cathodic materials are characterised by Scanning Electron Microscopy (Zeiss Auriga FE-SEM).

2.3 Hydrometallurgical process for mixed NMC-LFP black mass at lab scale

The hydrometallurgical route for resynthesis of NMC cathodic materials is reported in Figure 3 putting in evidence the additional step for $FePO_4$ recovery after leaching. NMC-LFP mixed black mass (1:1 ratio in weight) were leached in thermos-stated jacked vessels under magnetic stirring with 1.5 M sulfuric acid (VWR Chemicals, 95%ww) and 1/10 solid liquid ratio in different operating conditions of H_2O_2 dosage (0 and 15% as % volume added to the suspension of 30%ww H_2O_2 solution, Sigma Aldrich), temperature (60 and 85°C), and time (3 and 5 h). Iron phosphate recovery was perfomed adding H_2O_2 (up to 600 mV) and increasing pH by 1 M NaOH solution (prepared from Sigma Aldrich pellets).

3. RESULTS AND DISCUSSION

The pilot-scale demonstration activities for the resynthesis of cathode materials from end-of-life Li-ion batteries

are still in progress within the activities of the LIFE DRONE project, which is scheduled to conclude in June 2024.

The following results pertain to the initial campaigns for the resynthesis of precursors at pilot scale and the transferability activities, at laboratory-scale, evaluating the application of the LIFE DRONE process using mixed NMC-LFP black mass.

3.1 Resynthesis at pilot scale of cathodic materials from NMC black mass

The starting electrode powder fed to the leaching section (black mass from S.E.Val) has the composition reported in Table 1. LFP scraps were composed by $LiFePO_4$ particles with V coating according to the following composition: 39±3 mg/g of Li, 330±30 mg/g of Fe, 180±20 mg/g of P, and 3.0±0.5 of mg/g V. Considering the stoichiometric ratios among nickel, manganese and cobalt this powder is equivalent to an NMC325 cathode material (not existing on the market and probably due to contamination effects as the mechanical plant is used also for the treatment of other types of batteries such as Li primary batteries and Ni metal hydride batteries. Fe, Al, and Cu contents in terms of atomic percentage (%at) are 1.5%, 4.3%, and 2.3%, respectively.

TABLE 1: Chemical composition of NMC black mass input material and NMC cathodes obtained by resynthesis routep.

Metal	Black mass (mg/g)	Cathodes (mg/g)
Li	40+/-3	50+/-20
Ni	96+/-6	200+/-30
Mn	77+/-2	150+/-20
Co	163+/-9	170+/-20
Fe	5.2+/-0.6	0.237+/-0.005
Al	7+/-2	5+/-3
Cu	9+/-2	9+/-2

NMC111 cathodes were obtained after correction of leach liquor composition by hydroxide precipitation and annealing in presence of Li salt. The stoichiometric coefficients of the NMC cathodes evaluated by chemical composition reported in Table 1 are 0.38, 0.30, and 0.32 for Ni, Mn, and Co, respectively, in line with the desired target stoichiometry (NMC111), while Li is under-stoichiometric (-17%). The atomic percentages of Fe, Al, and Cu are 0.04%, 2.1%, and 1.5%, respectively. The effect of such levels of metal impurities on electrochemical perfor-

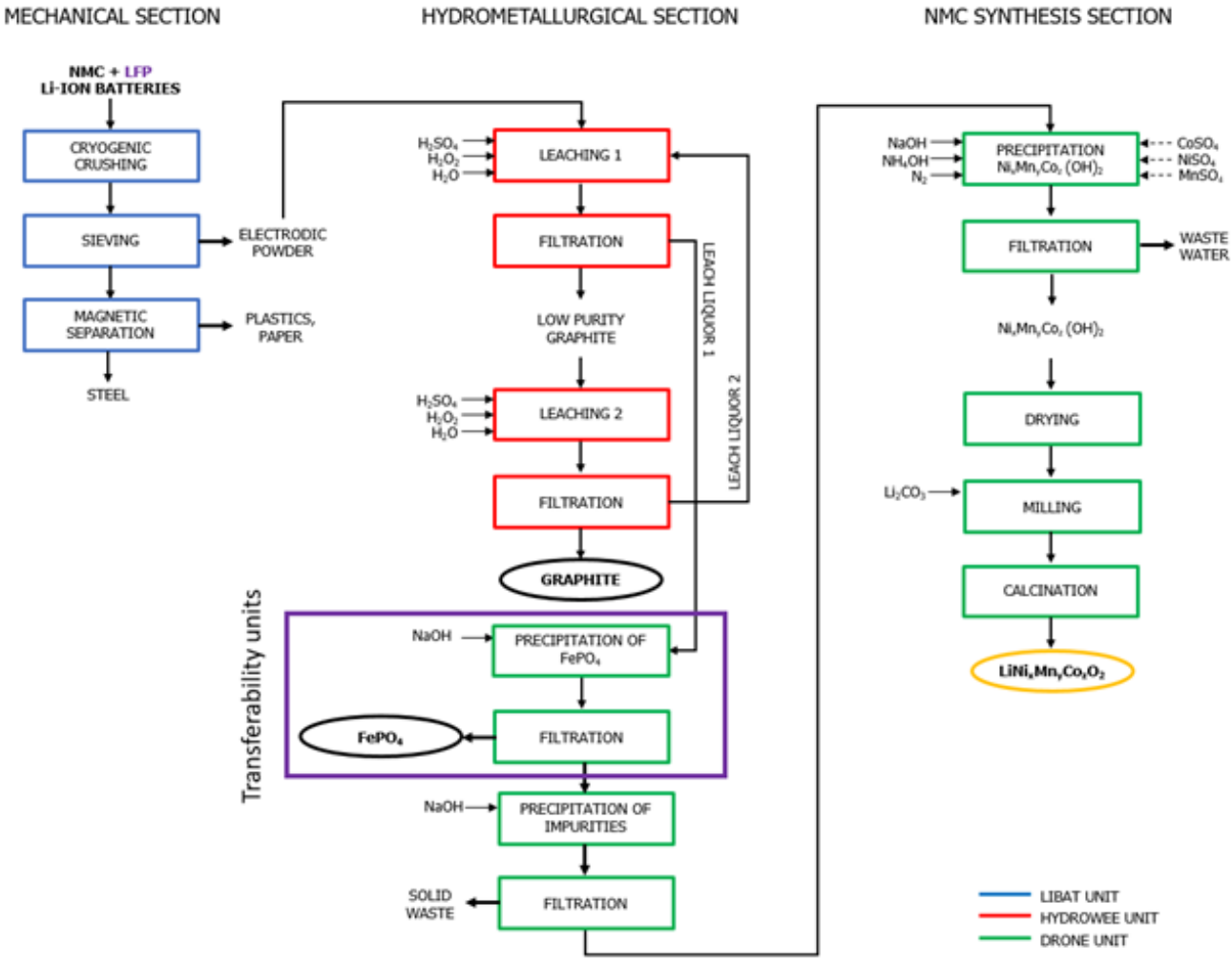

FIGURE 3: Process flow diagram for the integrated process of recycling of NMC-LFP black mass.

mances are still under evaluation. These metallic impurities present in the purified leach liquors are incorporated into the crystal lattice of the cathode material during coprecipitation. The presence of such metals can exhibit dopant effects below certain concentrations (Zhao et al., 2020; Sa et al., 2015), particularly for limit concentrations of 0.2% for aluminum (Zhang et al., 2020), 0.25% for iron (Park et al., 2018), and 1% for copper (Zhang et al., 2020). The simultaneous presence of different metal impurities requires further dedicated investigation as never reported in the literature.

SEM characterization of re-synthesized cathodic materials evidenced primary crystallites with size ranging from 200 to 300 nm, aggregating in larger structures (50-150 micron) as reported in Figure 4.

3.2 Transferability at lab-scale: leaching of mixed NMC-LFP black mass and $FePO_4$ recovery

Leaching of mixed NMC-LFP black mass by using the mildest conditions (60°C and 3h leaching) and without H_2O_2, enables achieving a metal extraction yield larger than to 90%, except for Mn and metal impurities (Al, Cu) as reported in Figure 5.

In particular, working without H2O2 at 60°C for 3 h the following yields of extraction were obtained: 89% for Ni, 69% for Mn, 89% for Co, 91% for Li, 90% for Fe, 100% for P, 56% for Al and 32% for Cu.

Average chemical composition of leach liquor is: 4400±800 mg/L for Li, 7000±500 mg/L for Ni, 7600±800 mg/L for Mn, 3000±300 mg/L for Co, 600±200 mg/L for Cu, 16000±1000 mg/L for Fe, 210±50 mg/L for Al, and 7700±900 mg/L for P.

$FePO_4$ recovery was performed by raising the pH of leach liquor to 2 provided the optimal option in terms of solid recovery (100% precipitation for Fe and P) and purity, as all metals except Al (60% precipitation) remain in solution at this pH. The presence of this impurity could be avoided by improving physical pretreatment (thus reducing initial amount of Al in black mass) or performing an initial basic leaching of the black mass.

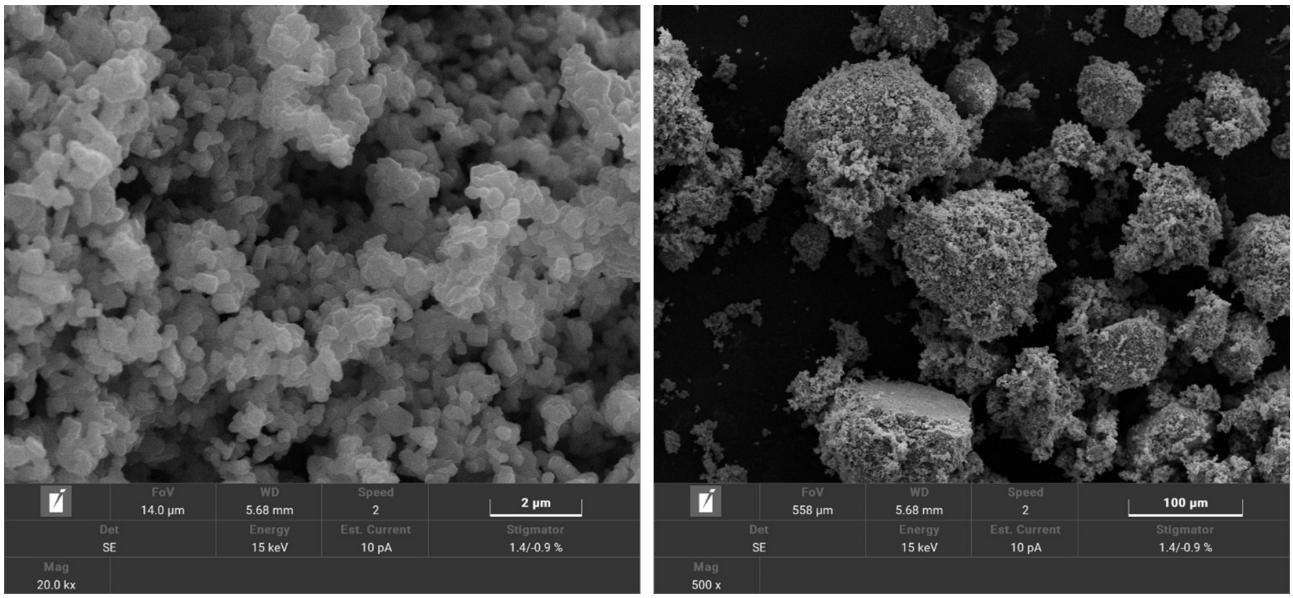

FIGURE 4: SEM characterization of re-synthetized cathodic materials at different magnifications.

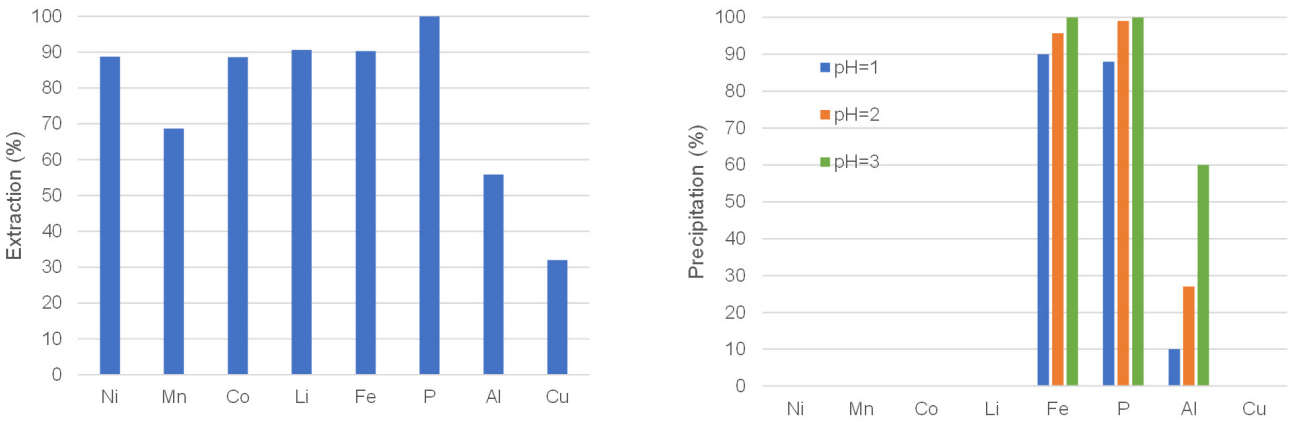

FIGURE 5: Metal extraction in NMC-LFP leaching (left); $FePO_4$ precipitation by pH increase (right).

4. CONCLUSIONS

The pilot-scale production activities of mixed cathodes through the resynthesis process are still ongoing, and the electrochemical performance of the obtained materials is also under evaluation, considering the presence of multiple metallic impurities resulting from the automated mechanical treatment process. In fact, currently, few literature information are available about the effect of metal impurities in the resynthesis route from EoL black mass. Electrochemical validation of produced materials could give new insight about the effect of simultaneous presence of different metallic impurities.

Even considering the necessary phases of process optimization, preliminary results have highlighted the effectiveness of the treatment regarding the ability to produce mixed cathodes with the desired stoichiometry starting from end-of-life Li-ion battery black mass with heterogeneous composition.

The lab-scale leaching tests of mixed NMC-LFP electrode powders have shown the possibility of extracting all solid metals quantitatively. Additionally, laboratory-scale tests have also highlighted the possibility of recovering iron before the precursor production process, allowing the treatment of mixed NMC-LFP black mass in the re-synthesis-based process.

AKNOWLEDGEMENTS

This work was co-funded by the EU LIFE+ program within the project "LIFE DRONE project: Direct pROduction of New Electrode materials from battery recycling (ENV/IT/000520) www.lifedrone.eu.

REFERENCES

Abo Atia, T., Elia, G., Hahn, R., Altimari, P., Pagnanelli, F., 2019. Closed-loop hydrometallurgical treatment of end-of-life lithium ion batteries: Towards zero-waste process and metal recycling in advanced batteries. Journal of Energy Chemistry, 35, 220-227. https://doi.org/10.1016/j.jechem.2019.03.022.

Domingues, A.M., Gabbay de Souza, R., Ometto, A.R., Silva, J.R.A., 2023. Life cycle assesment of scenarios for end-of-life management of lithium-ion batteries from smartphones and laptops Detritus, 25, 33-53 https://doi.org/10.31025/2611-4135/2023.18329

EU Regulation 2023/1542 of the European Parliament and of the Council of 12 July 2023 concerning batteries and waste batteries, http://data.europa.eu/eli/reg/2023/1542/oj

Gerold, E., Lerchbammer, R., Antrekowitsch, H., 2022. Parameter Study on the Recycling of LFP Cathode Material Using Hydrometallurgical Methods. Metals 12, 1706. https://doi.org/10.3390/met12101706

Li, H., Xing, S., Liu, Y., Li, F., Guo, H., Kuang, G., 2017. Recovery of Lithium, Iron, and Phosphorus from Spent LiFePO4 Batteries Using Stoichiometric Sulfuric Acid Leaching System. ACS Sus.Chem.Eng. 5, 8017- 8024 http//doi.org/10.1021/acssuschemeng.7b01594

LIFELIBAT project: Recycling of primary LIthium BATtery by mechanical and hydrometallurgical operations" Life LiBat - LIFE16 ENV/IT/000389 (https://www.lifelibat.eu/it)

LIFE DRONE project: Direct pROduction of New Electrode materials from battery recycling (ENV/IT/000520) (www.lifedrone.eu)

Pagnanelli, F., Moscardini, E., Altimari, P., Abo Atia, T., Toro, L., 2016. Cobalt products from real waste fractions of end of life lithium ion batteries. Waste Manag. 51, 214-221. https://doi.org/10.1016/j.wasman.2015.11.003.

Pagnanelli, F., Schiavi, P.G., Altimari, P., Beolchini, F., Amato, A., Coletta, J., Forte, F., Moscardini, E., Toro, L., 2023. Economic and Environmental Sustainability of an Innovative Cryo-Mechano-Hydrometallurgical Process Validated at Pilot Scale for the Recycling of Li Batteries. Metals, 13, 497. https://doi.org/10.3390/met13030497

Park, S., Kim, D., Ku, H., Jo, M., Kim, S., Song, J., Yu, J., Kwon, K., 2019. The effect of Fe as an impurity element for sustainable resynthesis of Li(Ni1/3Co1/3Mn1/3)O2 cathode material from spent lithium-ion batteries. Electrochimica Acta 296, 814-822, https://doi.org/10.1016/j.electacta.2018.11.001

Sa, Q., Heelan, J.A., Lu, Y., Apelian, D., Wang, Y., 2015. Copper Impurity Effects on LiNi1/3Mn1/3Co1/3O2 Cathode Material ACS Applied Materials & Interfaces 7 (37), 20585-20590. https://doi.org/10.1021/acsami.5b04426

Schiavi, P.G., Branchi, M., Casalese, E., Altimari, P., Navarra, M.A., Pagnanelli, F., 2021. Resynthesis of NMC111 cathodic material from real waste lithium ion batteries. CET, 86, 463 – 468 https://doi.org/10.3303/CET2186078

Song, S.L., Liu, R.Q., Sun, M.M. et al. 2023 Hydrometallurgical recovery of lithium carbonate and iron phosphate from blended cathode materials of spent lithium-ion battery. Rare Met. https://doi.org/10.1007/s12598-023-02493-9

Wang, M., Liu, K., Dutta, S., Alessi, D.S., Rinklebe, J., Ok, Y.S., Tsang, D.C.W., 2022. Recycling of lithium iron phosphate batteries: Status, technologies, challenges, and prospects, Renewable and Sustainable Energy Reviews, 163, 112515. https://doi.org/10.1016/j.rser.2022.112515.

Xu, Y., Zhang, B., Ge, Z., Zhang, S., Song, B., Tian, Y., Deng, W., Zou, G., Hou, H., Ji, X., 2024. Advances and perspectives towards spent LiFePO4 battery recycling. Journal of Cleaner Production, 434, 140077. https://doi.org/10.1016/j.jclepro.2023.140077

Zhang, R., Zheng, Y., Yao, Z., Vanaphuti, P., Ma, X., Bong, S., Chen, M., Liu, Y., Cheng, F., Yang, Z., Wang, Y., 2020. Systematic Study of Al Impurity for NCM622 Cathode Materials. ACS Sustainable Chemistry & Engineering 8 (26), 9875-9884 http://dx.doi.org/10.1021/acssuschemeng.0c02965

Zhang, R., Meng, Z., Ma, X., Chen, M., Chen, B., Zheng, Y., Yao, Z., Vanaphuti, P. Bong, S., Yang, Z., Wang, Y., 2020. Understanding fundamental effects of Cu impurity in different forms for recovered LiNi0.6Co0.2Mn0.2O2 cathode materials. Nano Energy 78, 105214 https://doi.org/10.1016/j.nanoen.2020.105214.

Zhao, Y., Yuan, X., Jiang, L., Wen, J., Wang, H., Guan, R., Zhang, J., Zeng, G., 2020. Regeneration and reutilization of cathode materials from spent lithium-ion batteries. Chemical Engineering Journal, 383, 123089 https://doi.org/10.1016/j.cej.2019.123089.

Zheng, R., Zhao, L., Wang, W., Liu, Y., Ma, Q., Mu, D., Li, R., Dai, C., 2016. Optimized Li and Fe recovery from spent lithium-ion batteries via a solution-precipitation method. RSC Adv. 6, 49 http://dx.doi.org/10.1039/C6RA05477C