Innovative technologies for spent lithium-ion batteries recovery, based on the microwave

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INTRODUCTION

To enable a major shift to bring transportation and power to greenhouse gas neutrality the coupling of both sectors for the first time in history is mandatory: batteries can enable 30% of the required reductions in carbon emissions in the transport and power sectors. However, the supply of the raw metals for batteries is precarious because of limited natural reserves of several raw materials and their local distribution. Thus, technologies that can stably secure strategic metals must be developed, as for example urban mining, which allows recovery of metals from secondary sources. However, at the moment, the waste recovery processes of battery wastes are complicated and require high resources consumption in terms of energies and chemicals necessary for metals extraction. In line with the European Green Deal, the Circular Economy Action Plan, and the Industrial Strategy, the Tech4lib project aims to work for a competitive, circular, sustainable, and safe value chain for lithium-ions batteries (LIBs), by developing an innovative and sustainable technological solution finalised to establish the circularity of these resources.

The principal goals of Tech4Lib are:

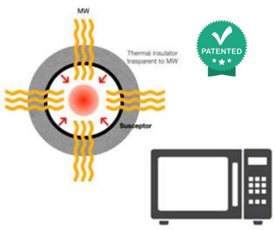
- Microwave (MW) thermal treatment, which is realised by using an unconventional MW heating system, that allows to enhance the potentialities of a MW-supported carbothermic reactions, due to the increased temperature that can be reached;
- Extracting Li by using only a water solution, and the other metals (such as Co, Mn, and Ni) by combining leachate streams obtained by food waste;
- Applying an eco-design procedure to select the most sustainable technological parameters.

EXPERIMENTAL

Pre-treatment

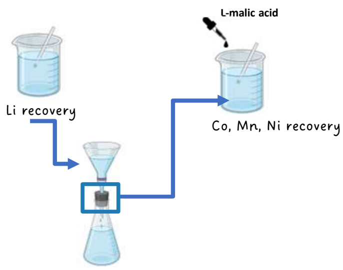
- The recovery experiments were done on the finest black mass (BM) fraction (granulometry <0.5 mm), that was obtained after drying (100 °C for 1h) and sieving;

Microvawe treatment



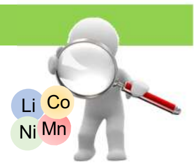
- 0.4 g of black mass;
- Power and time:
  - -1000 W for 4 min
  - -600 W for 8 min
  - -440 W for 12 min

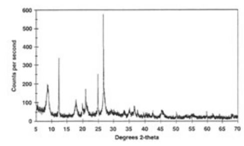
Metal extraction



- Water leaching (40 g/L) → Li extraction
- L-malic acid (1.2 M) leaching on the residue (40 g/L) → Co, Mn and Ni extraction;

Characterization





XRD pattern

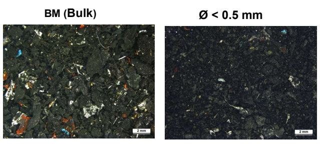
- XRD analysis allows the comparison between black mass before and after MW treatment;
- Graphitic carbon and Li-Co, Li-Ni, and Li-Mn oxides intensity evaluation;

Inductively coupled plasma-optical emission spectometry (ICO-OES)

- Metals (Li, Co, Mn, Ni, Al, and Cu) quantification in the BM fine fraction and in the leaching solutions;
- Sample was prepared by acid digestion with aqua regia.

RESULTS AND DISCUSSION

Optical microscopy analysis



wt (%)	Al	Co	Cu	Fe	Mn	Ni	Li
BM	5.4±0.1	5.2±0.2	5.3±0.1	0.7±0.1	5.1±0.1	8.5±0.2	2.2±0.1
BM < 0.5 mm	2.9±0.1	5.7±0.2	2.7±0.1	0.8±0.1	6.1±0.1	9.9±0.2	2.6±0.1

Elemental analysis of the pristine BM before and after sieving

- ✓ Ni, Co, and Mn are the main constituents of the LIB cathodes;
- ✓ Li is around 2.6%;
- ✓ Fe origins from battery casing contamination.

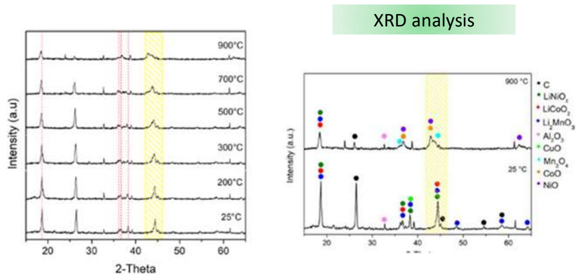
Leaching test

Sample	Al	Co	Cu	Fe	Mn	Ni	Li
A1000	204	<0.01	0.02	0.02	<0.01	<0.01	517.6
A600	273.9	<0.01	0.28	0.02	0.01	0.01	773.2
A440	185	0.01	0.07	0.02	0.03	0.04	869.6
MA1000	831.2	3420	214	270.8	3360	4383	1053
MA600	771.9	2959	4.48	367.3	3413	2910	838.9
MA440	719.7	2854	1.89	352.9	3400	2538	920.9

Concentration of metals (mg/L) in the leaching solution, after microwave treatment at different time and power, and water leaching (A) and L-Malic acid leaching (MA).

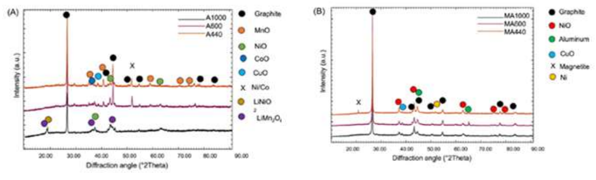
- ✓ Acid leaching of the residual solid previously treated in water allows for the simultaneous extraction of Al, Co, Mn, and Ni;
- ✓ Complete extraction (>95%) of Li, Co, and Mn.

XRD analysis



XRD patterns collected at different temperature on BM: a) evolution of XRD patterns from 25 °C to 900 °C b) detailed phases attribution of XRD patterns collected at 25 °C and 900 °C.

- ✓ (Li-Co, Li-Ni, and Li-Mn oxides) decreased their intensity in favor of the formation of Ni, Mn, and Co oxide, when high temperatures are reached.

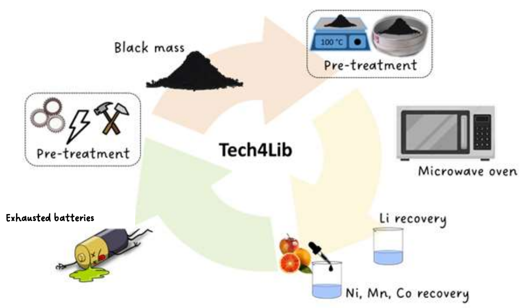


A) XRD patterns collected on samples after MW treatments and water leaching B) XRD patterns collected on samples after MW treatments and water and L-Malic acid leaching

- ✓ Graphitic carbon in the samples is not completely consumed, due to the presence of residual graphite peaks, also after the reactions;
- ✓ At 440 W and 600 W no peaks attributed to LMO, LNO, and LCO, indicating that carbothermic reactions have caused the formation of corresponding metal oxides.

CONCLUSIONS

- ✓ Possibility to avoid the separation of the anode and cathode materials in the pre-treatment process;
- ✓ The dedicated device for carbothermic reductions allows to increase the efficiency of carbothermic process, in comparison to those obtained with conventional oven;
- ✓ The choice of L-Malic acid relied on the sustainable management of this chemical after the treatment (recoverable) and for its neglecting secondary emissions (compared to the inorganic acids), making it suitable for future environmentally friendly applications;
- ✓ The subsequent leaching in water and L-Malic acids enables the efficient recovery of the metallic species (mainly Li, Co, and Mn).



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Tech4Lib website: https://tech4lib.unibs.it/