Italian National Agency for New Technologies, Energy and Sustainable Economic Development

MISSION INNOVATION
accelerating the clean energy revolution

IEMAP Project Italian Energy Materials Acceleration Platform
WP2: Sustainable materials for electrochemical energy storage

MINISTERO DELL'AMBIENTE
E DELLA SICUREZZA ENERGETICA

Materials recovery from end-of-life lithium-ion batteries: results and perspectives

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Department for Sustainability (SSPT)

The Department for Sustainability develops, implements and promotes the **eco-innovation in production and consumption systems**, contributing to the definition and implementation of Country's strategies and policies within the overall framework of **transition towards a more sustainable use of the resources and emissions reduction**.

- Climate changes
- Air quality and health
- Territorial security
- Protection and enhancement of the artistic, historical and architectural heritage
- Closure of cycles, industrial areas and circular economy
- Natural capital and sustainable tourism
- Innovative health products and systems
- Sustainable supply chains and food systems
- Materials and processes for competitive manufacturing industry
- Sustainable cities
- Biotechnological systems, products and processes

Division Resource Efficiency (USER)

ENEA supports the Country in the **transition towards new production and consumption systems** based on sustainable supply and use of resources and on reduction of industrials emissions and social impacts. Closing the loop approach is pursued as a necessary goal to move towards a Circular Economy at various levels: wihin production processes, in industrial areas, on urban and extra-urban areas.

Product Eco-Innovation

- Eco-design
- Life Cycle Thinking (LCT, LCA,..)
- Recyclability, durability, easy disassembly
- Raw Materials: nanomaterials, biomaterial, recycled materials, critical and hazardous raw materials substitution

System Eco-Innovation

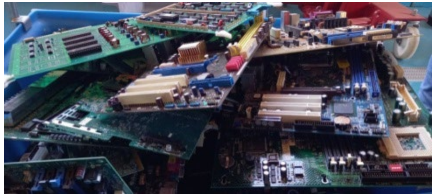
- Industrial symbiosis
- Sharing economy (Remanufacturing, second hand products, from goods posses to services)
- Waste management
- Urban mining/landfill mining
- Reuse/Remanufacture/Recycling

Process Eco-Innovation

- Low resource consumption
- Low energy consumption
- Low emissions
- Clean technologies

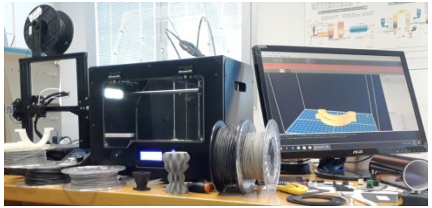
Laboratory Technologies for the Reuse, Recycling, Recovery and valorisation of Waste and Materials (T4RM)

1. Recovery of materials from complex matrices (industrial by-products, EoL products, waste streams, etc.)



Metal recovery from waste printed circuit boards

2. Valorization of plastic waste



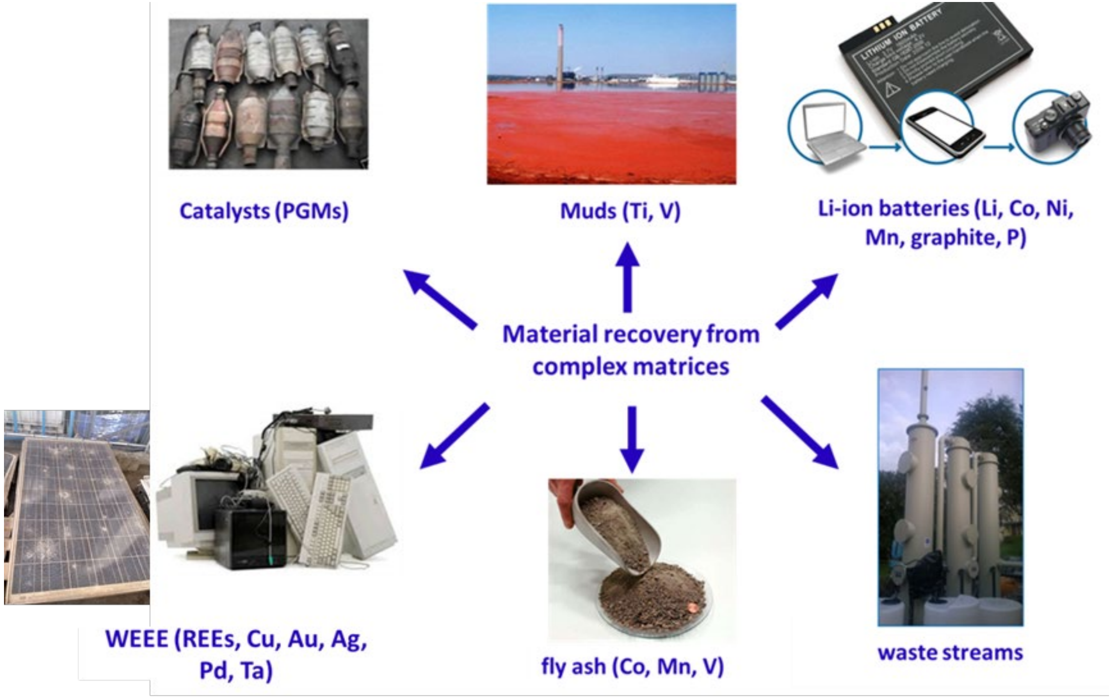
WEEE plastic recovery for the production of 3D printing filaments

3. Valorization of the organic fraction for compost production

Low-cost sensors for compost analysis

Laboratory Technologies for the Reuse, Recycling, Recovery and valorisation of Waste and Materials (T4RM)

Development of technologies for the valorization of complex matrices



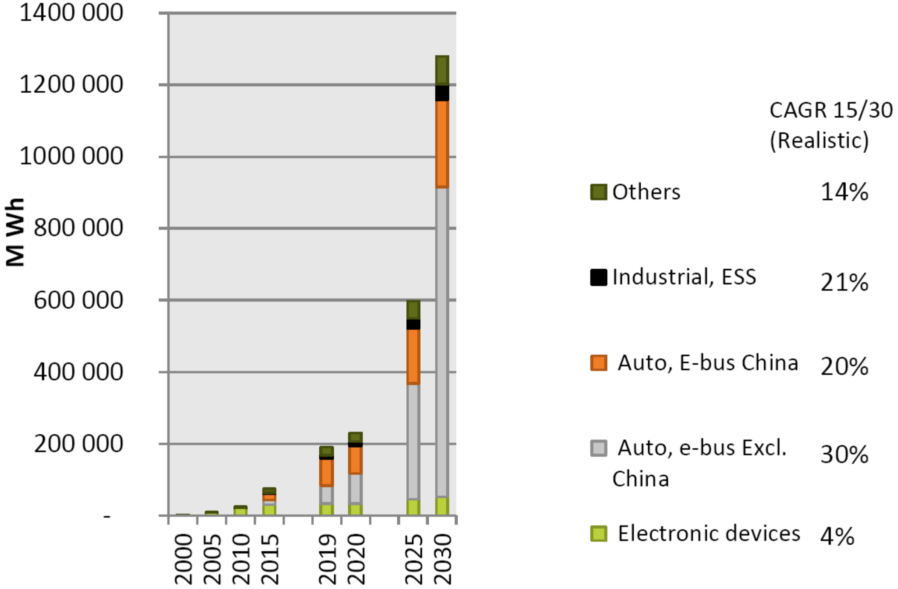
Lithium-ion batteries: market forecasts

e-mobility

consumer electronics

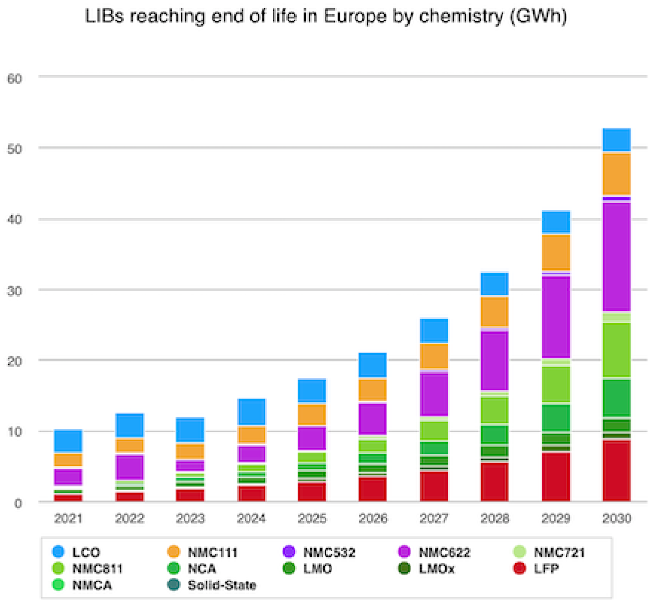
stationary energy storage systems

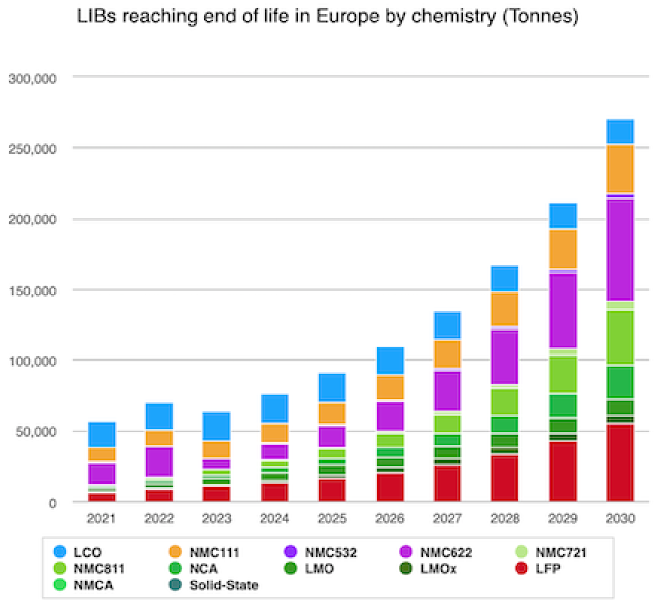
Li-ion batteries sales, worldwide, 2000-2030 (MWh)



Source: C. Pillot. The rechargeable battery market and main trends 2020-2020. Avicenne Energy, 2021.

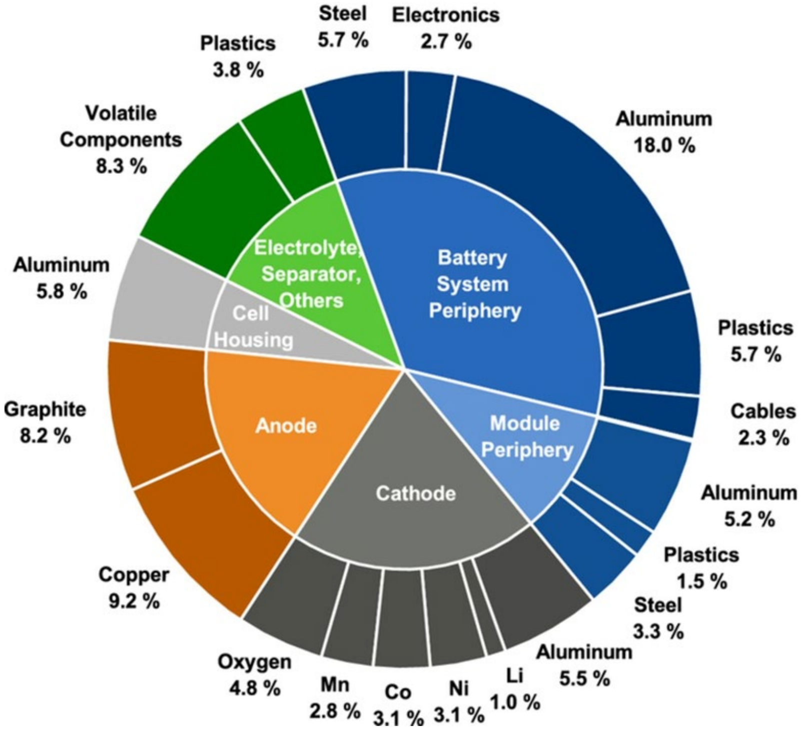
Lithium-ion batteries: end-of-life volumes





Source: Circular Energy Storage, 2023.

Materials recovery from EoL Li-ion batteries



In order to be sustainable, a recycling chain needs to be oriented to the valorization of the whole waste: not only the ***cathode*** materials, but also the ***anode*** (graphite) and the ***electrolyte*** should be valorized, according to the principles of Circular Economy:

PRODUCT-CENTRIC APPROACH

Source: J. Diekmann, C. Hanisch, L. Frobose, G. Schalicke, T. Loellhoeffel, A.S. Folster and A. Kwade. Ecological Recycling of Lithium-Ion Batteries from Electric Vehicles with Focus on Mechanical Processes. Journal of The Electrochemical Society 2017, 164, A6184-A6191.

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Due to the high cost of Co, its availability and the criticalities related to the extraction conditions from primary sources, the scientific community is currently moving towards a decreasing content of Co in ***Lithium-Nickel-Manganese-Cobalt-Oxide*** batteries ($LiNiMnCoO_2$, NMC) as well as to the use of Co-free batteries, such as ***Lithium-Iron-Phosphate*** batteries ($LiFePO_4$, LFP).

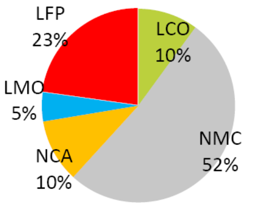
Regarding the treatment of EoL LIBs, materials recovery is mainly carried out by means of pyrometallurgical processes, which however allow only some fractions to be recovered (Ni, Co and Cu). Fractions such as Al, Li, graphite and the electrolyte are not usually recovered. The hydrometallurgical processes currently available in the literature are applied predominantly at laboratory scale and are focused on the recovery of materials from LIBs with defined sub-chemistry.

The scientific innovation within LA 2.10-2.12 lies in the development of a recovery process which can be applied to LIBs under continuous technological evolution. The experimental activity is carried out on NMC cathodes characterized by decreasing concentrations of Co, Mn and Ni and on LFP cathodes. The goal is the definition of an eco-innovative treatment process for the recovery of materials from LIBs currently produced, but which takes into account also the future trend towards Co reduction in LIBs.

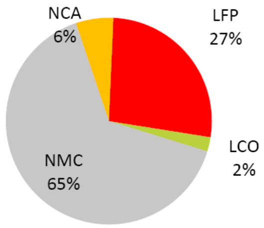
- ❖ **2021-2022 LA2.10**: Materials chemical characterization (NMC and LFP cathodes characterization methods)
- ❖ **2022-2023 LA2.11**: Materials recovery process development (NMC and LFP cathodes materials recovery processes)
- ❖ **2023-2024 LA2.12**: Process validation at pilot scale (TRL 4-5)

LA2.10
Materials chemical characterization (NMC and LFP cathodes characterization methods)

Cathode active materials in 2020
450 000 Tons

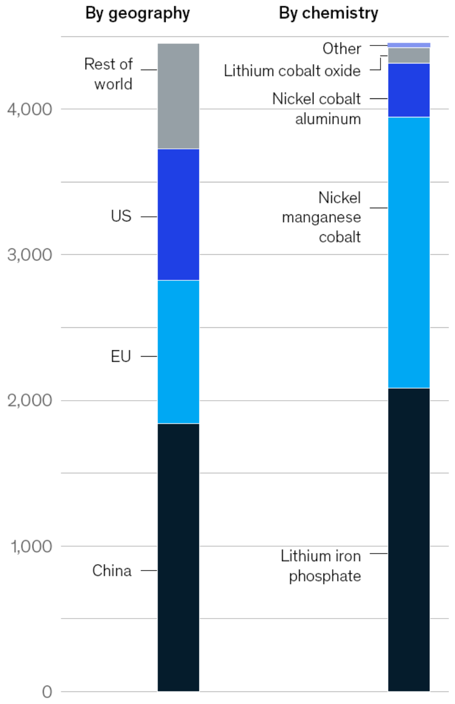


Cathode active materials in 2030
2 100 000 Tons



Source: C. Pillot. The rechargeable battery market and main trends 2020-2020. Avicenne Energy, 2021.

Breakdown of demand, 2030, GWh



Source: McKinsey & Company, 2022.

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LA2.10: Materials chemical characterization (NMC and LFP cathodes characterization methods)

A methodology for the chemical characterization of the cathode material has been developed. An analytical protocol has been defined for the chemical species of interest which takes into account, for example, the interfering chemical species and the detection limits of the instruments. Specific procedures has also been developed for the preparation of samples to be subjected to instrumental analyses.

NMC cathode characterization method

❖ Definition of NMC cathode powders sampling protocol

- metal oxides Li_2O, MnO, MnO_2, CoO, NiO have been employed to reproduce typical target metal content of NMC cathodes
- based on metals stoichiometric ratio of three different NMC cathode generation, NMC111, NMC622 and NMC811 cathodes powders have been reproduced.

❖ Definition and optimization of NMC cathode powders characterization protocol

- Analytical technique choice: Microwave Plasma Atomic Emission Spectroscopy (MP-AES)
- Solubilization conditions identification: lixiviant agent (acqua regia), temperature, Liquid-to-solid ratio (L/S)
- Analytical technique optimization: optimal wave lengths and optimal analytes detection ranges.

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LA2.10: Materials chemical characterization (NMC and LFP cathodes characterization methods)

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LFP cathode characterization method

❖ Commercial LFP powder has been employed

❖ Definition and optimization of LFP cathode powders characterization protocol

- Analytical technique choice: Microwave Plasma Atomic Emission Spectroscopy (MP-AES), Total organic carbon measurement (TOC), pH measurement, moisture measurement
- Solubilization conditions identification: lixiviant agent, temperature, Liquid-to-solid ratio (L/S)
- Analytical technique optimization: optimal wave lengths and optimal analytes detection ranges, as previously defined for NMC cathode characterization.

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LA2.11: Materials recovery process development (NMC and LFP cathodes materials recovery processes)

The hydrometallurgical process is being developed according to a "product-centric" approach, aimed at recovering the greatest number of materials through innovative, efficient and circular technological solutions. The quality of the obtained products, potentially usable to synthesize new active materials, will be demonstrated by chemical characterization. The enhancement of process outputs will also be studied, according to the principles of the circular economy.

LFP recovery process

❖ Commercial LFP powder has been employed

❖ Definition of the hydrometallurgical recovery process steps

- Leaching
- Solid/Liquid separation
- Precipitation

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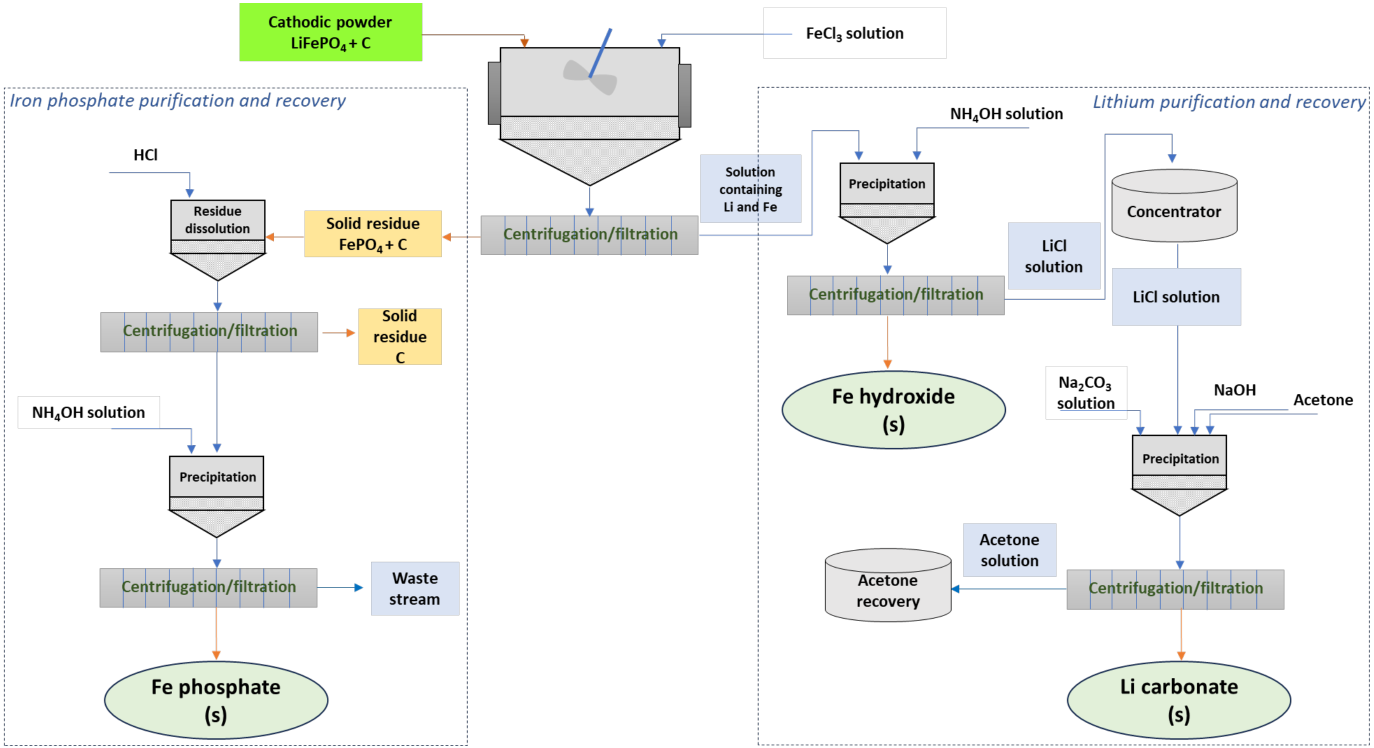
LA2.11

Materials recovery process development (NMC and LFP cathodes materials recovery processes)



Materials recovery from EoL LFP batteries: preliminary flow sheet

Conclusions

- 2021-2022 LA2.10: Materials chemical characterization (NMC and LFP cathodes characterization methods) - *concluded*

- 2022-2023 LA2.11: Materials recovery process development (NMC and LFP cathodes materials recovery processes) – *work in progress*

- 2023-2024 LA2.12: Process validation at pilot scale (TRL 4-5)

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Thank you for your attention!

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