

MATERIALS RECOVERY FROM END-OF-LIFE ELECTROCHEMICAL STORAGE SYSTEMS: PRELIMINARY RESULTS FROM THE IEMAP PROJECT

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ABSTRACT: Within the framework of the IEMAP (Italian Energy Materials Acceleration Platform) Project, a hydrometallurgical process was developed for the recovery of cathodic materials contained in lithium-ion batteries. The experimental activity is carried out on Lithium-Nickel-Manganese-Cobalt-Oxide cathodes characterized by decreasing concentrations of cobalt and on Lithium-Iron-Phosphate cathodes. The goal is the definition of an eco-innovative treatment process for the recovery of cathodic materials from batteries currently produced, taking into account also the future technological trends.

Keywords: Lithium-ion batteries; hydrometallurgy; circular economy

1. INTRODUCTION

Lithium-ion batteries (LIBs) represent a breakthrough point in technology of electrochemical storage since they can replace any other type of battery in the various applications; they can also be used for electric traction automotive and the leveling of loads in high-power networks. Every year in the EU around 800,000 tonnes of car batteries, 190,000 tons of industrial batteries and 160,000 tons of portable batteries are placed on the market ¹.

The global LIBs market is growing steadily and is expected to multiply in the next twelve years going from about 1,000,000 tons of LIBs placed on the market in 2018 to 7,500,000 tons in 2030.² Today only a small part of the exhausted LIBs is correctly collected, while the remaining is intended for “informal” operations.³ Many fractions could be recycled in the production processes, avoiding the dispersion of dangerous substances in the environment and reducing dependence from non-EU suppliers.⁴ It is therefore evident the need of creating a complete LIBs value chain, according to the principles of the circular economy.⁵

Due to the high cost of cobalt, its availability issues and the criticalities related to the extraction conditions from primary sources, the scientific community is currently moving towards a decreasing content of cobalt in Lithium-Nickel-Manganese-Cobalt-Oxide batteries (LiNiMnCoO₂, NMC) as well as the use of cobalt-free batteries, such as Lithium-Iron-Phosphate batteries (LiFePO₄, LFP).

Within the framework of the IEMAP (Italian Energy Materials Acceleration Platform) Project⁶, the research activities here reported refer to the development of a recovery process applicable to LIBs under

continuous technological evolution. The experimental activity is being carried out on NMC cathodes characterized by decreasing concentrations of cobalt as well as on LFP cathodes, thus considering materials from LIBs currently produced and also the future technological trends. The results here reported refer, in particular, to the recovery process applied on LFP cathodes.

2. MATERIALS AND METHODS

Commercial LFP powder was employed as starting material. The powder was characterized by dissolution in acidic media followed by analysis of metal content by Microwave Plasma Atomic Emission Spectroscopy (MP-AES).

Metal recovery from the LFP powder was performed by means of hydrometallurgy. Leaching was carried out by contacting the powder with a solution of $\text{FeCl}_3 + \text{H}_2\text{O}_2$. After solid/liquid separation by means of filtration/centrifugation, Fe recovery from the leachate was investigated by precipitation with NH_4OH . Li recovery was performed by precipitation with Na_2CO_3 .

The valorization of the leaching residue was studied as well by means of leaching with mineral acids followed by alkaline precipitation.

3. RESULTS

The flowsheet of the proposed recovery process is reported in **Figure 1**.

Regarding the leaching step, it was found that the use of $\text{FeCl}_3 + \text{H}_2\text{O}_2$ solution as lixiviant allowed to leach both Li and Fe within a short time (30 min) at room temperature.

Fe precipitation from the obtained leachate with a NH_4OH solution allowed its recovery as hydroxide.

Li recovery from the lithium chloride solution obtained after Fe removal was then performed by means of precipitation with a water/acetone solution of Na_2CO_3 . pH adjustment was performed by adding NaOH .

The solid residue containing the C fraction was valorized as well by a purification step carried out through a leaching with HCl solution followed by precipitation with a NH_4OH solution. Fe was thus recovered as FePO_4 , leaving the carbon fraction in the leaching residue.

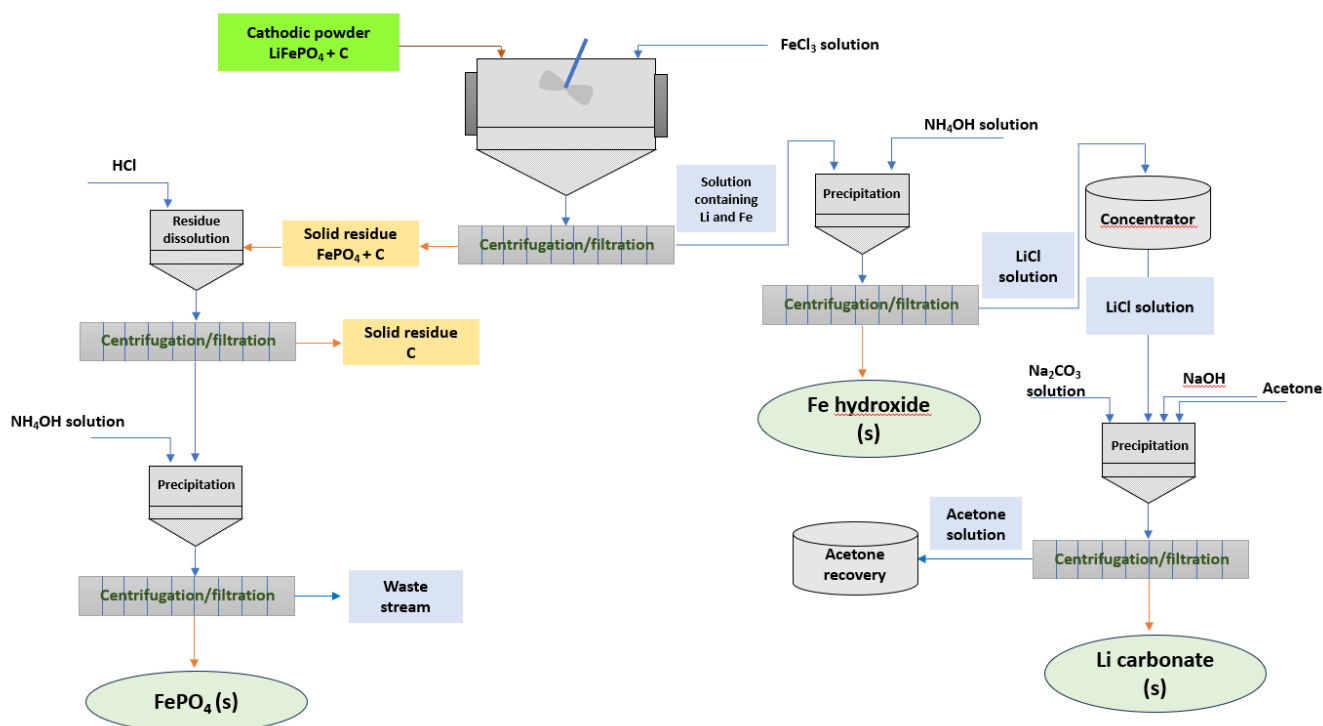


Figure 1. Preliminary LFP recovery flowsheet

4. CONCLUSIONS

The research activities here reported refer to a preliminary hypothesis of a treatment process for LFP cathodic material performed within the IEMAP project. 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 preliminary results here reported will be further optimized in the following activities foreseen in the project. The possible improvement of the process outputs quality will be studied as well, according to the circular economy principles.

REFERENCES

<https://ec.europa.eu/environment/waste/batteries/index.htm>
 Christophe Pillot, Avicenne Energy. The Rechargeable Battery Market and Main Trends 2018-2030. Stockage Batterie Conference, 28 May 2019 <https://tinyurl.com/yeqr3qw>
http://prosumproject.eu/sites/default/files/DIGITAL_Final_Report.pdf
 EC, 2017. Third list of Critical Raw Materials to the EU
 COM(2015) 614 final
<https://mission-innovation.it/iemap/>