End-of-Life Electric Vehicle Lithium-Ion Batteries: Physical Methods for the Recycling

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1. Introduction

For the European Union (EU) it is reported that 74,900 t of lithium-ion batteries (LIBs) are placed on the EU market in 2019, of which 51% are industrial and automotive batteries (European Commission, 2019). The International Energy Agency (IEA, 2021) estimates that the amounts of end-of-life (EoL) or spent LIBs, expressed in gigawatt hours (GWh), will increase from approximately 400 GWh in 2035 to 1,300 GWh in 2040.

On the one hand, there are supply risks for lithium and cobalt (European Commission, 2022; Windisch-Kern et al., 2022). On the other hand, LIBs are seen as excellent secondary resources for the recovery of these critical raw materials (European Commission, 2022). Besides, spent LIBs contain hazardous metals such as nickel and manganese, toxic and corrosive electrolytes, metal casting, and polymer binders that pose a serious threat to the environment and human health (Raj et al., 2022). For this reason, EU member states should achieve a minimum collection rate for LIBs of 70%, a recycling rate of 95% for nickel, copper, and cobalt, as well as 70% for lithium by 2030 (European Commission, 2020). Therefore, more efforts should be made to recover metals through recycling methods (Castelvecchi, 2021).

A LIB is composed of a cathode, an anode, an organic electrolyte, a separator, and an iron shell (Lain, 2001). An anode is usually a copper foil coated with a mixture of graphite, a conductor, a binder, and an electrolyte. The binder is usually made of polyvinylidene fluoride (PVDF), and the electrolyte is a solution of lithium-containing salt (such as $LiPF_6$, $LiClO_4$) dissolved in an organic solvent (such as ethylene carbonate, or dimethyl carbonate). Similarly, the cathode is an aluminum foil coated with cathode materials, a conductor, a PVDF binder, and fluoride salt. To prevent a short circuit between two electrodes, a separator (polypropylene and polyethylene) is placed between the anode and cathode as a barrier (Liu et al., 2019). There are different types of currently used LIBs, the distinction of which is based on the chemical composition of the cathode material, such as a Lithium Nickel Manganese Cobalt Oxide (NMC) cell and a Lithium Iron Phosphate (LFP) cell (Zhao et al., 2021).

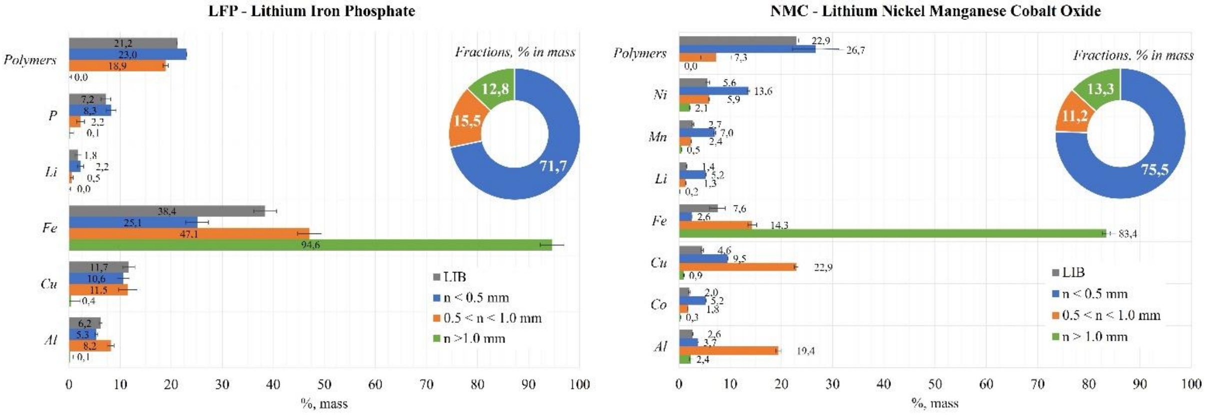
2. Material and methods

Two different brands of cylindrical lithium-ion batteries, a Lithium Nickel Manganese Cobalt Oxide (NMC) cell and a Lithium Iron Phosphate (LFP) cell were subjected to chemical characterization as well as to the mechanical separation process by milling and sieving. First, approximately 500 g of cells of each type were comminuted in a Retsch model SM300 knife mill (rotation speed of 1500 rpm), passing once through each grid, from the largest to the smallest, whose opening sizes were 9.5, 5, 2, 1, 0.75, and 0.5 mm. This sequence of screens was used so as not to damage the mill and to intensify the separation of the cathode materials from the cathode support. The ground material was quarried twice, and 25 % (by mass) was identified as the ground whole Lithium Ion Battery (LIB). The remaining material (75% by mass) was placed on a sequence of bench sieves with a vibration system, whose apertures were 1.0 and 0.5 mm. Then, the initial sample resulted in 3 different fractions: the Fine Fraction (FF: $n<0.5$ mm), the Intermediate Fraction (IF: $0.5 < n < 1.0$ mm), and the Coarse Fraction (CF: $n > 1.0$ mm). The mass of each fraction was measured to calculate the mass percentage in relation to the whole sample without sieving. Six samples of approximately 5 g of each fraction (LIB, FF, IF, and CF), totaling 24 samples, were submitted to 600 ºC for 1 hour to verify the percentage of polymers present, corresponding to the identified mass loss. Subsequently, these samples were subjected to acid leaching with aqua regia (75% HCl and 25% HNO_3) for 2h, with heating (temperature 70-80ºC), and a solid-liquid ratio of 1/40. After filtration, the liquid fraction containing the solubilized metals was analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

3. Results and discussion

The mass percentages of metallic elements and polymers in the integral lithium-ion battery (LIB) and the fractions obtained (FF, IF, CF) after the grinding and sieving process of the NMC cell and the LFP cell are shown in **Figure 1**. The mass percentage of each fraction in relation to the LIB sample is also informed. Metals that are not reported were below the detection limit.

Figure 1. Composition of the two lithium batteries studied and the fractions obtained by milling and screening.



It is observed that the applied treatment had better results for the NMC cell than for the LFP. The proposed separation process allowed the cathodic materials to become more concentrated in granulometry smaller than 0.5 mm (FF) in both cell types. The FF of the NMC cell had 3.6, 2.4, 2.6, and 2.5 times more respectively lithium, nickel, cobalt, and manganese than the LIB. Copper from the anode support and aluminum from the cathode support tended to remain in the granulometry 0.5 < n < 1.0 mm (IF). IF had 7.4 times more aluminum and 5.0 times more copper than LIB for the NMP cell. The fraction n > 1.0 mm (CF) has more than 80% iron, especially from the robust housing, in addition to having no polymers in its composition. For cell NMC, CF has 11 times more iron. The polymers were concentrated in a particle size smaller than 1.0 mm.

4. Conclusions

The mechanical separation process by grinding and sieving indicated that cathode materials tend to concentrate in the particle size smaller than 1.5 mm, copper and aluminum tend to be in 0.5 <n< 1.0 mm, and iron from the robust cell housing concentrates in n > 1.0 mm. Mechanical treatment has shown more promise for NMC cells than LFP cells. Although the process needs improvement, the information obtained gives a north about the behavior of these materials.

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