Thermal treatment of lithium concentrated fraction from end-of-life $LiFePO_4$ automotive batteries as a prior process for lithium recovery

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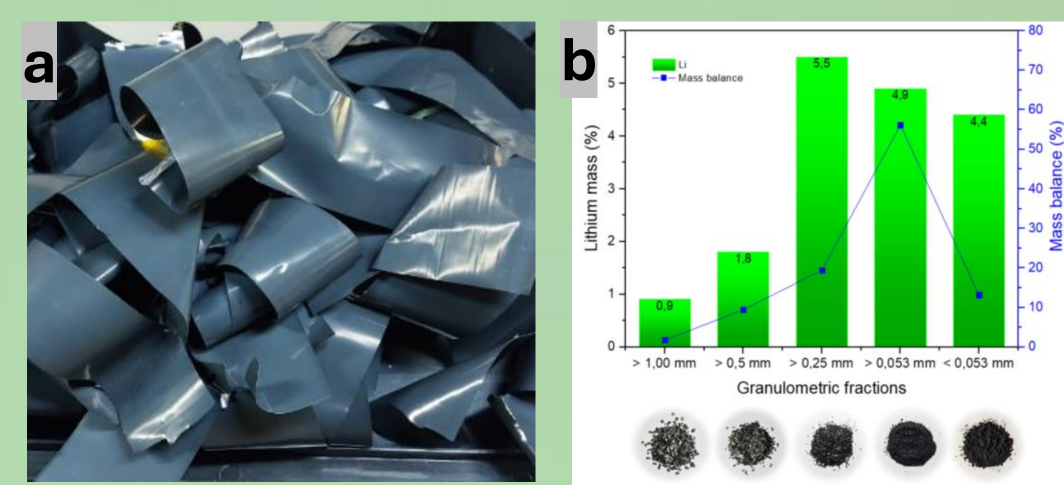
Introduction

In recent years, the **demand for lithium-ion batteries (LIBs) has experienced remarkable growth**, driven primarily by the **increasing adoption of electric vehicles** (EVs), renewable energy storage systems, and portable electronic devices. In pursuing sustainable solutions for the burgeoning challenge of end-of-life electric vehicle batteries, this research explores a novel approach for the **recovery of lithium compounds combining thermal treatment and microwave assisted leaching process** for **concentration of lithium solutions** derived from **spent $LiFePO_4$ (LFP) automotive batteries** scrap fraction.

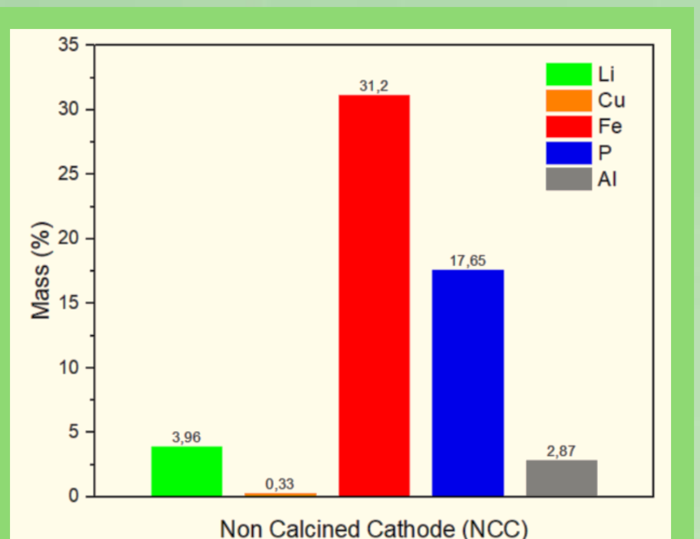
Materials and method

This study starts with the collection of **end-of-life LFP automotive batteries** which were **discharded** for safety manipulation. The **cathodic material, after being separated**, was beneficiated through **grinding, and sieving** to concentrate powdered **fraction rich in lithium**. The resulting material, so called "non calcinated cathode" **(NCC)** was **thermal treated at 300°C (C300), 400°C (C400), 500°C (C500), 600°C (C600), 700°C (C700), 800°C (C800), and 900°C (C900) in air atmosphere** and was subsequently subjected to a **microwave-assisted hydrometallurgical process** in **sulfuric acid** with **different concentration** as the leaching agent for **selective lithium extraction**.

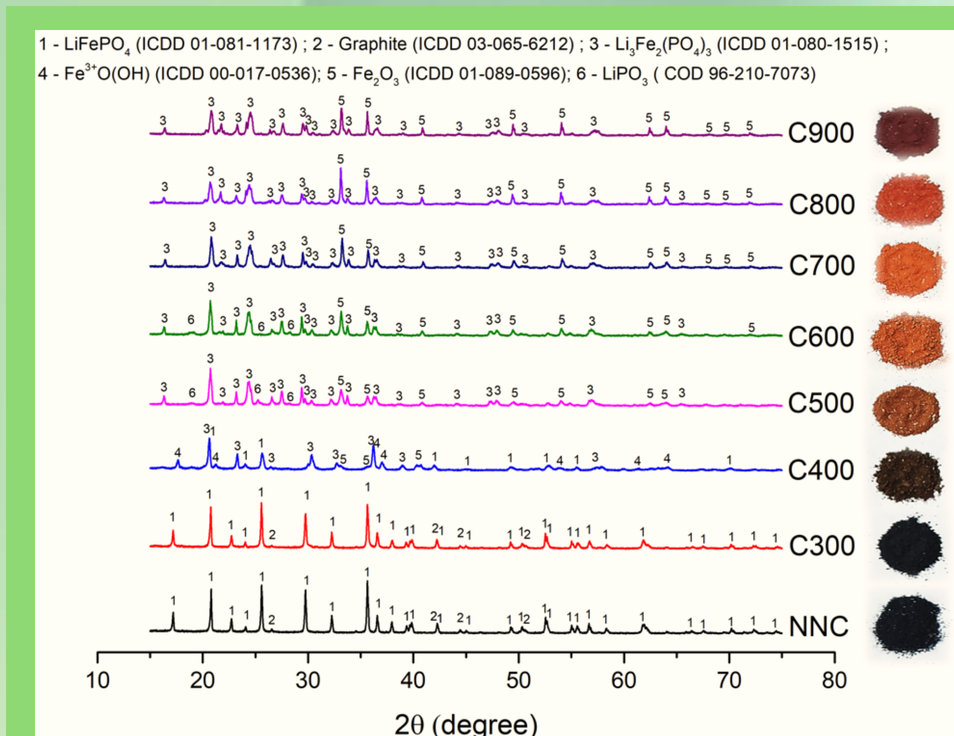


Cathodic material (coils) separated by manual processing (a), lithium mass content in the granulometric fractions obtained after grinding and sieving process and their respective mass balance (b).

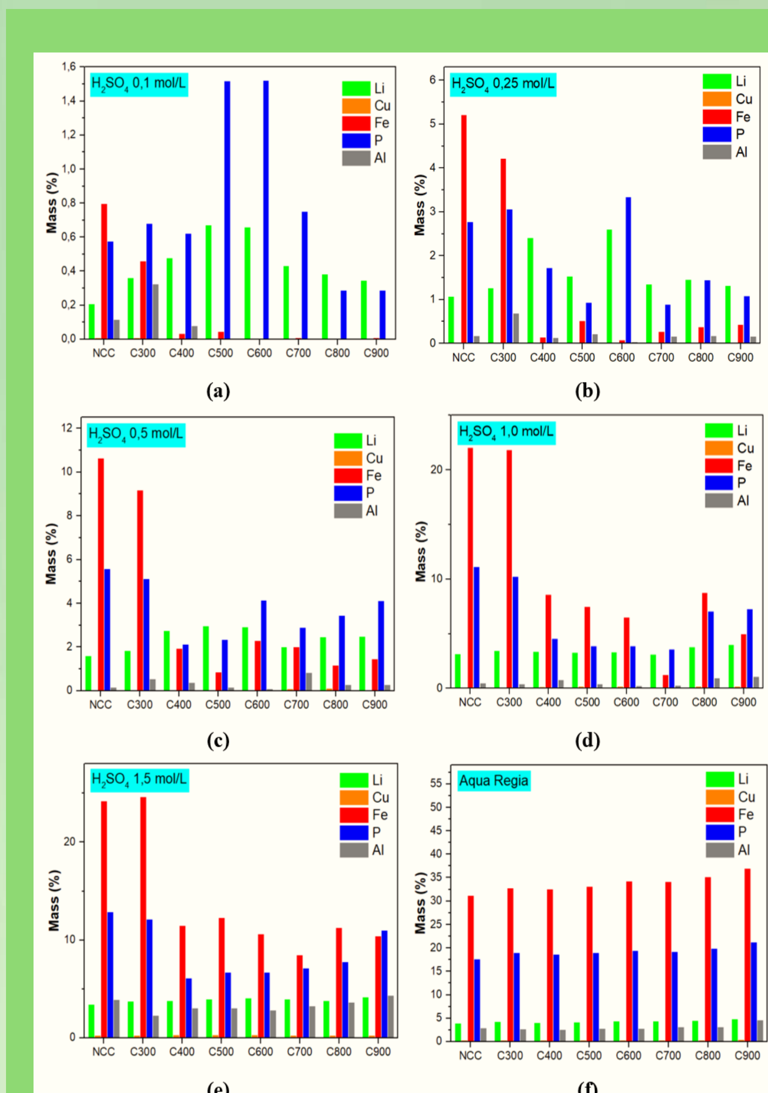
Results and discussions



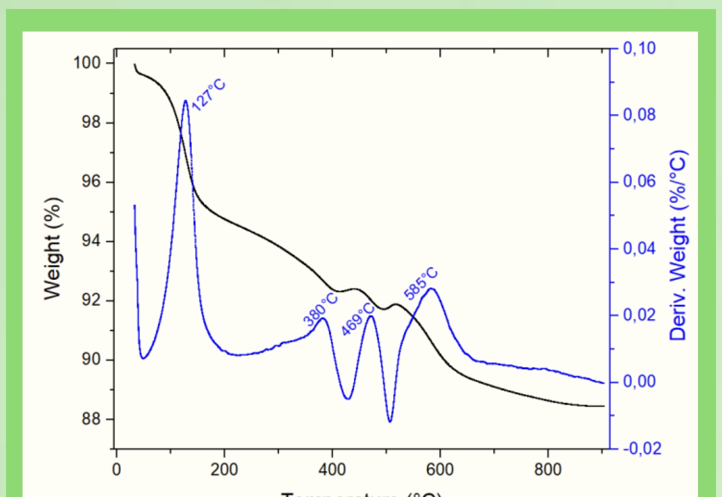
Elemental **chemical composition** of interest in the raw material base of this study, called NCC. (Aqua regia leaching at S/L ratio of 30 g/L). Highlighting the mass **content of lithium** in the starting sample is **3.96%.**



X ray diffractograms reveals that **thermal treatment start to modify crystal structure at 400 °C from $LiFePO_4$ to $Li_3Fe_2(PO_4)_3$** by the formation of intermediary phases such as iron hydroxide and iron oxide. From **500 °C onwards, the formation of $Li_3Fe_2(PO_4)_3$** arises together with iron oxide and lithium metaphosphate. **Above 700°C only $Li_3Fe_2(PO_4)_3$ and Fe_2O_3 were observed.** The oxide increases its presence as the temperature rises.



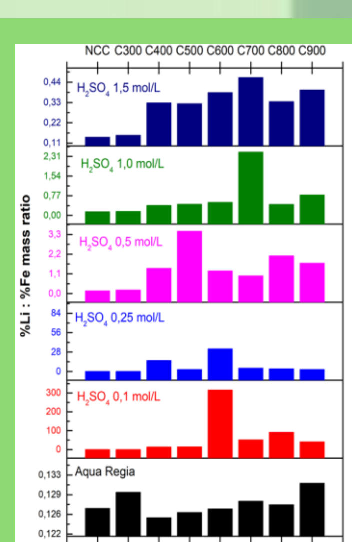
Aqua regia leaching (f), the mass extraction of Li, Fe, P, Al, and Cu **remain constant for all calcination temperatures** of the cathodic material. However, **with sulfuric acid at the proposed different concentrations, a significant selectivity is evident,** mainly al low concentration, such as 0.1 (a), 0.25 (b) and 0.5 (c) mol/L. **With cathode calcined at 600°C was possible to produce a leachate with 2,6% of Li, 0,08% of Fe, 3,35% of P, 0,04% of Al, and 0.01% of Cu,** microwave assisted leaching at **0.25mol/L sulfuric acid** solution (b).



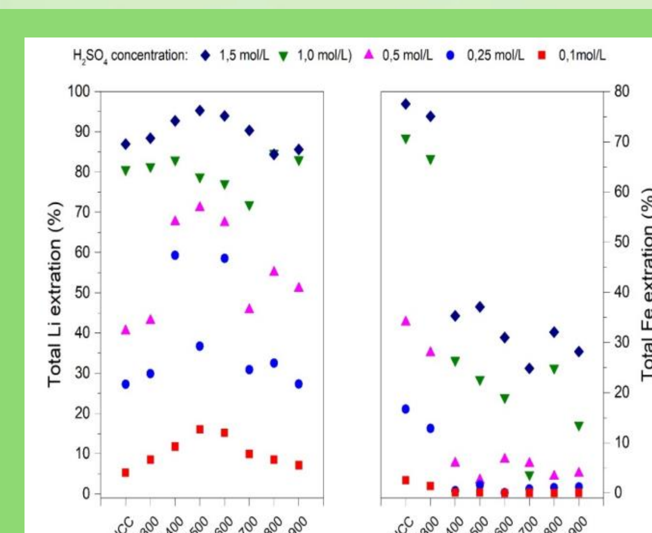
TGA reveals **two main decomposition events** of the NCC material:

1: **From 100 °C to 350 °C**, associated with the **remaining electrolyte**.

2: **From 350°C to 750°C attributed to** the **binder (PVDF) degradation** process.



In this scenario as higher, the value obtained on the ordinate axis, the greater the selectivity in lithium extraction. **Leaching with 0.10 mol/L sulfuric acid with the cathodic material calcined at 600°C yields the best results, with lithium extraction being 300 times higher than iron extraction.** However, the mass contents, for lithium: 0,67% and for iron: 0,0021%. **Excellent selectivity but with low efficiency.**



The **total lithium extraction** for **all proposed conditions** (compared to the complete leaching with aqua regia), is **highlighting a clear trend of selective lithium extraction** for **all sulfuric acid concentrations.** Thus, cathode calcined at 600°C and leached with 0.25mol/L sulfuric acid was possible to **extract 60% of all Li and only 0,23% of all iron.**

Conclusions

With a **grinding and sieving process was possible to concentrated 96% of all lithium content in powdered fractions smaller than 0,5 mm**. By thermal treatment of this powder, starting **from 500°C, is observed a crystal structure transformation of $LiFePO_4$ to $Li_3Fe_2(PO_4)_3$**, in which there is a **greater quantity of lithium available per unit cell and the consequent formation of iron oxide. Optimal lithium selectivity** was observed with samples **calcined at 600°C and leached with 0.25 mol/L sulfuric acid. Under this conditions 60% of all Li, 0.23% of all Fe**, 17% of all P, 2.2% of all Cu and 1.33% of all Al extraction. **In terms of mass content in this solution: 2,6% Li, 0,27% Fe,** 3,4% P, 0,01% Cu and 0,04% Al was reached, **revealing a promise selectivity.**

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