



Article

Selective Leaching for the Recycling of Lithium, Iron, and Phosphorous from Lithium-Ion Battery Cathodes' Production Scraps

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Abstract: The market for lithium iron phosphate (LFP) batteries is projected to grow in the near future. However, recycling methods targeting LFP batteries, especially production scraps, are still underdeveloped. This study investigated the extraction of iron phosphate and lithium from LFP production scraps using selective leaching, considering technical and economic aspects. Two leaching agents, sulfuric acid (0.25–0.5 M, 25 °C, 1 h, 50 g/L) and citric acid (0.25–0.5 M, 25 °C, 1 h, 70 g/L) were compared; hydrogen peroxide (3–6%vv.) was added to prevent iron and phosphorous solubilization. Sulfuric acid leached up to 98% of Li and recovered up to 98% of Fe and P in the solid residues. Citric acid leached 18–26% of Li and recovered 98% of Fe and P. Totally, 28% of Li was precipitated for sulfuric acid process, while recovery with citric acid did not produce enough precipitate for a characterization. Sulfur is the main impurity present in the precipitates. The total operative costs associated with reagents and energy consumption of the sulfuric acid route were below 3.00 €/kg. In conclusion, selective leaching provided a viable and economic method to recycle LFP production scraps, and it is worth further research to optimize Lithium recovery.



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1. Introduction

Lithium iron phosphate (LFP) batteries are steadily expanding their share of the electric vehicle market [1], with a forecasted increase from 0.4 to 15.24 billion US\$ in the period 2017–2027 [2]. LFP batteries are characterized by low cost, long life cycle, and high-power capacity [3]. In addition, their manufacturing causes lower environmental impacts compared with batteries based on other cathode's chemistries [4]. However, LFP batteries do not include economically valuable metals, such as Co and Mn, and they are not able to overcome the economic costs of current recycling processes [5]. High energy demand, low efficiency, and high costs of state-of-the-art recycling processes make them not suitable to support the LFP-recycling sector [6]. Research on LFP cathodes' recycling has been increasing over the years and mostly focused on the optimization of leaching processes [5,7]. LFP hydrometallurgical recycling is commonly performed with sulfuric [5,8], hydrochloric [9], and phosphoric [10] acids, followed by chemical precipitation of lithium, iron, and phosphorous [11,12]. According to previous studies, sulfuric acid allows for leaching 98% of iron phosphate in the optimal leaching conditions [13], while the leaching efficiency reached with the combination of phosphoric and oxalic acid was 97% for lithium and 98% for iron [10].

Selective leaching was recently proposed as a viable solution to limit the environmental and economic impacts of hydrometallurgical recycling, and its application has been proposed to recover Li from different cathodes' chemistries, such as lithium manganese oxide

(LMO) [14], nickel manganese, and cobalt oxide (NMC) [15,16]. In detail, selective leaching applied to LFP cathodes is aimed at leaching lithium, while iron and phosphorous are left in the solid residue; this, compared to conventional hydrometallurgy, leads to shorter process time, lower acids' concentration, and limited energy requirements and waste generation [17]. Additionally, iron phosphate left in the leaching residues maintains its original olivine structure and could be directly reused as a precursor for cathodes' production, further limiting the process' costs [13]. Selective leaching of Li from LFP material involves oxidative leaching processes that aim to oxidize LiFePO_4 into FePO_4 , and releasing Li^+ into the solution for hydrometallurgical recovery [18]. The existing literature on selective leaching applied to LFP cathodes involves sulfuric acid combined with oxidizing agents, as hydrogen peroxide [19–21] or sodium hypochlorite [22], allowing for recovery of over 96% of Li, limiting Fe leaching between 0.027% [20] and 5% [19]. Comparable results were obtained with organic acids, such as formic acid combined with hydrogen peroxide, which achieved 99.98% Li-leaching efficiency [23], acetic acid and hydrogen peroxide leached between 95.5% of Li with a selectivity of 94.08% [24], and acetic acid leached almost 100% of Li [25]. Similarly, mechanochemical leaching of spent LFP cathodes with citric acid and hydrogen peroxide leached 99.35% of Li, limiting Fe leaching to 3.86% [26]. As an alternative to acid leaching, the application of CO_2 gas in the presence of an oxidizing solution allowed for selectively recovering 90% of Li as a bicarbonate [27].

As just mentioned, several studies recently investigated the optimization of LFP cathodes' recycling to improve environmental and economic sustainability [28]. However, they involved exclusively end of life cathodes, and production scraps from batteries' manufacturing are still overlooked. Indeed, scraps from batteries' manufacturing represent an additional source to recover critical raw materials in closed-loop processes [29]. Scraps represent up to 30% of LIBs' manufacturing capacity, and their generation is expected to grow accordingly with batteries' production rates in the next future [30]. Also, the materials' recovery from production scraps poses several advantages. Firstly, pre-treatments are simpler and safer, as discharge and dismantling are not necessary before recycling, and production scraps are already sorted according to specific chemistries [31]. Secondly, the morphological and chemical structure of production scraps is comparable with pristine batteries. However, because of the presence of the binder, their recycling is more challenging compared with end-of-life electrodes [32]. To the best of our knowledge, the few available studies exploring the recycling of LIBs' production scraps investigated the detachment of electrodes' active materials from current collectors through mechanical processes and dissolution with solvents [33,34] or thermal treatments [31,35]. These studies analyzed production scraps of NMC [34,35] and LMO cathodes [33]. Therefore, there is a knowledge gap related to the recycling of LFP production scraps. The novelty and objective of this study rely on the investigation of selective leaching applied to scrap LFP cathodes. Two routes, based on sulfuric and citric acids as alternatives, have been compared from the viewpoints of technical performance (leaching and recovery efficiencies for Li, Fe, and P; purity of the recovered phases) and operative costs.

2. Materials and Methods

2.1. Materials and Reagents

Production scraps of LFP cathodes have been supplied by the National Research and Development Institute for Cryogenic and Isotopic Technologies—ICSI Rm, Valcea, Romania. The LFP cathodes were prepared by coating aluminum foil with 93%wt. of LFP powder, 3%wt. of C65 conductive carbon black and 5% polyvinylidene difluoride (PVDF) in solution with N-Methyl-2-pyrrolidone (NMP). Leaching experiments employed sulfuric acid (Carlo Erba Reagents, Cornaredo (MI), Italy CAS: 7664-93-9, >96%), citric acid (Sigma Aldrich, Milano, Italy CAS: 77-92-9, >99.5%), hydrogen peroxide (Carlo Erba Reagents, Cornaredo (MI), Italy, CAS: 7722-84-1, 30%vv.), sodium hydroxide (Honeywell/Fluka, Charlotte, NC, USA, CAS: 1310-73-2, >98%), sodium carbonate (Sharlab, Lodi (MI), Italy,

CAS: 497-19-8, >99.8%), and deionized water, produced using a POBEL (Madrid, Spain) still 710 continuous distiller.

2.2. Experimental Procedure

The experimental design of this study (Figure 1) was aimed at the selective leaching of lithium from LFP production scraps (then recovered via chemical precipitation as Li_2CO_3 by adding 10 M NaOH and a stoichiometric amount of Na_2CO_3) and at the recovery of Fe and P in the leaching residues. LFP cathodes were heated at 200 °C for 30 min in a ZE V220 Prederi (Prederi, Milano, Italy) furnace and pre-treated in a Retsch (Hann, Germany) MM200 ball mill for 5 min at 14 Hz in 50 mL zirconia jars with two 10 mm beads in order to detach the active material from the current collector before leaching. The optimization of detachment of LFP powder from current collectors is reported in a previous study [36]. Leaching happened for 1 h at 25 °C with sulfuric acid (0.25–0.5 M) and hydrogen peroxide (3–6%vv.) and with citric acid (0.25–0.5 M) and hydrogen peroxide (3–6%vv.). The solid/liquid ratio was 50 g/L during leaching with sulfuric acid and hydrogen peroxide and 70 g/L during leaching with citric acid and hydrogen peroxide. Leaching tests were performed in triplicates on a heated magnetic stirrer Velp (Usmate (MB), Italy) AREX-6 DIGITAL PRO (Table 1). The solid residues were recovered through a Hermle Labortechnik (Wehingen, Germany) Z206A centrifuge, rinsed with deionized water, and dried overnight in an Argo Lab TCN 30 oven at 70 °C before characterization. The leachates' pH was adjusted to 12, adding 10 M NaOH, then heated 95 °C, and a stoichiometric amount of 10 M Na_2CO_3 was added to precipitate Li_2CO_3 .

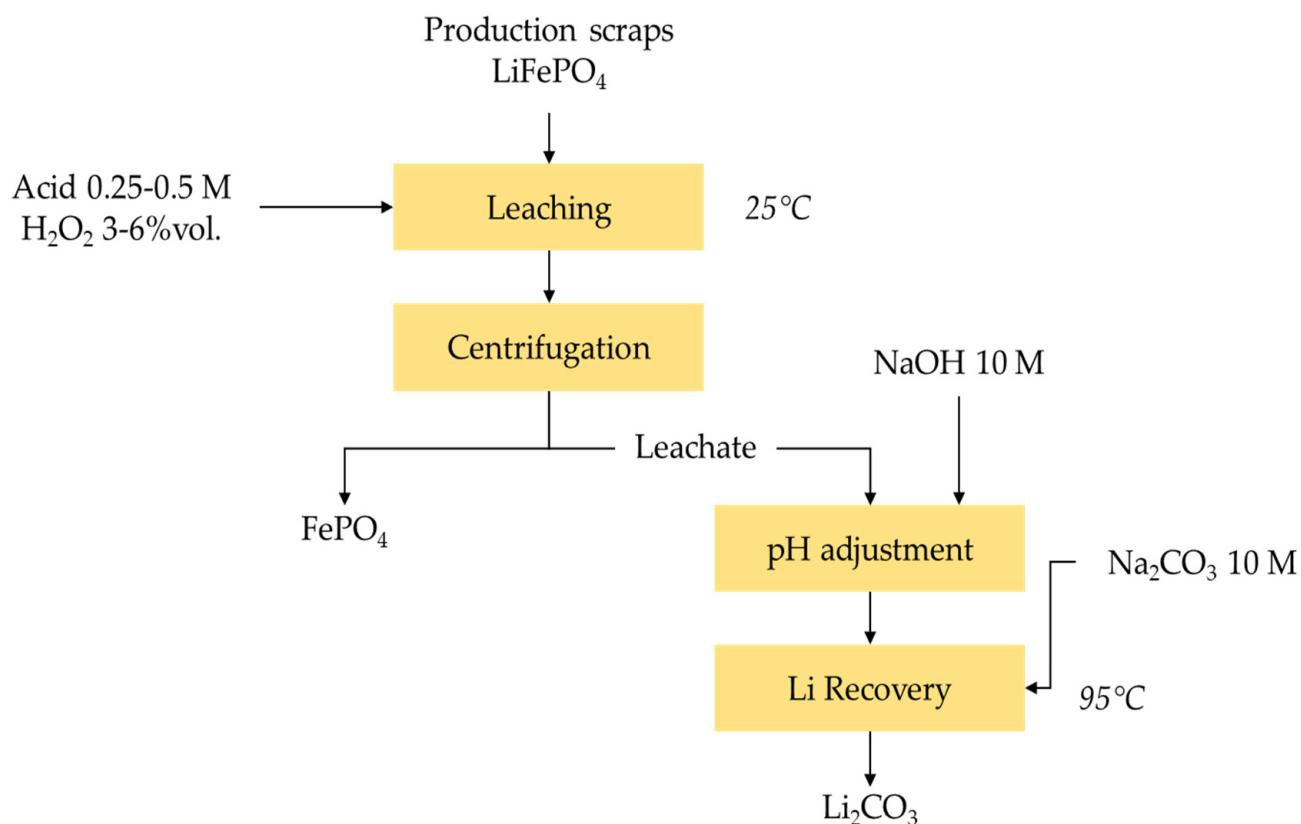


Figure 1. Outline of the experimental procedure to recycle Fe, Li, and P from LFP production scraps.

Table 1. Leaching conditions (concentration of leaching agents and hydrogen peroxide, temperature, contact time, S/L: solid to liquid ratio) applied in this study.

Leaching Agent	Concentration (M)	Concentration H ₂ O ₂ (%vv.)	Temperature (°C)	Time (h)	S/L Ratio (g/L)
Sulfuric acid	0.5	6	25	1	50
	0.5	3	25	1	50
	0.25	6	25	1	50
	0.25	3	25	1	50
Citric acid	0.5	6	25	1	70
	0.5	3	25	1	70
	0.25	6	25	1	70
	0.25	3	25	1	70

2.3. Analytical Methods

The chemical composition of the samples was analyzed with: X – ray Fluorescence (XRF) spectroscopy (NEX-DE, Rigaku, Tokyo, Japan) to measure the concentration (mg/kg) of Al, Ca, Cl, Co, Cr, Cu, Fe, Ni, P, S, Si, V, and Zn; and Flame Atomic Absorption (FAA) spectrometry (GFA-EX7, Shimadzu, Tokyo, Japan) to measure the concentration (mg/L) of Fe and Li. A ETHOS UP MILESTONE, Sorisole (BG), Italy) microwave digestor was used to prepare the samples for the FAA spectrometer treating 500 mg of each sample with 50 mL of 0.2 M HNO₃ and 0.8 M HCl at 230 °C for 25 min. The morphological structure of the samples was characterized via X-ray Diffraction (XRD) spectroscopy (X’Pert Malvern Pananalytical, Malvern, UK). FESEM analysis was carried out by a SUPRA TM 40, Zeiss (Oberkochen, Germany) with Gemini column and Schottky field emission tip (tungsten at 1800 K). Acquisitions were made at acceleration voltage of 3 kV and working distance (WD) between 2.1 and 8.5 mm, with magnification up to 300 KX.

2.4. Preliminary Economic Assessment

A preliminary economic assessment of the selective leaching routes considered the operative costs (e.g., reagents, water, and energy) scaled-up to 1 kg of LFP cathodes powder. This assessment was not aimed at evaluating the economic viability of the proposed recycling process but at a consistent comparison of the operative economic impacts of the proposed alternatives. A Maxcio PM10 power meter (Shenzhen Tiansuda Technology Co., Ltd., Shenzhen, China, www.maxcio.com, accessed on 24 October 2024) was used to measure the energy consumption of the lab equipment. The analysis of energy costs considered 0.1771 €/kWh, i.e., the average price of electricity for non-household consumers in Europe in 2023 [37]. The costs of reagents (deionized water, citric acid, sulfuric acid, hydrogen peroxide, sodium hydroxide, and sodium carbonate) were retrieved from Ecoinvent database [38]. A comprehensive analysis of the economic viability of the recycling process would benefit from including the costs associated with managing wastewater, waste gas, and waste residue, as well as capital expenses, maintenance, and labor costs. However, these factors were not considered in this study, as it was conducted at the laboratory scale.

3. Results

3.1. Samples’ Characterization

The composition of the LFP samples was 2.1 ± 0.1%wt. of Li, 29.5 ± 4.5%wt. of Fe, and 16.4 ± 2.5%wt. of P. The main impurities were as follows: 610 ± 157 mg/kg of Al, 179 ± 98 mg/kg of Ca, 346 ± 19 mg/kg of Cl, 61 ± 17 mg/kg of Cr, 92 ± 70 mg/kg of Co, 20 ± 4 mg/kg of Ni, 588 ± 28 mg/kg of S, and 1766 ± 124 mg/kg of V. Si, Cu, and Zn were not detected. The literature reported a composition of EoL LFP cathodes in the ranges 1.6–4.4%wt. of Li, 26.43–35.4%wt. of Fe, and 14.1–19.63%wt. of P [39–41], which is comparable with our results. The XRD spectra of the LFP samples (Figure 2) corresponded to Li-Fe Phosphate. The concentration of V (1766 ± 124 mg/kg) in the samples

is consistent with the characterization of LFP cathodes provided by other studies, which reported a V concentration of 0.24%wt. in one LFP sample, while in the other sample, V was below the detection limit [40]. According to literature, the presence of V could be attributed to possible V-doping of LFP cathodes, which has been shown to enhance electrochemical performance, improve thermal stability, and achieve specific capacities above 160 mAh g⁻¹ [42]. This doping has also been reported to increase electronic conductivity from $2.141 \cdot 10^{-2}$ S cm⁻¹ in undoped LiFePO₄ to $22.201 \cdot 10^{-2}$ S cm⁻¹ and prolong cycle life beyond 1000 cycles at high C-rates [43]. However, this information is not available for the samples used in this study.

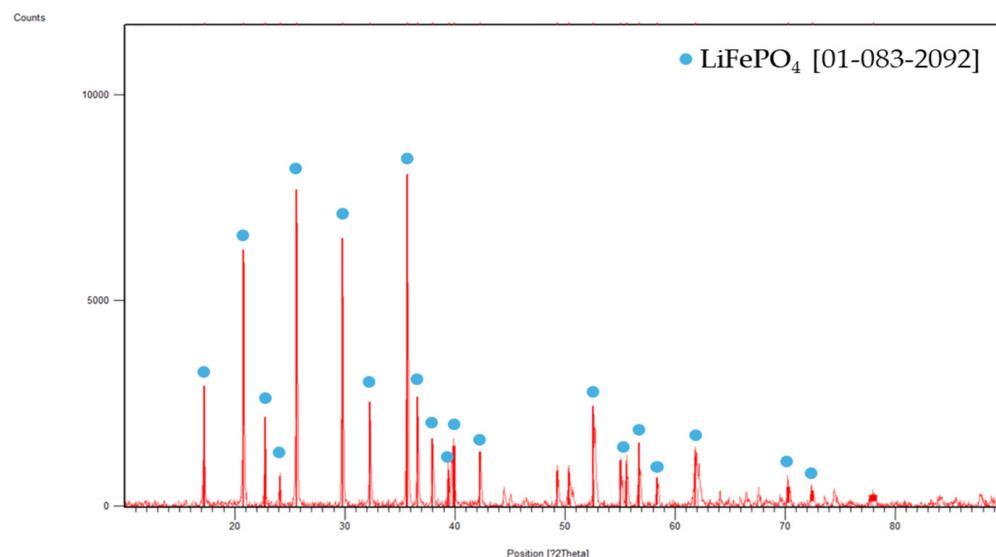


Figure 2. XRD spectrum of LFP cathodes' production scraps.

3.2. Selective Leaching of Lithium

The results of the leaching tests (Figure 3) showed that hydrogen peroxide prevented the solubilization of Fe and P in both routes, with higher leaching efficiency for Li achieved by sulfuric acid compared to citric. In detail, leaching with 0.5 M sulfuric acid and 6%vv. hydrogen peroxide solubilized $98 \pm 1\%$ of Li, $5 \pm 1\%$ of Fe, and $6 \pm 3\%$ of P. Similar results had been accomplished with different concentrations of sulfuric acid and hydrogen peroxide: $91 \pm 2\%$ of Li, $5 \pm 2\%$ of Fe, and $7 \pm 2\%$ of P were leached by 0.5 M sulfuric acid and 3%vv. hydrogen peroxide; $93 \pm 1\%$ of Li, $2 \pm 0.4\%$ of Fe, and $3 \pm 2\%$ of P were leached by 0.25 M sulfuric acid and 6%vv. hydrogen peroxide; and $90 \pm 3\%$ of Li, $2 \pm 1\%$ of Fe, and $3 \pm 1\%$ of P were leached by 0.25 M sulfuric acid and 3%vv. hydrogen peroxide.

Lower leaching efficiency has been achieved during leaching with citric acid and hydrogen peroxide, as follows: $25 \pm 1\%$ of Li, $1 \pm 0.4\%$ of Fe, and $2 \pm 1\%$ of P were leached by 0.5 M citric acid and 6%vv. hydrogen peroxide; $26 \pm 2\%$ of Li, $1 \pm 0.6\%$ of Fe, and $2 \pm 1\%$ of P by 0.5 M citric acid and 3%vv. hydrogen peroxide. A lower citric acid concentration reduced further Li-leaching efficiency: $18 \pm 3\%$ of Li, $1 \pm 0.4\%$ of Fe, and $2 \pm 1\%$ of P were leached by 0.25 M citric acid and 6%vv. hydrogen peroxide; $19 \pm 2\%$ of Li, $1 \pm 0.6\%$ of Fe, and $2 \pm 1\%$ of P were leached by 0.25 M citric acid and 3%vv. hydrogen peroxide.

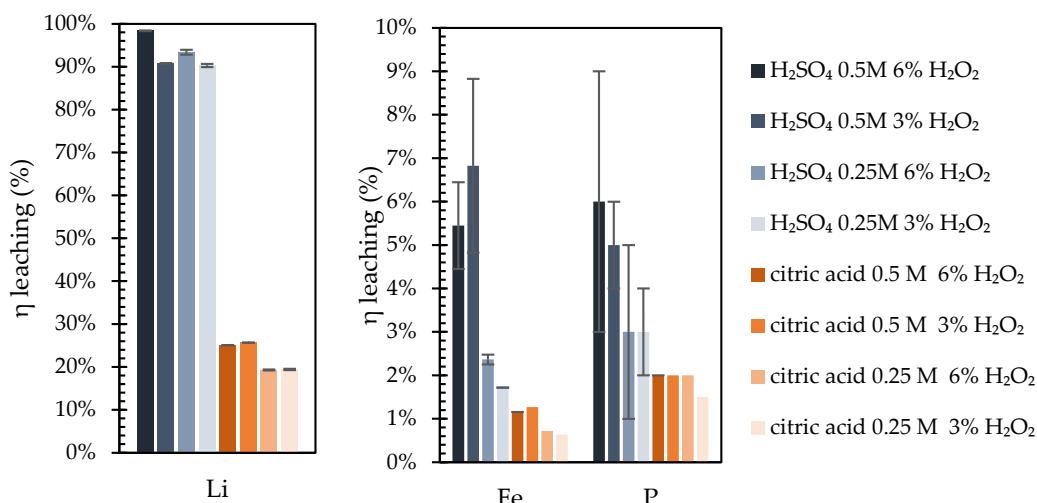


Figure 3. Leaching efficiency (%) of lithium, iron, and phosphorous achieved in the selective leaching tests with sulfuric and citric acids.

The concentration of sulfuric acid, at 0.25 M, was found to have no impact on the efficiency of Li leaching, demonstrating adequacy for the process while causing minimal solubilization of Fe and P. Lower sulfuric acid concentrations, and higher hydrogen peroxide concentrations, are expected to limit the leaching of Fe and P. Nonetheless, the sulfuric acid concentration influenced the selectivity of the leaching process towards Li. Specifically, reducing the sulfuric acid concentration to 0.25 M resulted in a 50% decrease in Fe and P leaching, without affecting the Li-leaching efficiency. On the contrary, citric acid proved ineffective for the hydrometallurgical recycling of LFP production scraps, due to low leaching performances and poor selectivity towards Li extraction.

3.3. Recovery of Iron and Phosphorous

The amount of Fe and P recovered by different leaching conditions was comparable between sulfuric and citric acid and applying different concentrations of acids or hydrogen peroxide. Analogously to the results presented in Section 3.2, the amount of Fe and P taken into solution during the selective leaching tests increased with the concentration of sulfuric or citric acid, to a larger extent with sulfuric acid; $95 \pm 6\%$ of Fe and $94 \pm 7\%$ of P were recovered in the solid residues obtained from selective leaching with 0.5 M sulfuric acid and 6% hydrogen peroxide, and $95 \pm 7\%$ of Fe and $93 \pm 4\%$ of P were recovered in the solid residues obtained from selective leaching with 0.5 M sulfuric acid and 3% hydrogen peroxide. Meanwhile, when the concentration of sulfuric acid was reduced to 0.25 M, $98 \pm 3\%$ of Fe and $96 \pm 4\%$ of P were recovered in the solid residues obtained from selective leaching with 6%vv. hydrogen peroxide, and $97 \pm 2\%$ of Fe and $98 \pm 5\%$ of P were recovered with 3%vv. hydrogen peroxide.

The solid residues after leaching with citric acid and hydrogen peroxide were composed as follows: $98 \pm 2\%$ of Fe and $97 \pm 4\%$ of P after leaching with 0.5 M citric acid and 6%vv. hydrogen peroxide, $98 \pm 3\%$ of Fe and $98 \pm 3\%$ of P after leaching with 0.5 M citric acid and 3%vv. hydrogen peroxide, $97 \pm 2\%$ of Fe and $96 \pm 3\%$ of P after leaching with 0.25 M citric acid and 6%vv. hydrogen peroxide, and $98 \pm 6\%$ of Fe and $95 \pm 2\%$ of P after leaching with 0.25 M citric acid and 3%vv. hydrogen peroxide.

The XRD analyses confirmed that Fe and P in the leaching residues were in form of iron phosphate (Figure 4). The crystalline olivine structure of the leaching residues remained unchanged after selective leaching of Li, as indicated also by previous studies [44,45]. The XRD spectra of leaching residues show peaks which align well with those observed in the LFP cathodes' production scraps, see Figure 2, which follows the standard orthorhombic olivine structure with the addition of peaks identified as crys-

talline FePO₄ [46]. The presence of both crystalline phases is consistent with a mixture of LFP and FePO₄ materials.

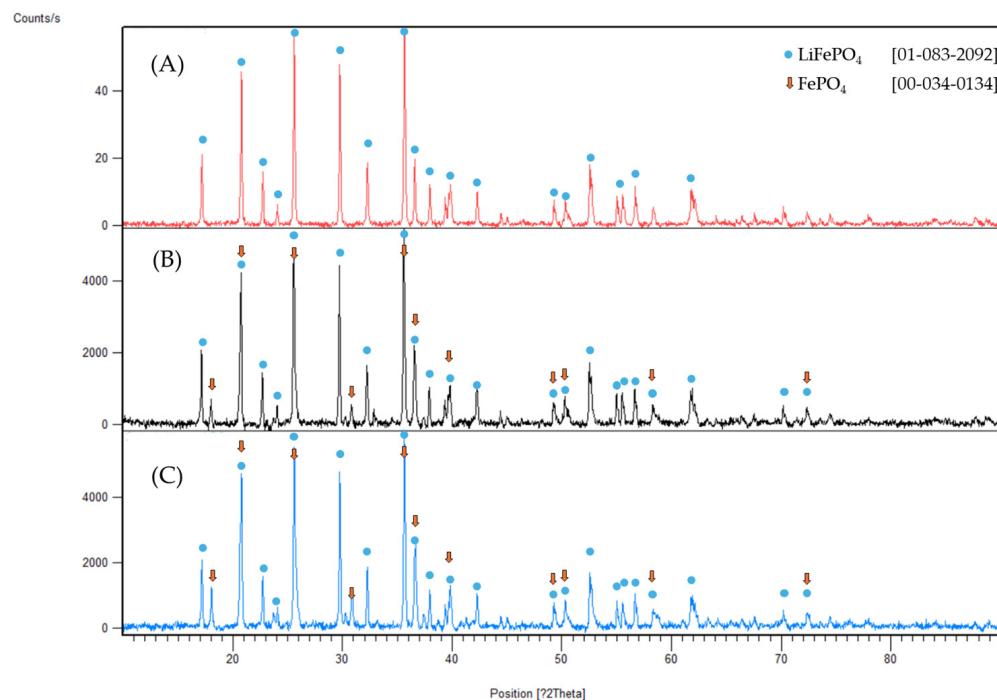


Figure 4. Comparison between XRD spectra of (A) initial sample of LFP cathodes' production scraps, (B) solid residues after leaching with sulfuric acid and hydrogen peroxide, and (C) citric acid and hydrogen peroxide.

The impurities' contents in the leaching residues were as follows: When sulfuric acid was used, the main impurity was sulfur: 4363 ± 581 mg/kg after leaching with 0.5 M sulfuric acid and 6%vv. hydrogen peroxide, $17,033 \pm 2173$ mg/kg after leaching with 0.5 M sulfuric acid and 3%vv. hydrogen peroxide. The sulfur concentration was lower after leaching with 0.25 M sulfuric acid: 1363 ± 835 mg/kg with 6%vv. hydrogen peroxide and 4586 ± 966 mg/kg with 3%vv. hydrogen peroxide. The sulfur concentration in the residues after citric acid leaching was 537 ± 29 mg/kg with 0.5 M citric acid and 6%vv. hydrogen peroxide, 561 ± 27 mg/kg with 0.5 M citric acid and 3%vv. hydrogen peroxide, 640 ± 38 mg/kg with 0.25 M citric acid and 6%vv. hydrogen peroxide, and 545 ± 37 mg/kg with 0.25 M citric acid and 3%vv. hydrogen peroxide. Other impurities (Al, Ca, Cl, Cr, Co, Ni, and V) were within the concentration range reported for the LFP sample (Section 3.1).

The morphology of the leaching residues has been compared with the original LFP sample by FESEM characterization (Figure 5). Residues recovered after sulfuric acid leaching presented a broader particle size distribution compared with the initial sample and residues after citric acid leaching, with larger crystals distributed throughout finer grains. The FePO₄ powders recovered after leaching with citric acid present inhomogeneous particles sizes, on average in the order of hundreds of nanometers, which is however consistent with the initial sample and the morphology of the leaching residues appears to maintain the crystallinity level of the initial sample.

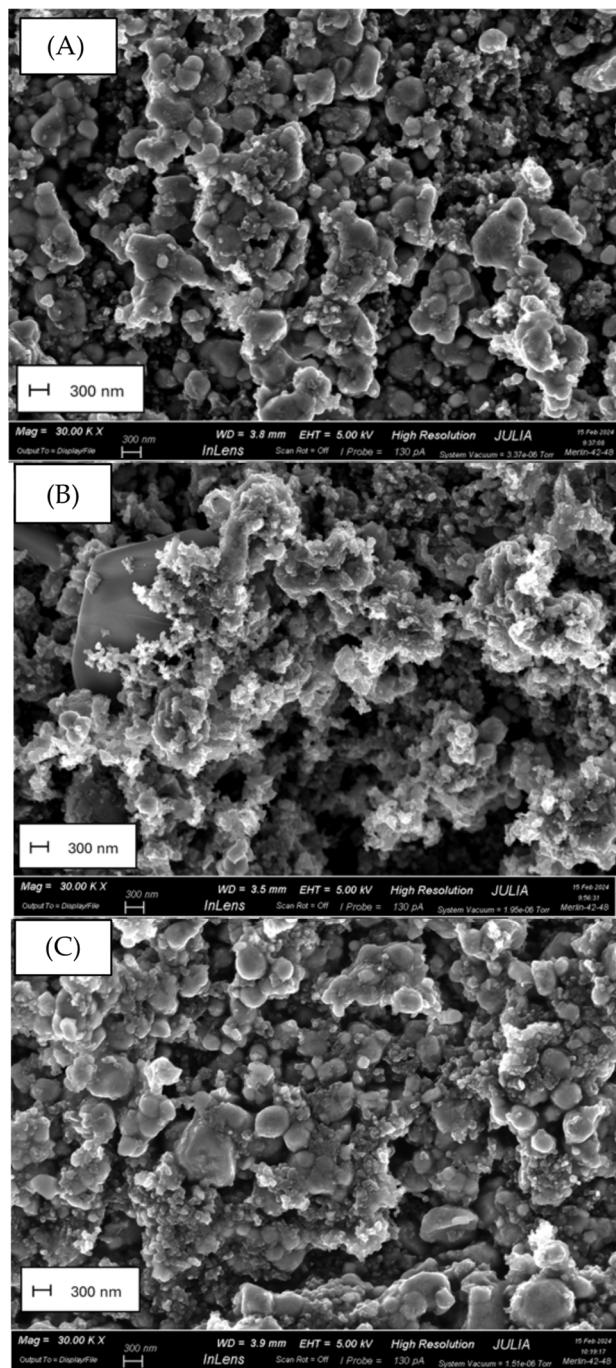


Figure 5. FESEM images of (A) initial LFP powder, (B) residues after sulfuric acid leaching, and (C) after citric acid leaching.

3.4. Recovery of Lithium

Lithium was recovered through chemical precipitation at 95 °C and pH 12, adding a stoichiometric amount of Na₂CO₃. The overall Li recovery efficiency was 28.6 ± 4% from the leachate with 0.5 M sulfuric acid and 6%vv. hydrogen peroxide, 25 ± 2% from the leachate with 0.5 M sulfuric acid and 3%vv. hydrogen peroxide, 26 ± 1% from the leachate with 0.25 M sulfuric acid and 6%vv. hydrogen peroxide, and 25 ± 6% from the leachate with 0.5 M sulfuric acid and 6%vv. H₂O₂. Unfortunately, chemical precipitation after citric acid leaching did not recover enough lithium to proceed with the characterization of the samples. Analogously to the leaching residues, the precipitates obtained from sulfuric acid leaching contained more impurities, with S concentration of 1770 ± 233 mg/kg with 0.5 M

sulfuric acid and 6%vv. hydrogen peroxide, 5250 ± 41 mg/kg with 0.5 M sulfuric acid and 3%vv. hydrogen peroxide, 3380 ± 163 mg/kg with 0.25 M sulfuric acid and 6%vv. hydrogen peroxide, and 9393 ± 775 mg/kg with 0.25 M sulfuric acid and 3%vv. hydrogen peroxide. The XRD analyses revealed the presence of lithium and sodium salts in forms of carbonates, sulfates, and phosphate (Figure 6).

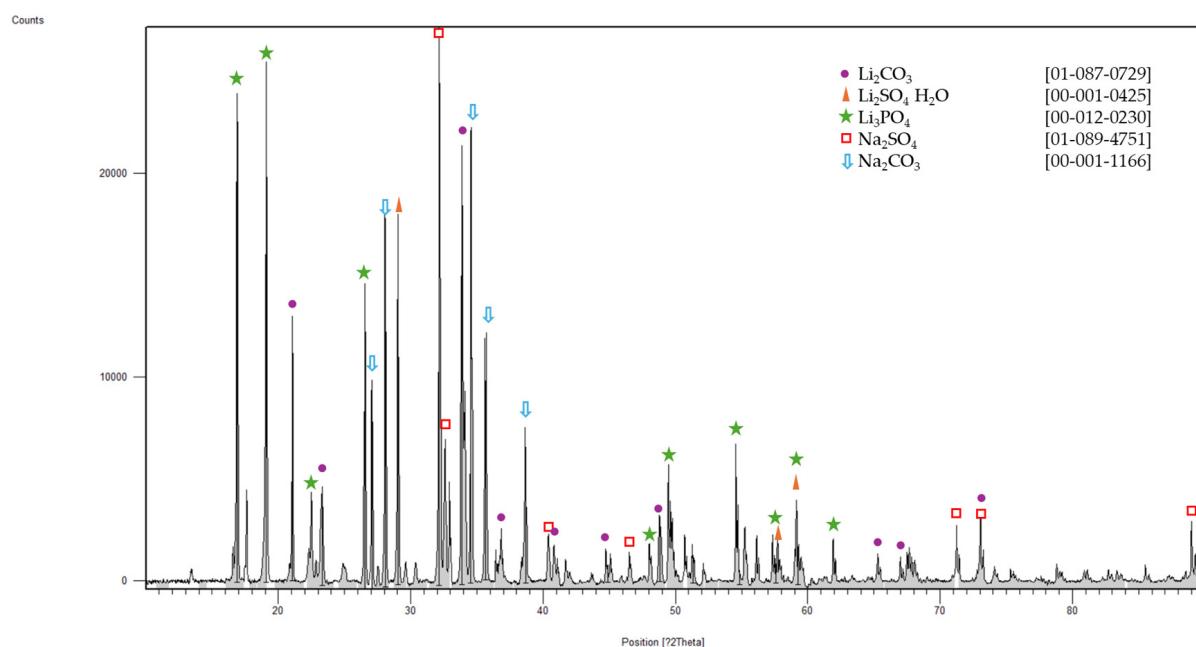


Figure 6. XRD spectrum of precipitate obtained at pH 12 from selective leaching with sulfuric acid and hydrogen peroxide.

3.5. Preliminary Economic Assessment

The operative costs associated with different experimental conditions (Figure 7) were in the range between 2.06 €/kg (0.25 M citric acid and 3%vv. hydrogen peroxide) and 2.55 €/kg (0.5 M sulfuric acid and 6%vv. hydrogen peroxide). The boundaries of the economic analysis are set by the leaching and precipitation processes. The economic and environmental implications of the pre-treatments to detach LFP-active material from current collectors have been reported in a previous study [32]. The costs associated with energy consumption were comparable for all routes, and the most expensive recycling step corresponds to Li chemical precipitation, which requires 95 °C. Indeed, the final stage of Li precipitation has been previously identified as the main bottleneck of the recycling process, due to its high energy demand [47]. The main difference among the routes was due to the cost of reagents, particularly hydrogen peroxide. Indeed, the cost of the process was 2.06 €/kg when hydrogen peroxide concentration was 3%vv. and between 2.47 €/kg and 2.80 €/kg with 6%vv. hydrogen peroxide.

The economic analysis presented in this study considered exclusively the process costs due to reagents and energy, which were directly measured during experimental tests as a comparison between different operative conditions. However, the economic feasibility of the process should be defined based on the scale-up of the process considering additional cost parameters: labor costs, management of waste streams, plant maintenance, and amortization of initial investments.

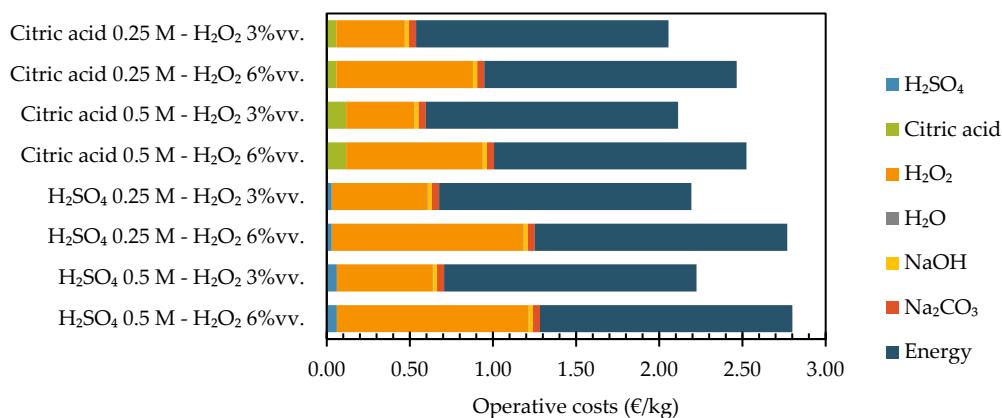


Figure 7. Operative costs of the considered routes applied to 1 kg of LFP cathodic material.

4. Discussion

4.1. Selective Leaching of Lithium from Production Scraps

Selective leaching of Li is critical in simplifying the recycling process of LFP cathodes; hence, various methods have been proposed to implement this strategy. For example, 97% of Li can be selectively recovered by mechano-chemical activation with ferric chloride [48], and 94.15% of Li can be extracted by carbothermic reduction followed by $\text{Na}_2\text{S}_2\text{O}_8$ leaching [49]. Nonetheless, these strategies are linked to the increase in reagents and energy consumption and in the generation of additional process wastes [50]. Thus, this work researches a viable solution by using a stoichiometric amount of leaching and oxidizing agents.

According to a previous study, selective Li leaching from end-of-life LFP cathodes using a stoichiometric ratio of sulfuric acid and hydrogen peroxide represent an economically valuable recycling strategy, due to a reduction in reagents consumption [20]. In this work, a similar approach is applied to production scrap cathodes, rather than end of life cathodes, analyzing the technical and economic comparison between a standard inorganic agent (sulfuric acid) and a greener alternative (citric acid). The results of this study imply that sulfuric acid and hydrogen peroxide, applied in mild concentration and at room temperature, are effective to selectively leach Li from LFP production scraps. The obtained results also confirmed the role of hydrogen peroxide in selective leaching; hydrogen peroxide acts as an oxidizing agent for Fe, oxidized to Fe (III), that forms phosphate salts that are not soluble at room temperature.

Moreover, previous studies proposed organic acids as sustainable leaching agents for Li-selective leaching, with oxalic acid reaching a leaching efficiency above 95% [51,52]. In this work, citric acid was selected as an alternative leaching agent, due to its lower price compared with other organic acids. Citric acid offers strong chelating properties, and it is often claimed as an effective leaching agent for end-of-life LIBs recycling [53], achieving dissolution rates of 96% of Li, 90% of Co, 94% of Mn, and 94% of Ni [54]. In addition, citric acid is biodegradable and lowly toxic, reducing the environmental impact associated with the management of process wastewater [55].

In this work, citric acid and hydrogen peroxide were significantly less effective than sulfuric acid in the selective leaching of Li from LFP production scraps. Previous studies, which compared the leaching efficiency of Li from end-of-life LIBs with traditional inorganic acids and with citric acid, reported higher leaching efficiencies for phosphoric acid [56] and for sulfuric acid [57] compared with citric acid. However, the slightly lower leaching efficiency of citric acid is overlooked since it is considered a more sustainable and cost-effective solution [58]. The results of this work, summarized in Table 2, comply with the notion that since pristine electrodes did not lose their structural and chemical integrity over time as end-of-life electrodes, recycling the former is more challenging [32]. In fact, citric acid was not effective for lithium-selective leaching from LFP production scraps. Whereas

sulfuric acid was identified as a better alternative because of the higher leaching efficiency and lower cost compared with citric acid. It should be noticed that the products recovered through sulfuric acid leaching presented higher contamination of S.

Table 2. Recovery efficiency (%) of Fe and P in the solid residues after leaching, leaching efficiency (%), and recovery efficiency of Li.

Leaching Agent	Concentration (M)	Concentration H ₂ O ₂ (%vv.)	Fe Recovery Efficiency (%)	P Recovery Efficiency (%)	Li Leaching Efficiency (%)	Li Recovery Efficiency (%)
Sulfuric acid	0.5	6	95 ± 6%	94 ± 7%	98 ± 1%	29 ± 4%
	0.5	3	98 ± 3%	96 ± 4%	91 ± 2%	25 ± 2%
	0.25	6	95 ± 7%	93 ± 4%	93 ± 1%	26 ± 1%
	0.25	3	97 ± 2%	98 ± 5%	90 ± 3%	25 ± 6%
Citric acid	0.5	6	98 ± 2%	97 ± 4%	25 ± 1%	-
	0.5	3	97 ± 2%	96 ± 3%	26 ± 2%	-
	0.25	6	98 ± 3%	98 ± 3%	18 ± 3%	-
	0.25	3	98 ± 6%	95 ± 2%	19 ± 2%	-

4.2. Preliminary Economic Analysis

From an economic point of view, selective leaching was proposed by this study to limit energy and reagents requirements and subsequently to decrease the costs related to recycling LFP powders from cathodes' production scraps. Mild conditions (0.25–0.5 M acids and 25 °C) have been selected, and the resulting operative costs were in the range 2.24–3.00 €/kg.

The hydrogen peroxide concentration has a huge impact on process cost, and 6%vv. was proposed [17] as an optimal concentration in the presence of organic acids. However, according to our study, the reduction in the hydrogen peroxide concentration from 6%vv. to 3%vv. did not alter the leaching efficiency of Li, Fe, and P. Indeed, our results proved that the leaching efficiency did not decrease when lower concentrations of sulfuric and citric acid (from 0.5 M to 0.25 M) and hydrogen peroxide (from 6%vv. to 3% vv.) were applied. Energy consumption was comparable between all recycling routes, with Li precipitation being the most energy-intensive step due to the high energy requirement. Thereby, Li precipitation should be improved to increase the overall economic feasibility of the recycling process.

Eventually, the economic analysis performed in this work is limited to process costs related to reagents and energy consumption. A more detailed evaluation of economic feasibility should consider other factors, such as labor costs, waste management, equipment maintenance, and amortization of capital investments [58]. Nonetheless, the comparison presented in this study is limited to lab scale in order to allow for a direct data collection during experimental analysis.

4.3. Practical Relevance of the Research

The practical implications of this study on selective leaching of Li from cathodes production scraps are relevant for different aspects of industrial recycling processes. LIBs manufacturing is rising exponentially due to increased demand for electric vehicles and renewable energy storage solutions, leading to an increase in demand for Li and in generation of production scraps. Therefore, cathodes production scraps could offer an additional source of Li supply for LIBs manufacturing, limiting reliance on mining primary raw materials. The recycling process presented in this study provides a solution both for managing LIBs production scraps and for securing supply of Li for manufacturing. Also, recycling of cathodic materials from production scraps entails several advantages compared with end-of-life LIBs, such as lack of discharge, dismantling and sorting necessity, availability of reagents, moderate process' temperature, and adaptability of recovered materials. Indeed, cathode scraps from production lines have not been assembled into batteries' cells yet, they have never come in contact with batteries electrolyte, which is flammable [59], and they do not contain residual voltage, which could lead to fire hazards [60], posing concerns for

workers safety [61,62]. Moreover, production scraps may hold higher contents of Li, since it has not been depleted during charge and discharge cycles [63], increasing their value as a Li source for recycling processes.

Additionally, the proposed recycling process requires the use of sulfuric acid and hydrogen peroxide, which are reagents commonly used in recycling facilities, thereby a full-scale implementation of selective leaching should be simplified, and the proposed recycling process requires lower operative temperature, which have a linear effect on energy expenses. The mild operative conditions (low acid concentration and room temperature) required to ensure selectivity of Li leaching, further enhance easy scalability of this process at industrial scale.

Ultimately, hydrometallurgical recycling of cathodes production scraps is a viable process to selectively recover lithium from other cathodes components and employ it as a secondary raw material to produce diverse cathodes chemistries.

5. Conclusions

LIBs recycling is commonly performed by hydrometallurgy; however, material recovery from cathodes production scraps is still an undeveloped topic. This study investigated the application of selective leaching for the recycling of active materials from LFP production scraps. Sulfuric and citric acid combined with hydrogen peroxide have been compared at different concentrations. Sulfuric acid provided higher leaching efficiency for Li (between $90 \pm 3\%$ and $98 \pm 1\%$), while citric acid could not exceed $26 \pm 2\%$. The optimal recycling process for LFP production scraps was leaching with 0.25 M sulfuric acid and 3%vv. hydrogen peroxide, at 25°C for 1 h, which allowed for leaching $90 \pm 3\%$ of Li and recovering $97 \pm 2\%$ of Fe and $98 \pm 5\%$ of P in the leaching residues. The main drawbacks of selective leaching with sulfuric acid were linked to the scarce Li recovery and to the presence of S impurities in leaching residues and precipitates. The operative costs of the proposed recycling processes were up to 3.00 €/kg, and they were reduced to 2.24 €/kg with the optimal leaching conditions.

In conclusion, this study presented a novel method to recover Li, Fe, and P from LFP production scraps, which represent an untapped resource to recover materials for batteries manufacturing. Further research is needed to optimize lithium recovery and limit impurities in the recovered materials.

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