Preliminary tests aimed at the recycling of Lithium Iron Phosphate (LFP) cathodes

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Introduction

Lithium Ion Batteries (LIBs) recycling is conventionally focused on the recovery of the most valuable metals (Co, Mn and Ni) from Cobalt-based cathodes (Larouche et al., 2020). However, Lithium Iron Phosphate (LFP) cathodes are expected to hold almost 35% of LIBs' market share by 2025 (Forte et al., 2020). A bottleneck of state-of-the-art LIBs' recycling technologies is the disadvantageous costs-benefits trade-off associated to the recovery of Li, Fe and P. LIBs' recycling at full-scale happens through pyrometallurgy, hydrometallurgy, or a combination of the two. Li, Fe and P recovery from LFP cathodes involves hydrometallurgy processes, based on acid leaching followed by a recovery phase. Excellent leaching efficiencies have been found for Li using inorganic acids, e.g., hydrochloric (Liu et al., 2023), phosphoric (Yang et al., 2017) and sulfuric (Li et al., 2017; Qin et al., 2019). The topic needs further research to improve the selectivity of Li recovery after the leaching phase (Forte et al., 2020).

This work describes some preliminary tests aimed at the leaching and recovery of Li, Fe and P from waste LFP cathodes. Acid leaching was explored by comparing two agents, e.g. sulphuric and citric acids. The process based on sulphuric acid involves Li, Fe and P leaching at 25-80°C (Dai et al., 2020; Wu et al., 2022; Larouche et al., 2020) and their further recovery as precipitates. On the other hand, citric acid entails selective leaching at 25°C of Li, then recovered as precipitate, while Fe and P remain in the solid phase (Kumar et al., 2020). Citric acid looks interesting as mild acidic leaching agent, but its use was preliminary investigated by few studies (Larouche et al., 2020). This work aims to search for further evidence, with the novelty of adding hydrogen peroxide to aid citric acid in the selective and efficient leaching of Li. Hydrogen peroxide has been reported by literature as auxiliary chemical in the leaching of Co, Ni and Mn from waste LIBs' cathodes (Larouche et al., 2020), but not yet applied to Li leaching.

Materials and methods

This study considered waste LFP cathodes provided by an Italian LIBs' producer. The waste cathodes have been pre-treated, to detach the active materials from the Al current collector, thermally (at 350°C for 0.5 hours) and mechanically (in a Retsch MM 200 ball mill in zirconia, at 14 Hz for 5 min). Two leaching agents have been compared, defining the experimental conditions according to literature (Larouche et al., 2020): 1M sulphuric acid at 40°C for 2 h, applying 50 g/L as solid-to-liquid ratio; 0.25M and 1M citric acid, eventually aided by 6%-vol H_2O_2, at 25°C for 1 h by applying 67 g/L as solid-to-liquid ratio. Recovery was achieved through chemical precipitation by adding 10M NaOH to adjust pH at 2, 6 and 12, obtaining three solid phases. The residual leachate was heated at 95°C for 2 h and mixed with Na_2CO_3 in stoichiometric amount to precipitate Li_2CO_3. All solid phases were dried, and analysed through a PANanalytical X'Pert XRD and a Perkin Elmer 7000 DV ICP-OES. The two leaching agents have been compared considering the recovery efficiencies of Li, Fe, and P.

Results and discussion

The results of the tests (Figure 1) showed excellent leaching efficiencies (95±3% for Fe and 94±3% for P) for sulphuric acid. On the other hand, the citric acid route is based on Li selective leaching and on leaving Fe and P in the solid phase. The achieved results showed that adding H_2O_2 to citric acid was crucial to avoid Fe and P leaching (90±3% for Fe and 91±1% for P with citric acid alone, and 23±5% for Fe and 30±8% for P with H_2O_2). A lower concentration of citric acid (0.25M instead of 1M) allowed to improve the process, and further limit Fe and P leaching to 1.4±1% and 5.3±1% respectively.

The powders recovered through sulphuric acid leaching were identified as mixtures of Iron Phosphate and Lithium Phosphate minerals, with overall efficiency values (involving leaching and further recovery) equal to 60% for Fe, 53% for P, and 25% for Li. These values suggest that even if the leaching was highly efficient, the recovery phase requires further research, particularly about Li.

The powders recovered through citric acid leaching aided by H_2O_2 were identified as Lithium Phosphate and Carbonate, while the residual solid phase was identified as Iron Phosphate, with overall efficiency values (involving leaching and further recovery) equal to 85% for Fe, 79% for P, and 15% for Li. These values confirmed the need to improve Li recovery from the leachate, however citric acid exhibited interesting performances about Fe and P.

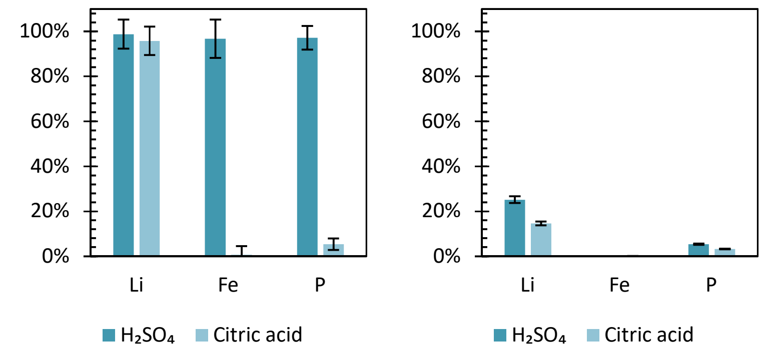

Figure 1. Process efficiencies for leaching (left), and final recovery (right) of Li, Fe and P with sulfuric acid 1M and citric acid 0.25 M and 6%-vol H_2O_2 leaching

Conclusions

Citric acid has been found to be a valid alternative to selectively recover Iron Phosphate and Lithium Carbonate from spent LFP cathodes. Despite a full environmental assessment and cost analysis of the two alternatives is still to be performed, the main advantages of the application of citric acid is the limited energy demand (leaching at room temperature), the reduced number of steps to precipitate the desired precursors, and eventually the low concentration of impurities in the recovered materials.

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