

GREEN LITHIUM RECOVERY FROM LFP CATHODES: A STUDY ON AIR-ASSISTED ORGANIC ACID LEACHING

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Abstract

Lithium iron phosphate batteries are now getting increasing attention due to their low cost, good cycling stability and high safety characteristics. Enhanced batteries consumption is accompanied by their subsequent discard that, if poorly managed, may cause serious environmental damage as well as severe economic losses.

Since the first adoption of LiFePO_4 as a battery component in 1996, numerous cathode recycling methods have been developed, including traditional pyro/hydrometallurgical methods as well as direct regeneration approaches. This paper, after a short review of the most relevant spent cathode treatments, presents preliminary results of a green recovery process, based on the selective extraction of lithium from LFP powders through the combined action of malic acid and oxygen in a semi-batch reactor with continuous air blowing.

Introduction

Driven by the need to cut greenhouse gas emissions and address the depletion of fossil fuels, the adoption of clean technologies has surged at an unprecedented rate in recent years. This trend was accompanied by an increasing need for energy storage devices, which pushed lithium-ion batteries (LIBs) to the forefront.

Currently, the most used LIBs can be classified based on the crystal structure of their cathodes into three types: spinel, layered, and polyanion. Polyanionic compounds, particularly LiFePO_4 (LFP) cathodes, have gained increasing success in recent years. This tendency is explained by their low cost and by their long life and high safety due to the strong Fe-O and P-O bonds which make their olivine structure extremely stable [1]. It is natural to assume that such a significant increase in sales of LFP batteries will go hand in hand with an increase in their scrapping and, as their average life is 5-10 years, this will soon become a global issue. Failure to properly dispose of these devices would not only cause serious pollution problems due to the release of toxic compounds into the environment but would also lead to the loss of strategic elements such as lithium and phosphorus, which are considered critical raw materials by the European Union [2]. However, conventional recycling techniques for spent batteries are not as profitable as expected when applied to LFP cathodes due to the lower value of lithium and iron compared to nickel, cobalt and manganese. Researchers are therefore focusing on the development of shorter and less chemical-

intensive processes and the direct regeneration of such materials [3].

This paper presents a short review of the most significant existing literature on the recovery of LiFePO_4 cathodes, specifically focused on the most recent and environmentally friendly methods. Moreover, preliminary results obtained performing the selective extraction of lithium from LFP powders through the combined action of malic acid and oxygen in a semi-batch reactor with continuous air blowing was reported.

LiFePO₄ cathode recycling

Although not the main culprit in battery degradation, attention is focused on recycling LFP cathodes due to their valuable materials content and production complexity. As shown in Fig. 1a, the initial step to obtain spent cathode powder involves pre-treating retired batteries through discharging, dismantling, and separation. Once the active material is obtained, it is either recovered to restore its electrochemical properties or separated into its components.

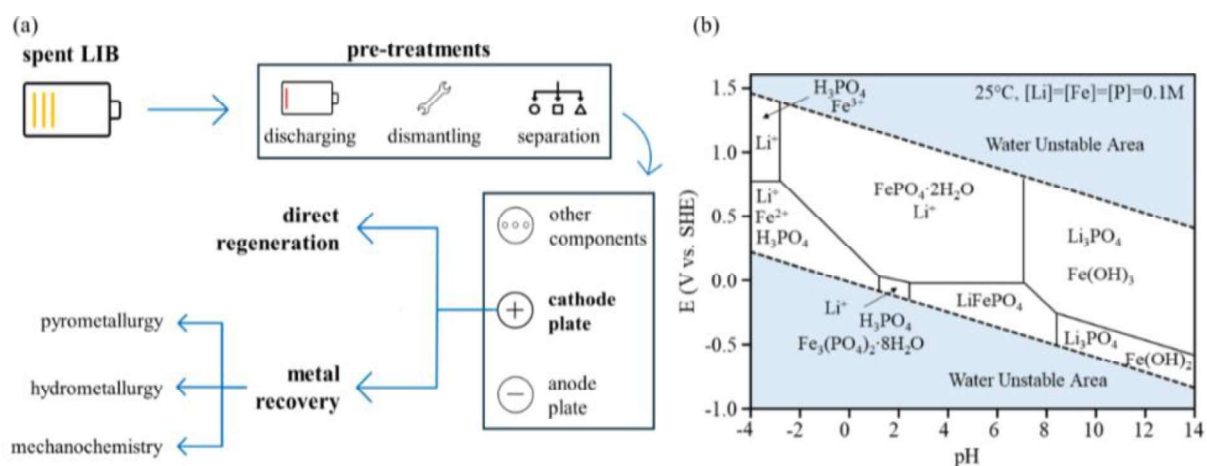


Figure 1. (a) Schematic representation of possible spent LIBs recycling routes. (b) Pourbaix diagram for the Li-Fe-P-H₂O system. Adapted from [4].

Metal Recovery

Following are the main techniques for recovering metals from spent LFP battery cathodes, including pyrometallurgy, hydrometallurgy and mechanochemistry.

Pyrometallurgy is a process that uses high temperatures to cause physical and chemical changes that allow for metal recovery [5]. It was traditionally used to extract valuable metals from ores but has become the go-to technology in the LIBs recycling industry due to its operational simplicity [6]. The extractive pyrometallurgical options used to process spent lithium-ion batteries are roasting/calcination and smelting [7], which differ mainly in operating temperature and atmosphere. Zhang et al. analysed LFP roasting in a sulphatising atmosphere [8]. Results showed that a mild temperature (600°C) reaction with sodium-bisulphate can convert lithium inside the olivine structure of the cathode into water-soluble sulphate, leaving Fe-P-O containing species in the solid state. Carbothermic

reduction (CTR) has also been investigated as a Li recovery procedure [24].

With the advantages of high metal recovery and reduced energy consumption, hydrometallurgical techniques are the preferred ones for spent LFP treatment. The typical hydrometallurgical process consists of a leaching step, aimed at dissolving all or part of the components of the cathode in an aqueous medium, followed by a purification stage. Based on the reagent used to solubilize the cathode, these processes can be categorized into inorganic acid leaching, organic acid leaching and acid-free leaching. An essential element in comprehending the distinctions between these leaching agents is the analysis of Pourbaix diagrams (Fig. 1b). Indeed, wet LFP recovery processes are contingent upon the thermodynamic equilibrium of the Li-Fe-P-H₂O system, which is a function of the pH and redox potential of the solution, as well as the temperature of the system and the liquid phase concentration of the species [4].

Strong inorganic acids can effectively leach Li, Fe and P out of the spent cathode at relatively low temperature as they provide suitable pH conditions for the generation of water-soluble species from the spent cathode powder. Sulphuric acid [9], phosphoric acid [10], pyrophosphoric acid [11] and hydrochloric acid [12] are examples of mineral lixiviants that researchers have investigated. Anyhow, being characterized by large acid consumption and non-selective extraction, these processes require the adoption of complicated metals separation steps and onerous wastewater treatments which limits their economic return. The use of oxidising agents or appropriate pre-treatments can alleviate these problems by enabling selective lithium recovery [4].

In view of the environmental risks associated with the use of mineral lixiviants, organic acids have become a major focus of research in the last few years [13]. This trend can be explained by the fact that, in addition to providing metal leaching efficiencies comparable to those of inorganic acids, these substances offer several advantages such as biocompatibility, mild operating conditions and facile downstream recovery [14]. Zhou et al. [15] proposed a closed-loop process exploiting the synergistic interaction between malic acid and hydrogen peroxide which enabled the occurrence of an in-situ reaction directly converting the olivine structure of LiFePO₄ to the olivine structure of FePO₄. In the work of Yang et al. [16], relatively cheap acetic acid was used, together with H₂O₂, to achieve Li recovery. By using the cathode plate directly as starting material rather than the previously scratched powder, researchers were able to simplify the recycling process, demonstrating the high selectivity of organic lixiviants towards Al impurities. Leaching with formic acid/H₂O₂ systems was explored by Mahandra and Ghahreman [17]. An oxidant free organic acid treatment was proposed by Chai et al. [18]. Using oxalic acid alone, more than 99% of the lithium present in the spent cathode powder, with only 2.4% Fe moving to the liquid phase, was extracted through a reaction carried out at 90°C for 60 minutes. Attempts to avoid using H₂O₂ are noteworthy because, although it only gives off oxygen and water as decomposition products, it cannot be considered a green reagent due to its energy-

intensive production process [19]. Kumar et al. [20] investigated the possibility of using citrus fruit juices as leaching agents. Lemon juice, paired with hydrogen peroxide, stood out as an excellent reagent owing to its high citric acid content, which provides a suitable pH for selective lithium extraction.

Preliminary results on a green process for lithium recovery from cathodes

In this study, the extraction of lithium from LFP powders was achieved through the combined action of malic acid and oxygen in a semi-batch reactor with continuous air blowing.

Single factor experiments were employed to optimize the leaching parameters.

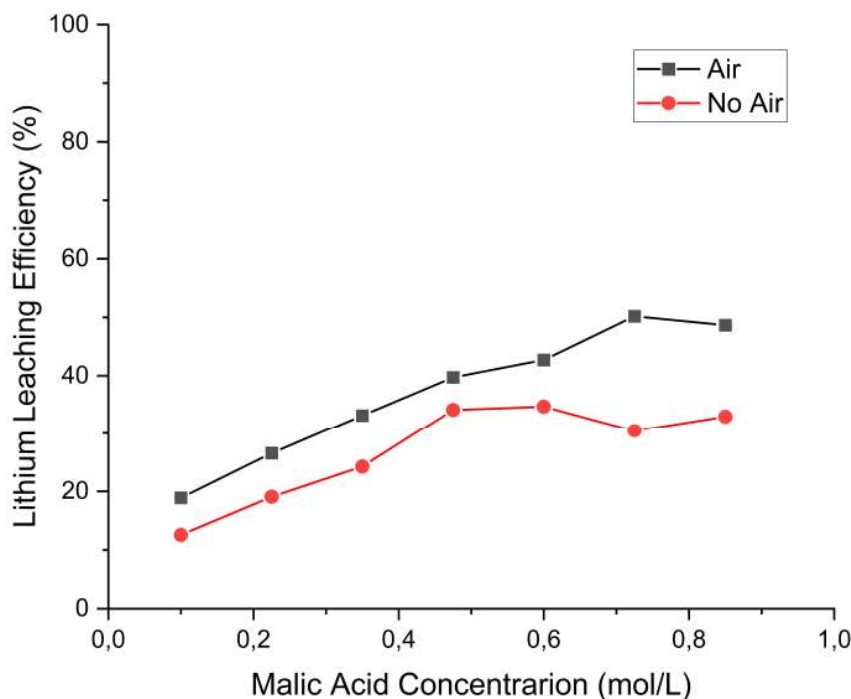


Figure2. Effect of air bubbling on lithium leaching efficiency at $T=25^{\circ}\text{C}$, $S/L=50\text{ g/L}$, reaction time=3 h, air flowrate= 1 L/min.

The following techniques were used to characterize the raw materials and products of the reaction to evaluate the leaching efficiency and to investigate possible reaction mechanisms: inductively coupled plasma-optical emission spectroscopy (ICP-OES), X-ray diffraction (XRD), X-ray fluorescence spectrometry (XRF), and Fourier transform infrared spectroscopy (FT-IR).

Final remarks

The short review presented in this paper set out to explore the most relevant strategies for spent LFP batteries recycling, highlighting novelty, limitations and possible improvement opportunities. The importance of selective Li extraction together with

the necessity to explore organic acids and inorganic salts as eco-friendly leaching agents has been underlined. This paper also reports preliminary results on air-assisted lithium leaching using malic acid. The obtained results show that continuous air bubbling enhances the ability of malic acid to extract Li from LFP cathodes, suggesting that the proposed process could represent a sustainable route for waste cathodes recovering. Further work is underway to optimise leaching time, temperature and solid-to-liquid ratio, with a view to exploring the deferred addition of acid. This should help to keep the pH constant, thereby improving selectivity for lithium.

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