A FACTORIAL DESIGN FOR THE EVALUATION OF THE OPTIMAL CONDITIONS FOR LiCoO$_2$ PARTICLES DISSOLUTION

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ABSTRACT: The hydrometallurgical leaching process for the recovery of valuable metals from the cathode active materials of spent lithium batteries was evaluated. Experiments were carried out using LiCoO$_2$ which is one of the most used cathodes in lithium-ion batteries. With the aim of optimizing the most relevant parameters (solid to liquid ratio, the concentration of the extracting agent and the concentration of the reducing agent) for the extraction process, a factorial experimental design was carried out to evaluate the effect of them in the dissolution process. Batch experiments were performed using 0.1 and 1 M HCl solution as extracting agent, solid to liquid ratio of 5 and 50 g L^{-1} and in absence and presence of reducing agent, i.e. 5% H$_2$O$_2$. The kinetic of LiCoO$_2$ dissolution was studied in batch experiments using as extracting agent 2.5 M of HCl, achieving an extraction of 52% and 87% of cobalt and lithium, respectively.

Keywords: Lithium-ion battery, LiCoO$_2$, Critical raw materials; leaching.

1. INTRODUCTION

Lithium ion batteries (LIBs) are extensively used nowadays in portable electronic devices and electric vehicles due to their advantageous characteristics, such as high energy density, small volume, light weight and low self-discharge efficiency. In our time, the accelerated updating of consumer electronics and the continued promotion of LIBs in electric vehicles has caused the amount of spent LIBs to increase. LIBs consist of a cathode, an anode, an organic electrolyte and a separator. Some of the materials used in LIBs such as metals and toxic electrolytes, present a threat to ecosystems and human health. In addition, spent LIBs have a high economic value because they contain valuable metals such as lithium, nickel, cobalt, and manganese. The recovery of these metals entails significant economic benefits which promotes the development and optimization of recycling processes (Zheng et al., 2018). Some important companies, such as Umicore, Duesenfeld, Toxco and Recupyl have developed industrial-scale recycling processes (Choubey, Chung, Kim, Lee, & Srivastava, 2017; Foster, Isely, Standridge, & Hasan, 2014).

Depending on the metal extraction process, recycling technologies can be classified into pyrometallurgical, hydrometallurgical and combined techniques. Pyrometallurgy uses high temperature to separate valuable metals. Hydrometallurgy uses chemical acidic leaching, precipitation and solvent extraction. The leaching reagents used in industrial processes are mainly inorganic acids like HCl, HNO$_3$ and H$_2$SO$_4$, organic acids and alkaline solutions (Liu, Lin, Cao, Zhang, & Sun, 2019). With the aim of improving leaching efficiency, reducing agents, typically H$_2$O$_2$, are used to improve the reduction of Co^{3+} to Co^{2+} which could be readily dissolved (Zheng et al., 2018). Others factors influencing the

leaching process are the temperature, reaction time, concentration of leaching agents, solid-liquid ratio, and the concentration of reducing agents.

In this work, the study of cobalt and lithium recovery from $LiCoO_2$ was carried out using HCl as extracting agent. The influence of different factors, such as extracting agent concentration, solid to liquid ratio, reaction time and the use of reducing agent, in the leaching process were also evaluated. These results allow a better understating of the leaching processes involved in batteries recycling technologies.

2. MATERIALS AND METHODS

2.1. Extraction analysis

Batch extraction experiments were carried out in well-stirred 50 mL polypropylene vessels, containing $LiCoO_2$ powder suspended in a volume of 25 mL HCl solution. The vessels with the dissolution were agitated in a rotatory shaking table at room temperature during 21 days. After this time, samples were taken to determine the concentration of Co^{2+} and Li^+ in the aqueous phase. With the aim of determining the initial amount of metals, microwave-assisted acid digestion was carried out. All the samples were filtered using 0.60 μm glass-fiber and analyzed for Co and Li using Atomic Absorption Spectrophotometry.

The evaluation of the most relevant parameters influencing the $LiCoO_2$ dissolution process was carried out following the factorial design (2^3, *i.e.*, factors and 2 levels) varying the experimental conditions as showed in Table 1.

Table 1. Experimental conditions.

Test	[HCl]	Ratio S/L	[H$_2$O$_2$]
000	0.1 M	5 g/L	0% vol.
001	0.1 M	5 g/L	5% vol.
010	0.1 M	50 g/L	0% vol.
011	0.1 M	50 g/L	5% vol.
100	1 M	5 g/L	0% vol.
101	1 M	5 g/L	5% vol.
110	1 M	50 g/L	0% vol.
111	1 M	50 g/L	5% vol.

The kinetic of $LiCoO_2$ dissolution was studied in batch experiments using as extracting agent 2.5 M of HCl, $S/L = 50$ g L^{-1} and in absence of reducing agent. At selected times, samples were withdrawn to determine the concentration of Co^{2+} and Li^+ in the aqueous phase.

3. RESULTS AND DISCUSSION

3.1 Batch Experiments

3.1.1. Influence of the main parameters in LiCoO₂ dissolution.

The percentages of Li and Co recovered from the solid matrix at different experimental conditions are presented in Figure 1.
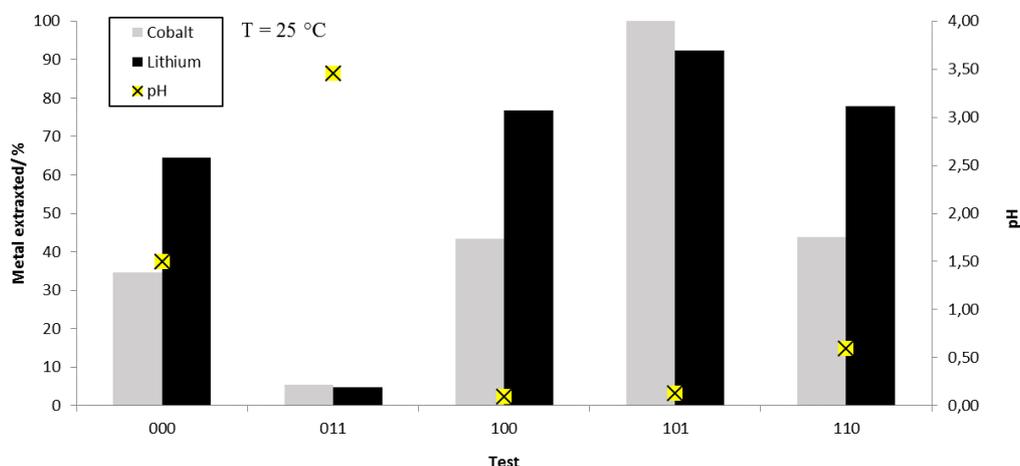

Figure 1. Percentage of extracted metal with respect to the amount in the initial solid.

First, 0.1 M HCl solution was used with a low solid/liquid ratio ($S:L$ = 5 g/L), obtaining an extraction of 35% and 64% of cobalt and lithium, respectively. Secondly, a $S:L$ = 50 g/L ratio was used with the same concentration of extracting agent, reaching an extraction of 5% of cobalt and 9% of lithium. The pH values increase from 1.5 to 3.5, which could be associated with the consumption of protons during the extraction process. In order to improve the extraction, HCl solution of 1 M was used in further tests, achieving a recovery of about 43% and 77% of cobalt and lithium, regardless of the solid-liquid ratio. Regarding the use of H_2O_2 as a reductant agent, an important increase of the extraction efficiency has been reported. Specifically, recovery increase from 77% and 43% in the absence of reductant agent for Li and Co, respectively, to 92% and 100% when 5% of H_2O_2 was added.

Results for the experiments 001 and 111 are not presented in the table because the data was not reliable. In particular, these experiments appear to have had a fast dissolution of the particles with significant release of gasses, which produced overpressure in the vials during within the shaking table and loss of material from the vials.

3.1.2. Kinetic study of LiCoO₂ in HCl 2.5 M solution

The time evolution of the dissolved metal (Co^{2+} and Li^+) from LiCoO₂ is presented in Figure 2. It could be concluded that the kinetics of particle dissolution is moderately quick reaching a plateau after, approximately, 2 hours to cobalt and 8 hours to lithium, reaching an extraction of 50% and 90% of cobalt and lithium, respectively. It has been also observed a non-equimolar proportion between Li^+ and Co^{2+}. The concentration of Li^+ in the equilibrium is, approximately, twice as high as the concentration of Co^{2+}.
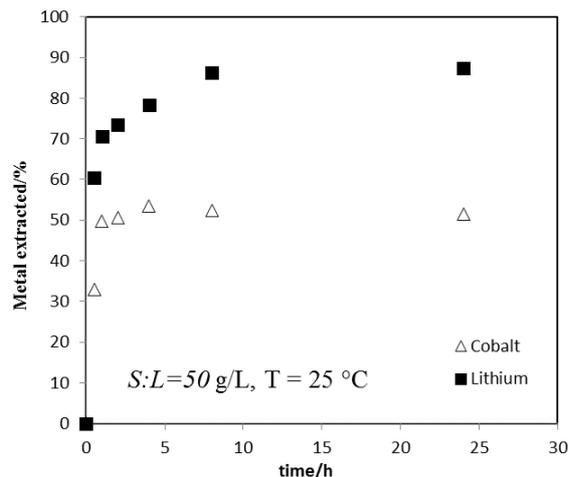
Figure 2. Time-transient values for the percentage of extracted metal with respect to the amount in the initial solid.

4. CONCLUSIONS

This work is focused on the implementation of hydrometallurgical extraction for the recovery of Li and Co from lithium-ion battery waste. Although tests have been carried out using $LiCoO_2$, the technique can be applied to different kinds of cathode from spent batteries. The results indicate that the recovery of Co and Li is viable at optimized experimental conditions. The results from the factorial design indicate clearly that the dissolution of LiCoO2 particles is faster and more extensive when using more acidic extracting solution and stronger reducing agents such as water peroxide. This Findings will be use in future stages of the investigation to design an optimized extraction procedure.

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