



Cathodes of spent Li-ion batteries: Dissolution with phosphoric acid and recovery of lithium and cobalt from leach liquors



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ABSTRACT

This paper presents the study of an innovative process: the reductive dissolution of mixed lithium cobalt oxide contained in the cathodes of spent Li-ion batteries with phosphoric acid. The studied parameters were: reaction time, temperature, stirring speed, solid-liquid ratio and concentrations of the leaching agent (H₃PO₄) and the reducing agent (H₂O₂). Reactants and products were characterized by atomic absorption spectroscopy (AAS), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The results showed that the reducing dissolution process with phosphoric acid is an efficient way for the extraction of lithium and cobalt, achieving dissolution values close to 100%. In addition, a recovery of 88% of Li + as Li₃PO₄ and 99% of Co⁺² as Co₂O₄, with purities of 98.3% and 97.8% was found respectively.

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1. Introduction

Today, Li-ion batteries (LIB) are used as energy sources for various portable devices such as mobile phones, laptops, cameras and camcorders, and hand tools among others. LIB are generally constituted by a graphite anode adhered to a copper sheet and lithium cobalt oxide (LiCoO₂) cathode adhered to an aluminum sheet, being both solids glued to these sheets by fluoro-polyvinylidene (PVDF). The electrodes are separated from each other by a plastic film, and covered by a metal casing wrapped in another plastic. Moreover, they are soaked in an electrolyte which may vary according to the brand and/or battery model, being LiClO₄, LiBF₄ and LiPF₆ the most commonly used (Xu et al., 2008).

In the last few years there has been a significant increase in the production of portable devices that use this kind of batteries that is why the demand for them has considerably grown, arousing great concern regarding their final disposal once their life time is over. At present, batteries are discarded along with domestic garbage, and then deposited in solid waste dumps which could lead to serious environmental problems, since the leaching of battery components caused by organic waste could contaminate soil, water and air, the last one when landfills are burnt (Greenpeace Argentina, 2010, Gudewort et al., 2013). Furthermore, the toxicity of their different components and the large waste volume generated by high demands and short average life (2 years) of

these batteries must be seriously taken into account (Li et al., 2010a). Nayaka et al., 2015 reported that Europe and the USA consume approximately 8 billion units per year. Consequently, the development of new methodologies for the recycling of various components of spent Li-ion batteries (LIBs) has become a main priority.

Most recently developed hydrometallurgical processes include stages of preparation and pretreatment of the sample. In them, batteries are firstly discharged, then opened and disassembled, separating their components, and then selecting cathodes, which have LiCoO₂, and taking off the aluminum sheet using NMP (Li et al., 2010a, 2010b) or dissolving it with alkalis (Wang et al., 2009 and Nayl et al., 2014). Afterwards, the obtained powder or paste is washed at 333 K for one day. The resulting solid is calcined at 975 K for 5 h and then it is taken into milling for a period of 2 h. The whole treatment is performed in order to increase the reactivity of the solid (Nayaka et al., 2015; Li et al., 2010a, 2010b; Xu et al., 2008).

Many researchers have investigated the process of LiCoO₂ reductive dissolution with numerous inorganic acids, and H₂O₂ as reducing agent. The tested acids were H₂SO₄ (Zhu et al., 2012; Nan et al., 2005; Nayl et al., 2014; Shin et al., 2005; Wang et al., 2009; Jha et al., 2013; Mantuano et al., 2006; Chen et al., 2011; Sun and Qiu, 2011; Kang et al., 2010) and HNO₃ (Lee and Rhee, 2003). In all the cases, the use of the reducing agent led to an increase in the dissolution of lithium cobalt oxide, because it facilitated the release of cobalt from the structure (Li et al., 2010a). The highest dissolution values, near 95% for both metals, were obtained when working with sulfuric acid. Cobalt recovery was achieved through precipitation, usually with NaOH (Nayl et al.,

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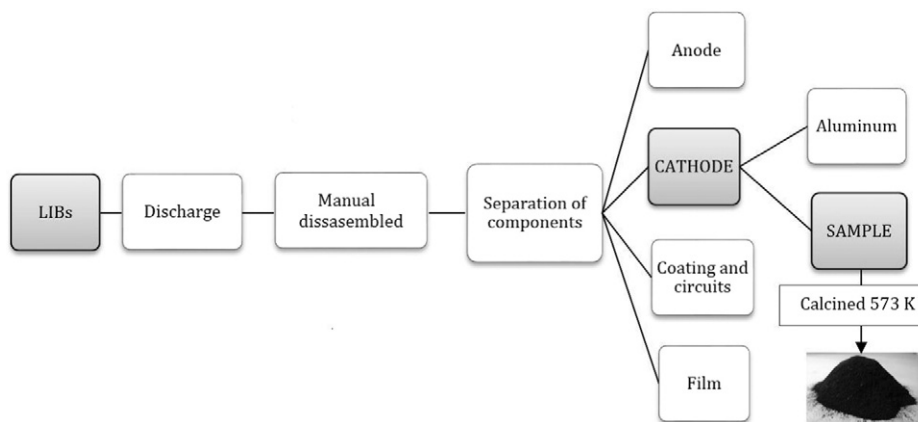


Fig. 1. Flow sheet of the sample preparation process.

2014; Wang et al., 2009; Contestabile et al., 2001), NH_4OH (Dorella and Mansur, 2007), $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (Wang et al., 2009; Zhu et al., 2012) and $\text{H}_2\text{C}_2\text{O}_4$ (Jian et al., 2012). The best recovery values for cobalt were between 80 and 90% for all precipitating agents. For lithium, the chemical reagent used was Na_2CO_3 with recoveries of about 90% (Zhu et al., 2012; Nan et al., 2005; Nayl et al., 2014 and Jian et al., 2012).

In a comprehensive literature review, researches on the dissolution of LiCoO_2 obtained from cathodes of LIBs using phosphoric acid as a leaching agent were not found. The use of this acid would be beneficial because the obtained products are of industrial interest. Furthermore, it is worth noting that the process for industrial production of Li_3PO_4 involves solutions of lithium salts, to which other salts containing the anion phosphate or phosphoric acid are added (Habashi, 1997).

The purpose of this paper is to look for an innovative process of LiCoO_2 reductive dissolution of the LIBs using phosphoric acid as leaching agent, obtained from a pretreatment with lower power consumption than those currently used, and to study the operational variables affecting the dissolution reaction and the recovery of high purity CoC_2O_4 and Li_3PO_4 as final products. This process has several advantages considering that it uses electronic waste, therefore it prevents pollution and mineral exploitation, moreover it decreases the number of steps needed to obtain lithium phosphate, since phosphoric acid is used directly as a leaching agent.

2. Experimental

2.1. Materials

The reagents used were phosphoric acid, oxalic acid, sodium hydroxide, ethanol and hydrogen peroxide, all of them with analytical grade.

The samples were obtained from LIBs from mobile phones of different brands and models.

2.2. Equipment

The dissolution tests were performed in a closed batch reactor of 800 mL built in Teflon® equipped with magnetic stirring and temperature control systems.

The reactants and products were characterized by X-ray diffraction (XRD) carried out in a diffractometer Rigaku D-Max III C. Morphological analysis was performed by SEM in a microscope LEO 1450 VP which was equipped with an X-ray dispersive spectrometer EDAX Genesis 2000 used to determine the semiquantitative composition of the synthesized compounds by electron probe microanalysis (EPMA). Composition quantitative determinations were performed by atomic absorption spectroscopy (AAS) using a Varian SpectrAA 55 spectrometer with a hollow-cathode lamp. The particle size was determined with an Analysette A-20 Fritsch scanning photosedimentography.

2.3. Experimental procedure

2.3.1. Preparation and characterization of the sample

Fig. 1 shows a flow sheet of the sample preparation and pretreatment stages. The sample was prepared using LIBs of 500 units of mobile phones of different brands and models, which were discharged with a saturated solution of NaCl (for 48 h at room temperature) and subsequently disassembled. Then, the components of the LIBs were separated, isolating the cathodes (Pinna et al., 2015) to obtain 3.7 kg of LiCoO_2 , later they were calcined at 573 K to remove the residual adhesives. The remaining parts of the batteries were stored for future studies.

Table 1 shows the quantitative composition of the sample determined by AAS.

In Fig. 2, the results of the characterization of the sample by XRD (Fig. 2a) and SEM (Fig. 2b) are shown. In the diffractogram the presence of a crystalline structure of lithium cobalt oxide (ICDD 01-077-1370) is observed. The presence of other crystalline compound has not been detected, so it could be inferred that the Mn detected by AAS is an impurity. Its presence may be explained since in the sample preparation some LIBs containing this metal were incorporated, it is worth mentioning that Mn is used to replace partially and in a low proportion the cobalt, when manufacturing the batteries. In Fig. 2b) it can be seen the particles sample morphology which have an irregular size and shape with rounded edges.

Analysis of particle size distribution by photosedimentography showed that the sample has the highest frequency in the 10 μm particle.

2.3.2. Procedure for the dissolution tests

For each test, 4.8 g of sample and calculated volumes of distilled water were introduced into the reactor. Upon attainment of the work temperature, the mixture was heated. Subsequently, calculated volumes of H_3PO_4 and H_2O_2 were added to obtain a final volume of 600 mL, and the reaction time began to be measured. At the end of this period, the solid was filtered, dried at 348 K, and weighed.

The dissolution efficiency was calculated by using the expression:

$$X\% = \left(\frac{m^0 - m^f}{m^0} \right) \times 100 \quad (1)$$

where: X% is the percent dissolution efficiency; m^0 is the initial mass of the solid reactant and m^f is the mass that remains unreacted after the reaction.

Table 1
The bulk composition of the sample.

Elements	Li	Co	Mn
%p/p	4.8	41.5	2.1

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