



# 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 (H<sub>3</sub>PO<sub>4</sub>) and the reducing agent (H<sub>2</sub>O<sub>2</sub>). 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 Li<sub>3</sub>PO<sub>4</sub> and 99% of Co<sup>+2</sup> as CoC<sub>2</sub>O<sub>4</sub>, 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 (LiCoO<sub>2</sub>) 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 LiClO<sub>4</sub>, LiBF<sub>4</sub> and LiPF<sub>6</sub> 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 LiCoO<sub>2</sub>, 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 LiCoO<sub>2</sub> reductive dissolution with numerous inorganic acids, and H<sub>2</sub>O<sub>2</sub> as reducing agent. The tested acids were H<sub>2</sub>SO<sub>4</sub> (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 HNO<sub>3</sub> (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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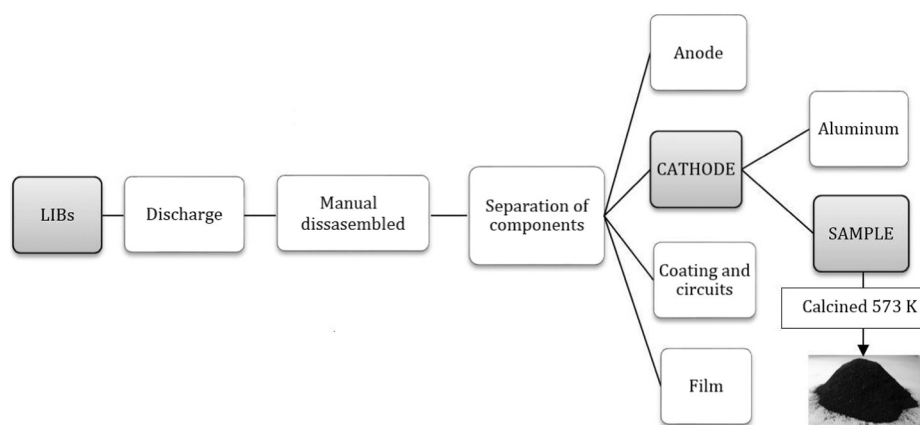


Fig. 1. Flow sheet of the sample preparation process.

2014; Wang et al., 2009; Contestabile et al., 2001),  $\text{NH}_4\text{OH}$  (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  $\text{Na}_2\text{CO}_3$  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  $\text{LiCoO}_2$  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  $\text{Li}_3\text{PO}_4$  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  $\text{LiCoO}_2$  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  $\text{CoC}_2\text{O}_4$  and  $\text{Li}_3\text{PO}_4$  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 photosedimentograph.

### 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  $\text{NaCl}$  (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  $\text{LiCoO}_2$ , 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  $\mu\text{m}$  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  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{O}_2$  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

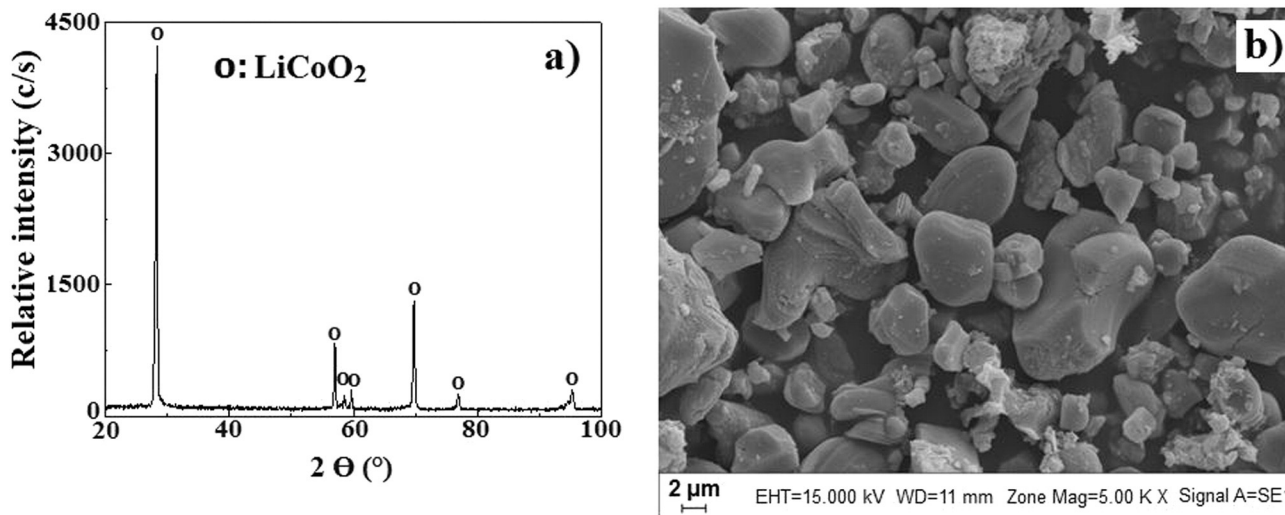


Fig. 2. a) Diffractogram and b) SEM micrograph of the sample.

In this research, an univariate analysis of each of the experimental leaching conditions was performed. Studied variables and intervals were: concentration of  $\text{H}_3\text{PO}_4$ , 1, 2, 3, 4 and 5% v/v; concentration of  $\text{H}_2\text{O}_2$ , 0, 1, 2, 4, 6 and 8% v/v; temperature, 288, 298, 318, 348 and 363 K; reaction time, 0, 15, 30, 60, 120 and 180 min; stirring speed, 0, 110, 330, 400 and 460 rpm, at two temperatures (298 and 348 K) and solid-liquid ratio, 2, 8, 17, 27 and 30 g/L.

### 2.3.3. Reactions proposed

Phosphoric acid is polyprotic and therefore it presents several dissociation reactions in aqueous solution, each species acting as an acid or as a base depending on the way in which Fig. 3 is analyzed, if it regards to the species on its right or on its left. These three equilibria of dissociation enable us to see that the first proton is readily detached even at an acidic pH, indicating that the  $\text{H}_3\text{PO}_4$  is a moderately strong acid. The second dissociation  $\text{pK}$  (7.2) has buffer action and the third  $\text{H}^+$  is dissociated in alkaline medium (Burriel Martí and Lucena Conde, 2008).

According to Fig. 3, probable dissolution reactions of  $\text{LiCoO}_2$  with phosphoric acid in reductive media were proposed. Furthermore,  $\Delta G_{298\text{ K}}$  values of each one were calculated with the software HSC Chemistry for Windows 5.0.

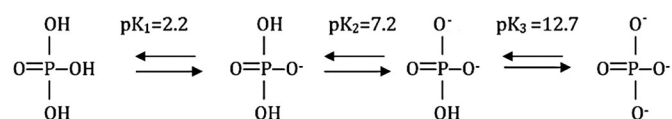
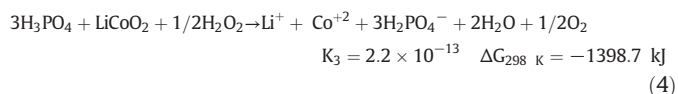
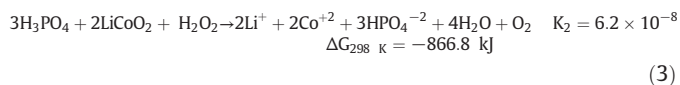
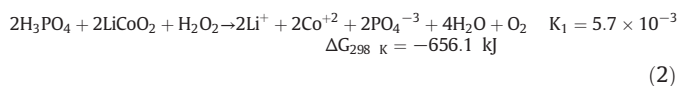


Fig. 3. Dissociation reaction of phosphoric acid.

### 2.3.4. Procedure for the recovery tests

The lithium and cobalt contained in the leach liquors from the dissolution with phosphoric acid and hydrogen peroxide were recovered as cobalt oxalate and lithium phosphate using oxalic acid and sodium hydroxide as precipitating agents, respectively.

These tests were carried out in two stages, the first stage was cobalt recovery through its precipitation with oxalic acid, and this precipitate was filtered and dried at 348 K. Then, in the second stage, the leach liquor obtained from step 1 was pre-concentrated by evaporation up to a concentration of  $\text{Li}^+$  of 10 g/L determined by AAS. The pH was adjusted to 13 by addition of NaOH, a few drops of ethanol were added and the solution was heated slightly until the appearance of a precipitated of lithium as  $\text{Li}_3\text{PO}_4$  which was filtered and dried at 348 K.

## 3. Results and discussion

### 3.1. Dissolution assays

#### 3.1.1. Effect of concentration of the leaching agent

In Fig. 4 the results of the effect of phosphoric acid concentration on the reaction dissolution were studied in a concentration range of 1 to 5%

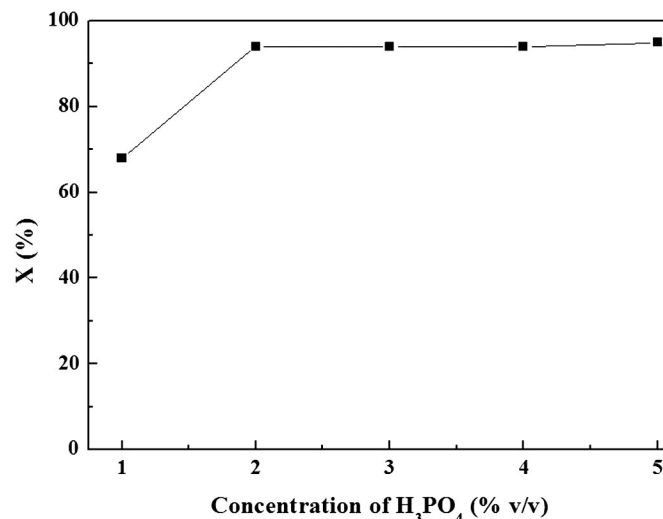


Fig. 4. Effect of concentration of  $\text{H}_3\text{PO}_4$  on the sample dissolution.

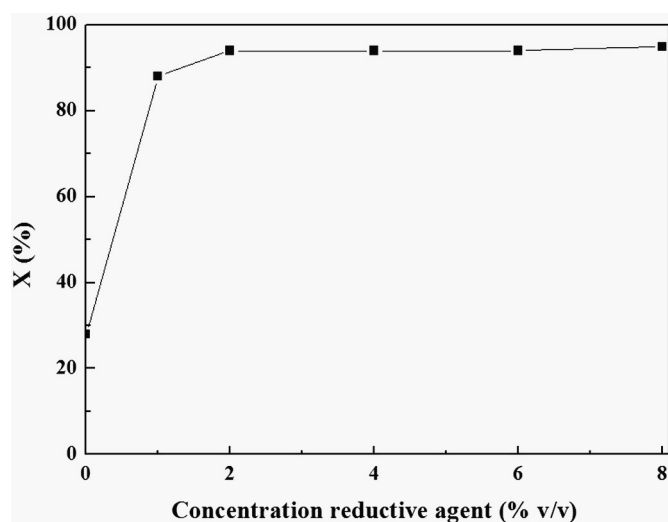


Fig. 5. Effect of concentration of the reductive agent on the sample dissolution.

v/v. The operating conditions of the dissolution process were: solid-liquid ratio, 8 g/L; stirring speed, 330 rpm;  $\text{H}_2\text{O}_2$  concentration of 2% v/v; temperature, 348 K and reaction time, 60 min.

The results presented in Fig. 4 show that increasing the concentration of phosphoric acid increases the dissolution of the sample to an acid concentration of 2% v/v, above which the dissolution of  $\text{LiCoO}_2$  remains constant. The range of concentrations selected for phosphoric acid was calculated according to the stoichiometry of the reaction given by Eq. (4). Furthermore, solutions obtained after the dissolution process had a pH equals to 3 which would indicate that the dominant species is  $\text{H}_2\text{PO}_4^-$ . This allows us to conclude that in our system,  $\text{H}_2\text{PO}_4^-$  is the mostly formed phosphate species, this should be taken into account in further analysis.

### 3.1.2. Effect of the concentration of the reductive agent

The study of the addition of hydrogen peroxide was carried out between 0 and 8% v/v. The tests were performed under the following conditions: solid-liquid ratio, 8 g/L; stirring speed, 330 rpm;  $\text{H}_3\text{PO}_4$  concentration, 2% v/v; temperature, 348 K and reaction time, 60 min. The results of these studies are presented in Fig. 5.

Fig. 5 shows that when incorporating a reducing agent, the dissolution process increases about 60% between the studied limits. It is also noticeable that increasing the concentration of  $\text{H}_2\text{O}_2$  above a value of

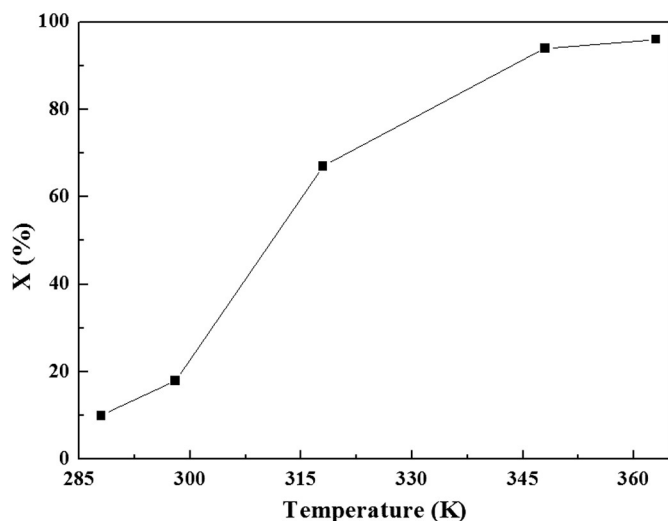


Fig. 6. Effect of temperature on the sample dissolution.

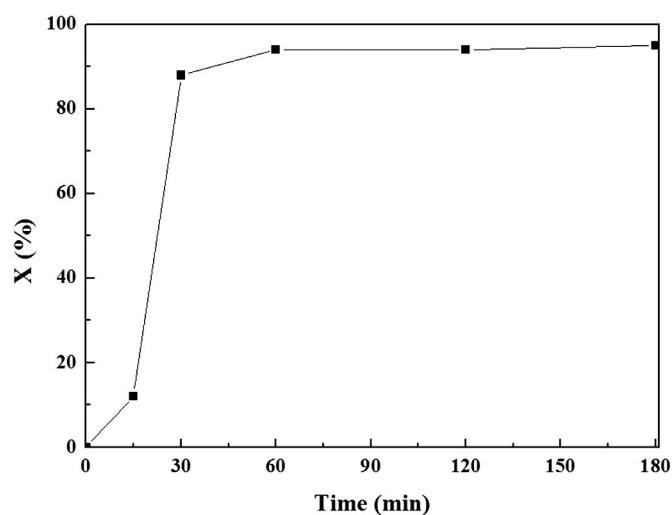


Fig. 7. Effect of the reaction time on the sample dissolution.

2% v/v has little effect on dissolution. Therefore, to study other parameters, we will work with  $\text{H}_2\text{O}_2$  2% v/v.

The decomposition of hydrogen peroxide produces oxygen, which reduces Co (III) to Co (II) despite being the chemical bond between Co (III) and O extremely strong. When reduction occurs, ionic radius of cobalt changes, then the strength of chemical bond decreases, facilitating Co expulsion from the structure and, therefore, the dissolution of the oxide is favored by a moderately strong acid. Moreover, as Co and Li are the main components of  $\text{LiCoO}_2$ , the dissolution of cobalt also promotes the dissolution of lithium (Li et al., 2010a, 2010b).

### 3.1.3. Effect of reaction temperature

The dissolution tests for studying the effect of temperature were performed under the following conditions: concentration of  $\text{H}_3\text{PO}_4$ , 2% v/v; concentration of  $\text{H}_2\text{O}_2$ , 2% v/v; reaction time 60 min; stirring speed, 330 rpm and solid-liquid ratio, 8 g/L. Experiments were performed in a temperature range between 288 and 363 K and results are presented in Fig. 6.

Fig. 6 shows the marked effect of temperature on the sample dissolution, increasing it significantly up to a value close to 95% at the highest temperature studied. This is explained due to the reactivity of the solid, since it increases with a rise of temperature.

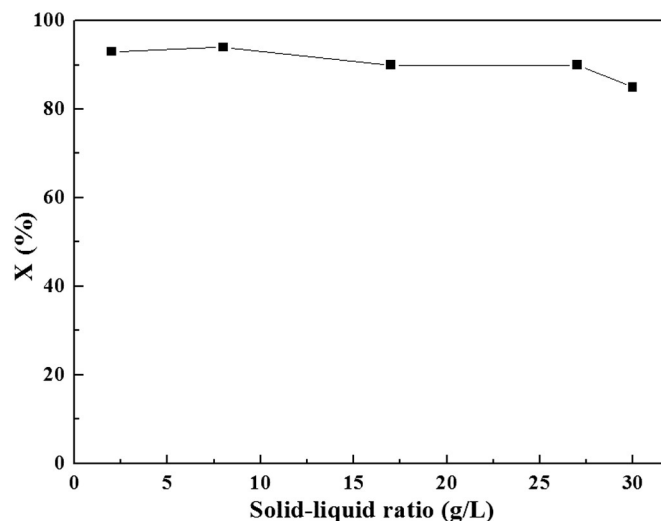


Fig. 8. Effect of solid-liquid ratio on the sample dissolution.

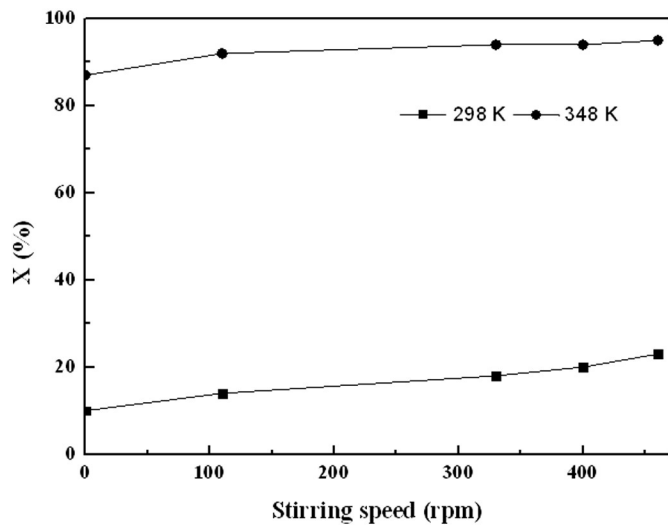


Fig. 9. Effect of stirring speed on the sample dissolution.

### 3.1.4. Effect of reaction time

The dissolution tests were conducted under the following conditions:  $\text{H}_3\text{PO}_4$ , 2% v/v;  $\text{H}_2\text{O}_2$ , 2% v/v; solid-liquid ratio of 8 g/L, 330 rpm and 348 K. The study of the time range was between 0 and 180 min and results are displayed in Fig. 7.

The results observed in Fig. 7 show that the dissolution of the sample increases with the reaction time; this is in agreement with the well known fact that for solid/liquid reactions increasing the contact time between reagents favors the dissolution reaction. An increase of almost 90% in the range studied can be appreciated. Furthermore, it can be seen that over the 60 min, reaction time does not affect significantly the dissolution value.

### 3.1.5. Effect of solid-liquid ratio

The study of the effect of solid-liquid ratio was performed under the following conditions: concentration of  $\text{H}_3\text{PO}_4$ , 2% v/v; concentration of  $\text{H}_2\text{O}_2$ , 2% v/v; reaction time, 60 min; stirring speed, 330 rpm and temperature, 348 K. The tests were carried out in a range of 2 to 30 g/L; the results are shown in Fig. 8.

The results plotted in Fig. 8 show that the solid-liquid ratio has a slight effect on the dissolution. When the solid-liquid ratio is over 8 g/L, the dissolution efficiency decreases slightly. A solid-liquid ratio of 8 g/L is considered to be optimal for both, economics and efficiency reasons.

### 3.1.6. Effect of stirring speed

The conditions in the process of dissolution were: solid-liquid ratio, 8 g/L; concentration of  $\text{H}_2\text{O}_2$ , 2% v/v;  $\text{H}_3\text{PO}_4$  concentration of 2% v/v; temperature, 288 and 348 K and reaction time 60 min. The study of the effect of stirring speed was performed in a range of 0–460 rpm and results are presented in Fig. 9.

The results shown in Fig. 9 indicate that when the stirring speed is over 330 rpm, the sample dissolution is slightly affected by the two

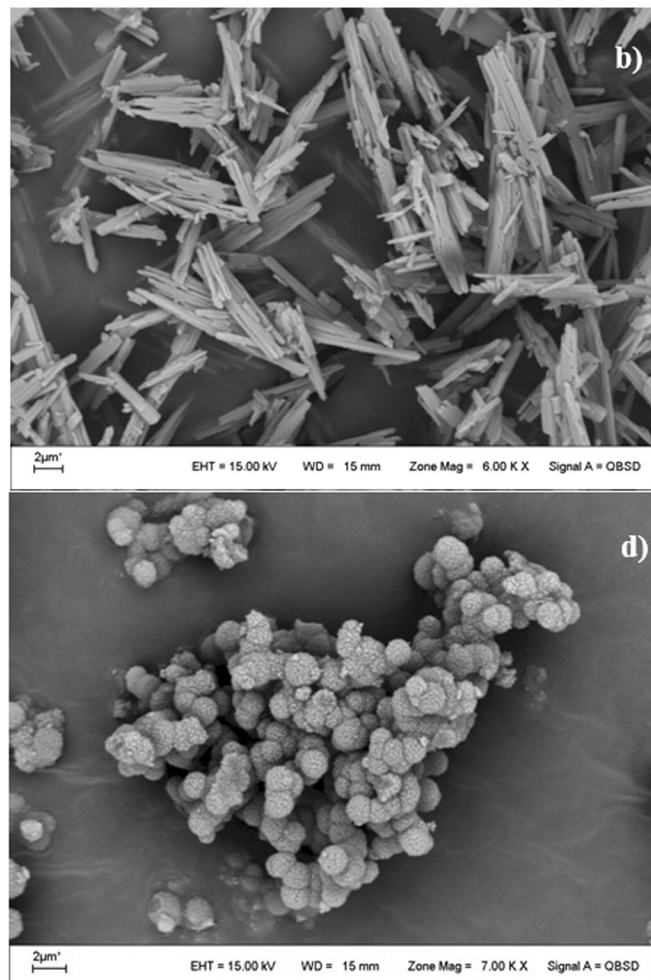
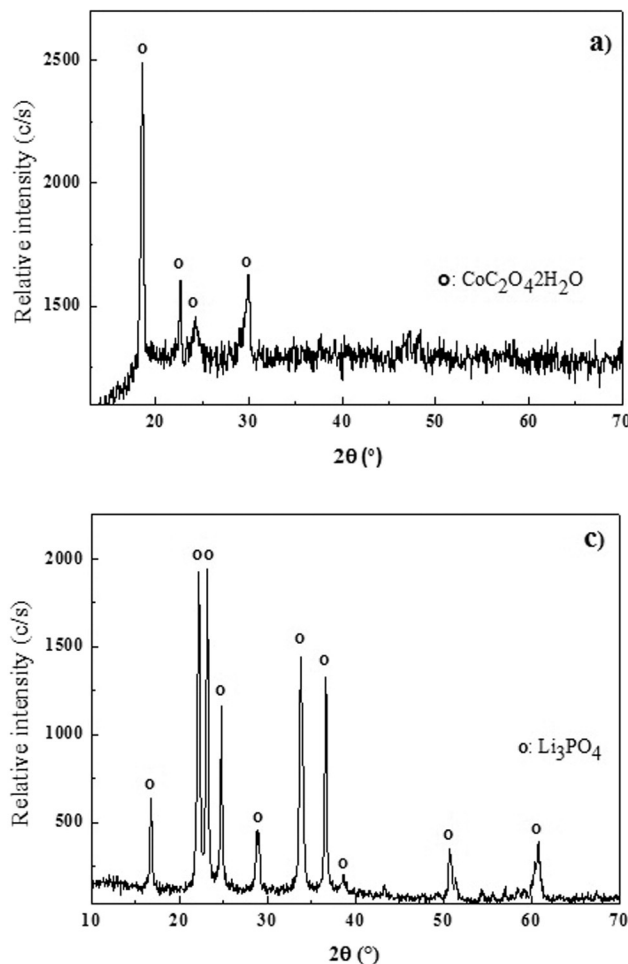


Fig. 10. a) XRD and b) SEM of the solid precipitated in step 1, c) XRD and d) SEM of solid precipitated in step 2.

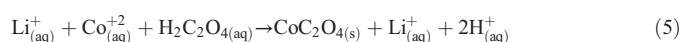
evaluated temperatures (298 and 348 K). This fact indicates that once this stirring speed has been reached, the thickness of the film surrounding the solid is minimal, and hence it does not affect the acid transfer rate from solution to particles surface. To continue the study of other operating parameters, 330 rpm was selected as the best stirring speed value.

### 3.2. Recovery assays

The obtaining of oxalate cobalt (step 1) was performed using an aliquot of leach liquor, heating it to 348 K and adding to it a stoichiometrically calculated amount of oxalic acid (determined by Eq. (5)). Then, the solution was stirred at 330 rpm for 60 min.

#### • Step 1:

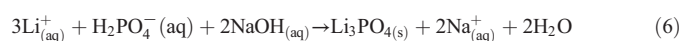
The following reaction has been proposed as the one for the recovery of cobalt with oxalic acid:



In the second step, an aliquot obtained from the above filtrate was used (step 1), this was previously pre-concentrated by evaporation at 348 K. Then, NaOH was added until reaching pH 13 with stirring at 330 rpm for 60 min.

#### • Step 2:

The following reaction has been proposed as the one for the recovery of lithium:



In Fig. 10 the results of the characterization of the solids obtained in the recovery steps are presented. In Fig. 10a) and b) XRD and SEM micrographs of the precipitates obtained in step 1 are depicted, whereas in Fig. 10c) and d) the ones of step 2 are shown. In Fig. 10a) it can be seen that the diffraction lines of the precipitated solid correspond to cobaltous oxalate dihydrate (JCPDS 014-0741).

Fig. 10b) shows that cobalt oxalate precipitates in form of agglomerated rods between 5 and 20  $\mu\text{m}$  in length with an acicular crystalline habit and organized in a layered sub-structure. Fig. 10c) shows that the precipitate formed in step 2 is  $\text{Li}_3\text{PO}_4$  (JCPDS 015-0760), which has an olivine structure with a diagonal length between 0.5 and 1  $\mu\text{m}$  (Fig. 10d)).

The percent recovery of the solid obtained in stage 1, of 99%, was calculated using Eq. (5). In the second stage, 88% recovery of Li was obtained, which was calculated with Eq. (6).

The solids obtained in both steps were washed and dried and then characterized by EDS and SEM. The results of these studies are shown in Table 2, from which it can be observed that both solids,  $\text{Li}_3\text{PO}_4$  and  $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , have high purities of 98.3% and 97.8%, respectively. The Mn detected in the cobalt oxalate is the one that was in the original sample; its presence in the precipitate obtained in step 1 does not significantly interfere in their potential uses. These solids are of industrial interest:  $\text{Li}_3\text{PO}_4$  is used for the synthesis of dental materials, catalysts and  $\text{LiFePO}_4$  cathode batteries, among others uses. As regards  $\text{CoC}_2\text{O}_4$ , it is used, for example, in the synthesis of cobalt powder, catalysts, cobalt oxide and  $\text{LiCoO}_2$  (Habashi, 1997).

**Table 2**

EPMA results of analysis of the solids precipitate shown in Fig. 10b) and d), in atom %.

Compounds	Purity	%Na	%K	%Co	%O	%C	%Mn	%P
$\text{CoC}_2\text{O}_4$	97.8	–	–	37.8	33.9	26.1	2.2	–
$\text{Li}_3\text{PO}_4$	98.3	0.9	–	0.8	64.8	–	–	33.5

Finally, based on the results obtained, it can be said that this process could be carried out in pilot-scale to evaluate its economic viability.

## 4. Conclusions

Experimental results show that the process using phosphoric acid as the leaching agent and hydrogen peroxide as the reducing one, achieves efficient dissolution of  $\text{LiCoO}_2$ , of about 99%.

The optimum conditions for the dissolution process were: temperature, 363 K;  $\text{H}_3\text{PO}_4$  concentration, 2% v/v;  $\text{H}_2\text{O}_2$  concentration, 2% v/v; reaction time, 60 min; stirring speed, 330 rpm and solid-liquid ratio, 8 g/L. Lithium recovered as  $\text{Li}_3\text{PO}_4$  was 88%, the solid showed a purity of 98.3%. Moreover, 99% of cobalt as  $\text{CoC}_2\text{O}_4$ , with a purity of 97.8%, was recovered.

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