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# ACID LEACHING OF LiCoO$_2$ FROM LIBs: THERMODYNAMIC STUDY AND REDUCING AGENT EFFECT

# LIXIVIACIÓN ÁCIDA DE LiCoO$_2$ PROVENIENTE DE LIBs: ESTUDIO TERMODINÁMICO Y DEL EFECTO DE UN AGENTE REDUCTOR

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## Abstract

This work shows the results of a comparative hydrometallurgical study of LiCoO$_2$ leaching, obtained from the cathodes of spent lithium-ion batteries (LIBs), with HF and HF/H$_2$O$_2$. The operational parameters researched were H$_2$O$_2$ and HF concentrations, solid-liquid ratio, stirring speed, temperature and reaction time. The experimental results indicated that the best working conditions, with dissolution values close to 100%, were 348 K, 330 rpm, 30 min, 8 g/L, HF 0.6 M and H$_2$O$_2$ 0.7 M. Thermodynamic study of the dissociation of HF in aqueous solution and E$_H$-pH diagrams for Li-H$_2$O, Co-H$_2$O and Li-Co-F-H$_2$O systems were performed. The results showed the feasibility of extracting and recovering metals contained in the sample.

*Keywords*: LiCoO$_2$, LIBs, reducing agent, thermodynamic.

## Resumen

En este trabajo se presentan los resultados del estudio comparativo de la lixiviación de LiCoO$_2$, obtenido desde los cátodos de baterías ion-litio (LIBs), con HF y HF/H$_2$O$_2$. Los parámetros operacionales investigados fueron: concentración de H$_2$O$_2$ y HF, relación sólido-líquido, velocidad de agitación, temperatura y tiempo de reacción. Los resultados experimentales mostraron que las mejores condiciones de trabajo, con disoluciones cercanas al 100%, fueron 348 K, 330 rpm, 30 min, 8 g/L, HF 0.6 M y H$_2$O$_2$ 0.7 M. Además, se llevó a cabo el estudio termodinámico de las reacciones de disociación del HF en solución acuosa y la construcción de los diagramas E$_H$-pH para los sistemas Li-H$_2$O, Co-H$_2$O y Li-Co-F-H$_2$O. Los resultados obtenidos indicaron que es factible extraer y recuperar los metales contenidos en la muestra.

*Palabras clave*: LiCoO$_2$, LIBs, agente reductor, termodinámica.

# 1 Introduction

Li-ion batteries are one of the main energy storage devices, currently used in a variety of portable electronic equipment and electric vehicles. Their applications rest on characteristics such as high specific energy and energy density, low self-discharge, long life cycle, high capacity and the possibility to be miniaturized (Zhang *et al*., 2015). Usually, spent lithium-ion batteries (LIBs) contain valuable metals, organic chemicals, plastics, etc., with variations according to the models and the brands. The most valuable part of LIBs is the cathode which contains metallic oxides of the "LiMO$_2$" kind (where M: Co, Mn, Ni or mixtures thereof) adhered to an aluminum sheet (Zheng *et al*., 2018). Eventually, when LIBs surpass their lifespan (of around 1000 charging-discharging cycles) they are discarded, which, considering that they contain heavy metals and possibly toxic organic compounds, brings about a potential threat to the environment and to human health.

Nowadays, there are several researches destined to the study of the previous treatment, extraction and recovery of the components of the lithium-ion batteries, once they are spent or in disuse. The preparation and pretreatment stages of the LIBs studied so far, involve an initial discharge in a NaCl aqueous solution and a subsequent opening and dismantling to separate their parts.

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Later, cathodes are selected to obtain $LiCoO_2$, which is taken off from the aluminum sheets with N-methylpyrrolidone (NMP) (Zheng *et al*., 2018) or dissolving the aluminum with alkalis (Nayl *et al*., 2017). Once the $LiCoO_2$ is isolated, it is washed at 333 K for 24 hours. Then, it is calcined at 973 K for 5 hours and it is finally ground for 2 hours. All treatments aim to increase the reactivity of solids and thereby to facilitate dissolution of the sample in different leaching media (Ordonez *et al*., 2016, Li *et al*., 2014).

Several methods have been proposed to treat LIBs in order to recover their valuable metals. One well-known way for the extraction and recovery of those metals is the hydrometallurgy employing inorganic acids, because of the high dissolutions values that are obtained. Among the inorganic acids studied in different reducing media ($H_2O_2$, $NaHSO_3$, $Na_2S_2O_3$ and $C_6H_{12}O_6$) there could be mentioned $HNO_3$ (Lee and Rhee, 2003); $H_3PO_4$ (Pinna *et al*., 2017, Chen *et al*., 2017) and $H_2SO_4$ (Nayl *et al*., 2017, Meshram *et al*., 2015, Meshram *et al*., 2016 a,b, Jha *et al*., 2013). Lee and Rhee (2002) reported extraction values over 93% for cobalt and lithium, when working with $HNO_3$-$H_2O_2$, whereas Jha *et al*., (2013) used $H_2SO_4$ and obtained leaching values of around 99% for lithium and 70% for cobalt. Pinna *et al*. (2017) obtained dissolutions of the mixed lithium cobalt oxide of nearly 100% working with $H_3PO_4/H_2O_2$.

The objectives of this work are: to calculate the thermodynamic parameters for the dissolution reactions of $LiCoO_2$ with HF and HF-$H_2O_2$ and to construct the Pourbaix diagram for the Li-Co-F-$H_2O$ system, applying these results to the study of the effect of a reducing agent on the operating parameters of the leaching process of the sample in these media, in order to optimize them to achieve a high dissolution of $LiCoO_2$, minimizing the use of chemical agents and reaction time.

# 2 Materials and methods

## 2.1 Materials

The sample was obtained from LIBs of mobile phones of different brands and models. All reagents used, hydrofluoric acid and hydrogen peroxide, were analytical grade.

## 2.2 Analysis techniques

The reactants and products were characterized by X-ray diffraction (XRD) carried out in a diffractometer Rigaku D-Max III C. Morphological analyses were 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 semi-quantitative 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. The particle size was determined with an Analysette A-20 Fritsch scanning photosedimentograph.

## 2.3 Thermodynamic evaluation and construction of $E_H$-pH diagrams

The thermodynamic study was carried out to determine the stability areas of the systems: Co-$H_2O$, Li-$H_2O$ and Li-Co-F-$H_2O$. Thermodynamic calculations were performed using the software HSC Chemistry 5.0 for windows.

## 2.4 Procedure of dissolution assays

The dissolution tests were performed in a closed batch reactor of 800 mL built in Teflon® equipped with magnetic stirring and temperature control systems. For each test, calculated amounts of sample and distilled water were introduced into the reactor. Then, the mixture was heated until the work temperature was reached. Subsequently, calculated volumes of HF or HF/$H_2O_2$ 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.

## 2.5 Preparation and characterization of the sample

The sample was prepared using 500 LIBs of mobile phones of 9 different brands, which were discharged by keeping them in a NaCl solution for 48 hours, and subsequently dismantled. Then, their components were separated and weighed. Those results are shown in Fig. 1. The mass of the 500 employed batteries was 10.23 kg, 3.8 kg corresponding to cathode from which 0.45 kg of aluminum and 3.35 kg of $LiCoO_2$ were obtained.
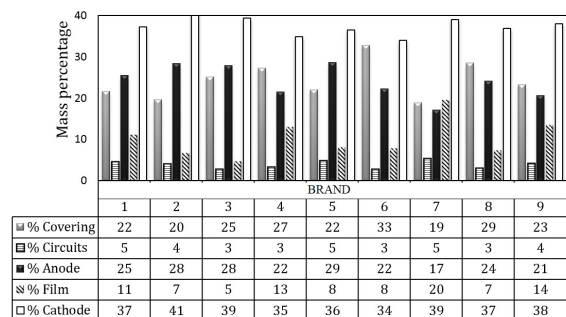
Fig. 1. Mass percentage of the components of LIBs.

The results presented in Fig. 1 show the percentages of each of the components obtained from the different brands of LIBs collected, being the mass percentage of the cathode between 34 and 41% in different brands. $LiCoO_2$ was obtained from such cathodes through manual scraping and it was calcined for 3 hours at 673 K to eliminate the present solvents. In addition, these batteries possess other recyclable components (stored for future studies), e.g. in the anodes, from which it can be recovered copper and graphite, whose mass percentage oscillates between 17 and 29%, according to the brand of the LIBs and the metallic cases or coverings (Al or steel for different brands) which represents between 19 and 33% of the mass.

Figs. 2 a)-b) present the results of the characterization of the sample by XRD and SEM-EPMA, respectively. The diffractogram shows the presence of a crystalline structure whose pattern coincides with the one of lithium cobalt oxide (ICDD 01-077-1370). In the SEM micrograph, Fig. 2 b), it can be observed the particles morphology, exhibiting irregular sizes and shapes, with rounded edges.
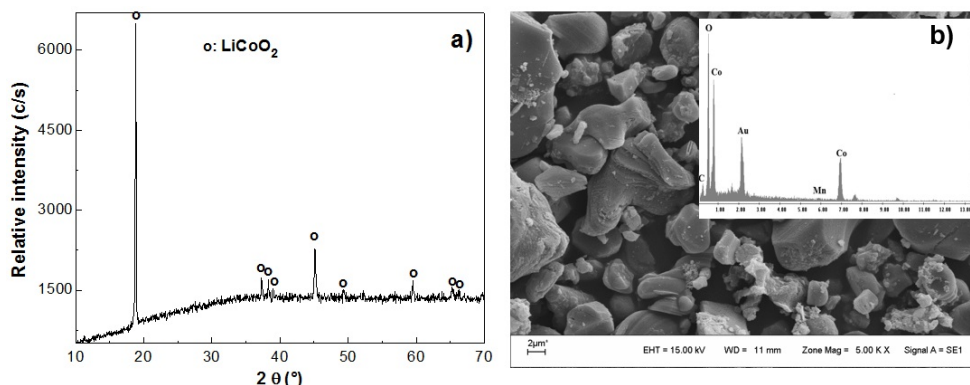
Table 1. The quantitative composition of the sample.

| Element | Li | Co | Mn | Ni |
|---------|-----|------|-----|-----|
| % w/w | 7.1 | 54.9 | 3.6 | 1.7 |

Moreover, an analysis of particle size distribution showed that the sample had the highest frequency in the 10 $\mu$m particle. Quantitative composition of the sample ($LiCoO_2$) determined by AAS is shown in Table 1.

# 3 Results and discussion

## 3.1 Thermodynamical study

The hydrofluoric acid shows an ionization equilibrium given by Eq. (1):

$$H_2O + HF_{(aq)} \longleftrightarrow H_3O^+_{(aq)} + F^-_{(aq)} \qquad (1)$$
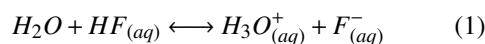
The dissociation and association degrees are represented by the following expressions:

$$\alpha_{F^-} = K_a/([H^+] + K_a) \qquad (2)$$

$$\alpha_{HF} = ([H^+]/([H^+] + K_a) \qquad (3)$$

where: $\alpha_{F^-}$ and $\alpha_{HF}$ are the dissociation or association degrees of $F^-_{(aq)}$ and $HF_{(aq)}$ species, respectively; $K_a$ is the dissociation constant for hydrofluoric acid and [$H^+$] is protons concentration.



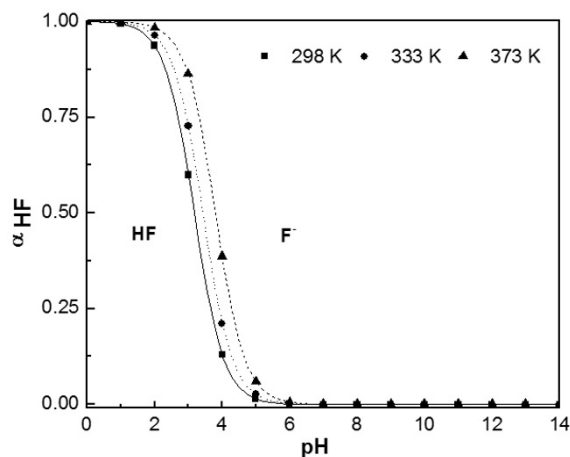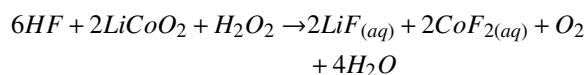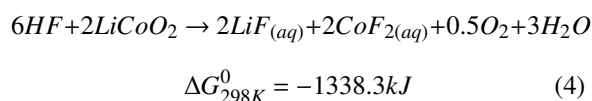Fig. 2. a) XRD and b) SEM-EPMA analysis of the sample (Au coating).

Fig. 3. Diagram of HF species distribution at different temperatures.

Fig. 3 presents the effect of temperature on the dissociation degree of HF. An increase in this variable leads to an increase in acid association, for pH values between 2 and 5. This fact can be explained taking into account that the dissociation reaction of HF is an exothermic one and, as a result, the Gibbs-Helmholtz expression indicates that the higher the temperature the lower the equilibrium constant, which according to Eq. 3, for a fixed concentration of protons, results in an increase in the association degree. Moreover, Le Chatelier principle states that an increase in the yield of the products is only favored by an increase of the equilibrium constant value. Therefore, the dissociation reaction of HF is not favored by an increase of temperature. Nevertheless, and as will be explained in Section 3.2.4, this temperature raise favors the dissolution of the solid because HF is the attacking species.

### 3.1.1 Reactions

The dissolution reactions of the sample were proposed from the results obtained in the $E_H$-pH diagram and what is reported in the bibliography (Suarez *et al.*, 2017). The reactions are shown in Eqs. (4)-(5) with their respective $\Delta G^0_{298K}$ values.

$$6HF + 2LiCoO_2 \rightarrow 2LiF_{(aq)} + 2CoF_{2(aq)} + 0.5O_2 + 3H_2O$$

$$\Delta G^0_{298K} = -1338.3kJ \tag{4}$$

$$6HF + 2LiCoO_2 + H_2O_2 \rightarrow 2LiF_{(aq)} + 2CoF_{2(aq)} + O_2 + 4H_2O$$

$$\Delta G^0_{298K} = -1455.3kJ \tag{5}$$

Both Gibbs energy values allow us to infer that $LiCoO_2$ dissolution reactions, using HF and HF-$H_2O_2$ are thermodynamically favored, Eqs. (4) and (5). Furthermore, this effect is remarkably noticeable when $H_2O_2$ is added to the leaching medium as a reducing agent. Similar $\Delta G^0$ values to the ones obtained in this work were reported by Meshram *et al.* (2016 a, b), for the reaction of $LiCoO_2$ with $H_2SO_4$-$H_2O_2$ at 368 K. From its $\Delta G^0$ value ($\Delta G^0 = -651.2$ kJ) they were able to conclude that this reaction was thermodynamically feasible. Takacova *et al.* (2016) also performed thermodynamic calculations for $LiCoO_2$ reactions with HCl and $H_2SO_4$, concluding that the dissolution reaction was thermodynamically feasible.

It is worth noting that in the proposed equations $F_{2(g)}$ formation is not produced, which is in accordance with the fact that in the performed tests, the release of this gas was not evident.

### 3.1.2 $E_H$-pH diagram

Fig. 4 a) shows $E_H$-pH diagram for the Co-$H_2O$ system, (concentration 1 molal, temperature of 298-373 K) the species present are: $Co_{(s)}$, $Co(OH)_{2(s)}$, $Co(OH)_{3(s)}$, $Co_3O_{4(s)}$ and $Co^{2+}_{(aq)}$. In zone 1, the metallic Co is thermodynamically stable, that is, it does not suffer corrosion. In zone 2, it is dissolved in its stable phase $Co^{2+}_{(aq)}$ up to pH 6. When the temperature increases, a decrease occurs in the area of predominance of the species up to pH 5. At alkaline pH, zone 3, cobalt is found as hydroxide $Co(OH)_2$ in the solid state and the system acquires very low potentials; at this potential the species $Co(OH)_2$ can be oxidized even by environmental oxygen. The oxidation products can be $Co(OH)_3$, black or dark brown, or oxides of the same color, more or less hydrated $Co_2O_3$ or $Co_3O_4$ (mixture of Co(II) and Co(III)).

Fig. 4 b) presents the $E_H$-pH diagram for the Li-$H_2O$ system for a temperature range of 298-373 K and 1 molal lithium solution. Changes are not observed in the present species nor in the regions of predominance of these in the analyzed conditions. Since the charge/radius ratio (q/r) for $Li^+$ is small, water hydration molecules are weakly bound to this and there is practically no interaction between them. Thus, lithium is in the cationic $Li^+$ form over a wide pH range.
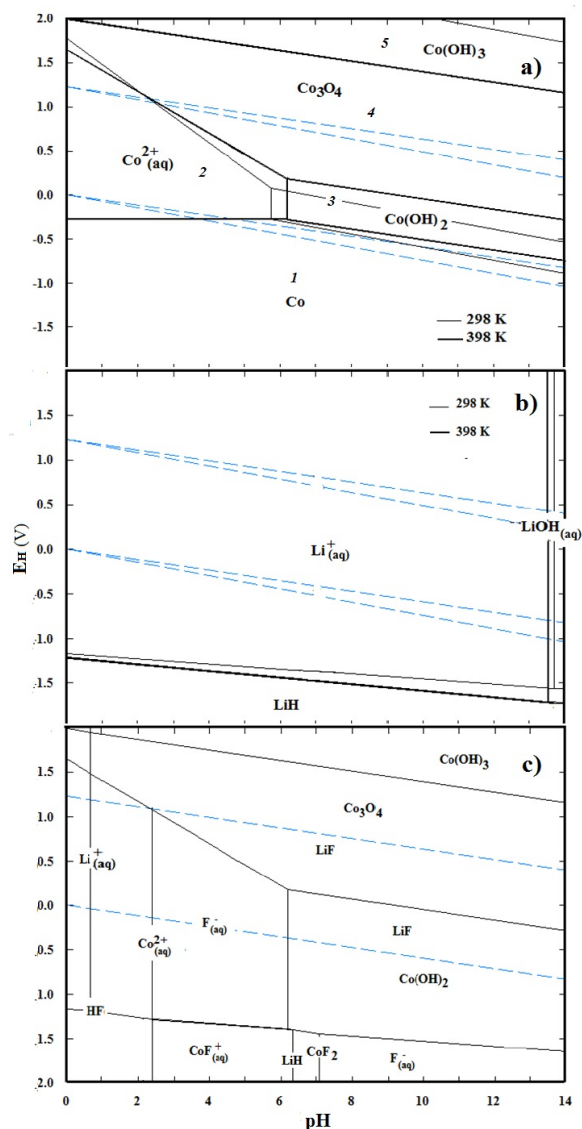
Fig. 4. $E_H$-pH diagram of the systems: a) Co-H$_2$O, b) Li-H$_2$O and c) Li-Co-F-H$_2$O.

Fig. 4 c) exhibits the $E_H$-pH diagram for the Li-Co-F-H$_2$O system, where it can be appreciated the stability of ions in aqueous medium. It can be observed that the dissolution of cobalt and lithium is theoretically possible when working with HF at pH below 6. When working at low pH values, we find lithium and cobalt solubilized as Li$^+$ and CoF$^+$, respectively. An increase in pH above 6 produces Co precipitation as Co(OH)$_2$, while lithium precipitates as LiF. Diagrams at different temperatures, between 298 and 373 K, show a slight displacement of the area of predominance of the different species of 0.15 unit to the right on the pH axis, approximately.

## 3.2 Comparative dissolution assays

The study of the effect of different operational variables on the dissolution of the sample was performed in the following ranges: solid-liquid ratio (5-66 g/L), stirring speed (0-460 rpm), HF concentration (0.6-9 M), temperature (298-363 K) and reaction time (0-180 minutes). Previously, a study to determinate the effect of concentration of hydrogen peroxide (as reducing agent) in range of concentrations comprised between 0-3 M was analyzed. The conversion of the solid was followed using the Eq. (6), (Habashi, 1980, Pinna *et al.*, 2017):

$$X(\%) = ((m^0 - m^r)/m0)100 \qquad (6)$$

where: $X$ is the dissolution of the solid; $m^0$ is the initial mass of the solid reactant and $m^r$ is the mass which remains unreacted after the reaction. This equation is valid according to Habashi (1980) when the reaction of dissolution does not yield solid products. This condition is fulfilled in our reaction system since unreacted sample was the only compound found in the residual samples of each leaching experiment, as confirmed by XRD.

### 3.2.1 Effect of reducing agent concentration

The effect of the reducing agent concentration was evaluated in the following conditions: reaction time, 60 minutes; stirring speed, 330 rpm; HF concentration 1.1 M, 348 K and solid-liquid ratio of 8 and 13 g/L. Fig. 5 a) shows that increasing the concentration of the reducing agent increases the dissolution of the sample and for concentrations equal or higher than 0.7 M it is observed that the maximum dissolution is reached for both solid-liquid ratio. According to Meshram *et al.* (2015) the leaching efficiency of cobalt depends on the concentration of the used reductant. Reductant converts Co$^{3+}$ to Co$^{2+}$ state for effective dissolution and subsequent recovery by different methods (Lv *et al.*, 2018, He *et al.*, 2017). It is evident from the $E_H$-pH diagram for the Co-H$_2$O system, Fig 4 a), that Co(II) remains stable in solution in the pH range 1-6.

### 3.2.2 Effect of solid-liquid ratio

The study of the effect of solid-liquid ratio was performed in the following conditions: concentration of reducing agent 0.7 M; HF concentration, 1.1 M; reaction time, 60 minutes; stirring speed, 330 rpm and temperature, 348 K. The tests were carried out in a range from 5 to 66 g/L. The results are shown in Fig. 5 b).
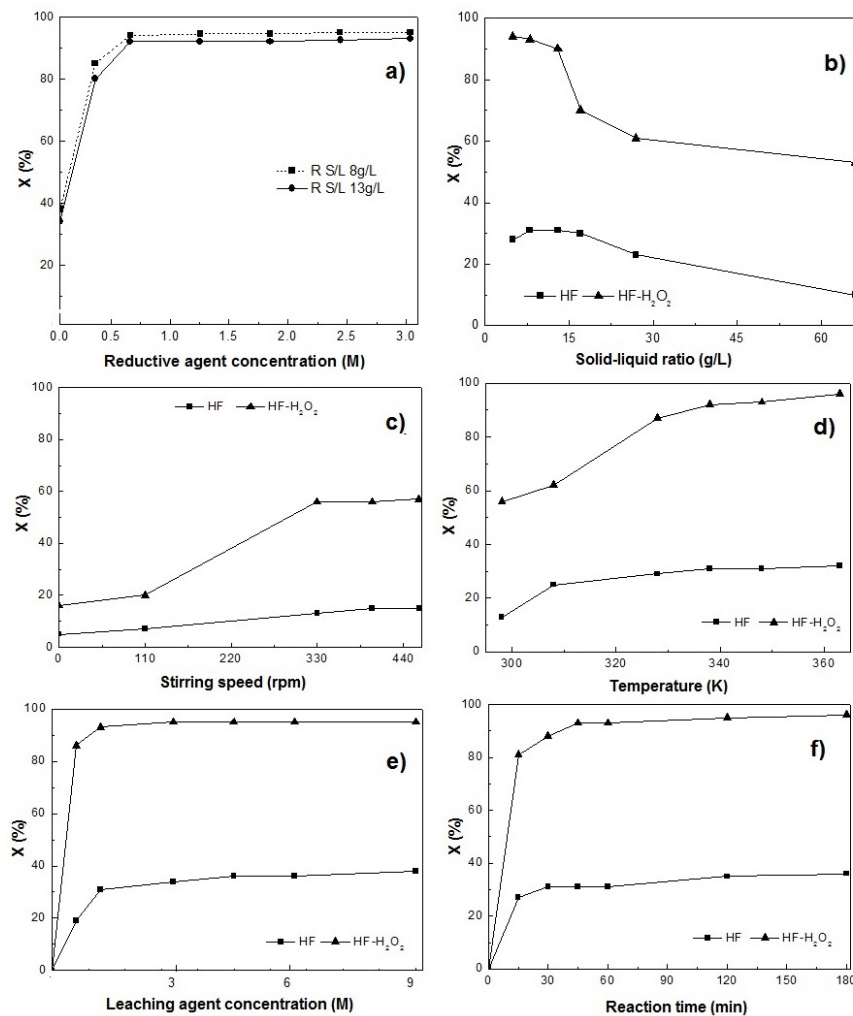
Fig. 5. Effect of the: a) reducing agent concentration, b) solid-liquid ratio, c) stirring speed, d), temperature e) HF concentration and f) reaction time.

The results plotted in Fig. 5 b) 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.

### 3.2.3 *Effect of stirring speed*

The effect of stirring speed was studied under the following working conditions: temperature, 298 K; reaction time, 60 minutes; HF concentration, 1.1 M and solid-liquid ratio of 8 g/L. Also, the reducing agent used was $H_2O_2$, 0.7 M. The results presented in Fig. 5 c) indicate that, for both systems, the increase in stirring speed produces an increase in the dissolution

of the lithium cobalt oxide up to 330 rpm, above which, the conversion of the solid remains constant for both systems.

Remarkably, for the HF-$H_2O_2$ system, an increase between 110 and 330 rpm leads to an increase in $LiCoO_2$ dissolution, which can be explained since an increase in the stirring speed causes an increase in the diffusion rate of the peroxide and the acid, due to the diminution of the thickness of the limit layer. The reactants that reach the surface of the solid cause the reduction of Co(III) to Co(II), followed by the breakage of the Co-O bond. This instability in the net allows HF to react at a higher speed, leading to an increase in the dissolution of the solid. From these results, and for the study of further variables, 330 rpm was selected as the optimum stirring speed.

### 3.2.4   Effect of temperature reaction

The study of the effect of temperature was carried out under the following conditions: reaction time, 60 minutes; stirring speed, 330 rpm; HF concentration, 1.1 M; solid-liquid ratio of 8 g/L. When hydrogen peroxide was employed, its concentration was 0.7 M. The obtained results are shown in Fig. 5 d). It can be seen that when HF was used, there was not a significant rise in the dissolution of the solid with the increase of temperature. Meanwhile, when HF-$H_2O_2$ was used, temperature had a bigger influence on the dissolution of the solid, close to 100%, when working at 348 K. Above this temperature, according to literature, the leaching efficiency stagnates or decreases slightly. This is, according to He *et al.* (2017), becouse $H_2O_2$ is unstable when heated and increasing the temperature over 343 K would accelerate its decomposition.

### 3.2.5   Effect of leaching agent concentration

Fig. 5 e) shows the results of the study of the effect of HF concentration on $LiCoO_2$ dissolution at 348 K, 330 rpm, reaction time 60 minutes and solid-liquid ratio of 8 g/L. When hydrogen peroxide was employed, its concentration was 0.7 M. The exposed results enable us to state that a marked increase in the dissolution occurs in both media. Nevertheless, when hydrogen peroxide was employed, the dissolutions of the solid were almost complete, whereas without the reducing agent, the maximum dissolution reached was close to 40%. This difference in the dissolution of the solid when using a reducing agent can be explained, according to Pinna *et al.* (2017), by the fact that the generation of oxygen from the decomposition of $H_2O_2$ reduces Co(III) of $LiCoO_2$ to Co(II); this change in the oxidation state is accompanied by a diminution of its ionic radius that leads to the destabilization of the crystal lattice and favors the dissolution of the oxide in the presence of a weak acid such as HF. Additionally, considering that Co and Li are the main components of $LiCoO_2$, the dissolution of one of them promotes the same for the other. In consideration of these results, the optimum HF concentration was selected to be 0.6 M, which was used for the rest of the assays.

It is also worth mentioning that the results in Fig. 5 e) highlight a significant benefit in comparison to the use of other leaching agents, since high dissolution values are achieved while working with low HF concentrations in reducing media, whereas for conventionally studied agents, $H_2SO_4$ and $HNO_3$ in reducing media, the best results are obtained using concentrations of 4 and 2 M, respectively. Also, the use of HCl gives off chlorine gas, differently from the system studied in this work, which advantageously releases $O_2$ (Zheng *et al.*, 2018, Lv *et al.*, 2018). Besides, Suarez *et al.* (2017) used HF as leaching agent for $LiCoO_2$, in absence of a reducing agent and obtained sample dissolutions close to 60% with HF concentrations of 7.5 M and a reaction time of 120 min.

### 3.2.6   Effect of reaction time

Fig. 5 f) shows the results of the assays performed for different times of reaction. For this study, the following parameters were kept constant: temperature, 348 K; stirring speed, 330 rpm; HF concentration, 0.6 M; solid-liquid ratio of 8 g/L. When hydrogen peroxide was employed, its concentration was 0.7 M. Plots in Fig. 5 f) show, for both reaction systems, an important increase in $LiCoO_2$ dissolution when increasing reaction time up to values of 30 minutes, while for higher reaction times oxide leaching is slightly affected. It is worth noting that in the first 15 minutes of reaction, high conversion values are obtained, close to 80%, when a reducing agent is used. This might be attributed to the fact that in that time interval, most of the reduction of Co(III) to Co(II) occurs, thus increasing the dissolution of the solid. Both dissolved metals can be recovered from dissolution by using chemical precipitation as reported by Suarez *et al.* (2017). They recovered cobalt as $Co_3O_4$ and lithium as LiF with recoveries of 98 and 80%, respectively. In addition, they proposed that the fluoride remaining in the effluent is precipitated with the addition of $CaCO_3$.

### 3.2.7   Characterization of dissolution residues

Figs. 6 and 7 present the SEM-EPMA analysis and diffractograms, respectively, of the residues obtained at 348 K; 330 rpm, 60 minutes, solid-liquid ratio of 8 g/L, HF concentration of 0.6 M and $H_2O_2$ concentration of 0.7 M, when this reducing agent was employed.

Figs. 6 a) and b) show particles with different degree of attack depending on the presence or not of the reducing agent, for the same dissolution conditions. In Fig. 6 a) it can be observed particles attacked, but they still preserve their size and shape.
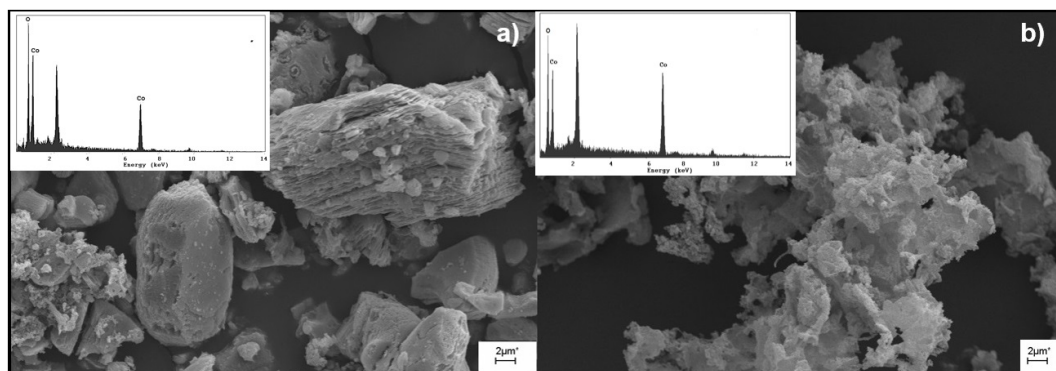
Fig. 6. SEM-EPMA analysis of leach residue with: a) HF and b) HF-$H_2O_2$ (Au coating).
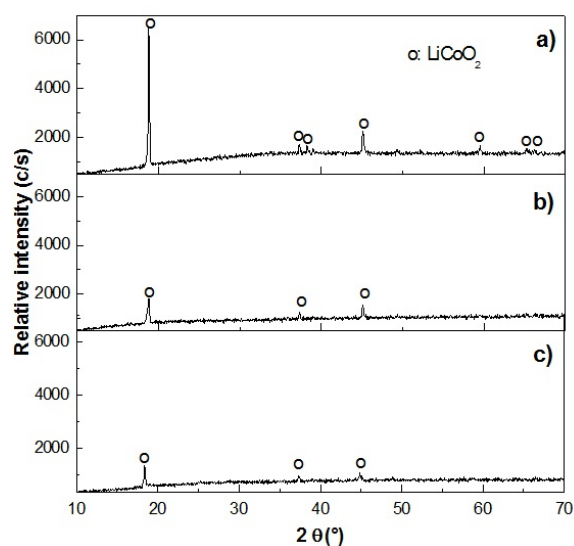
## Conclusions

This work presents the results of a comparative study of the leaching of $LiCoO_2$ with HF and HF/$H_2O_2$. The dissolution reaction of $LiCoO_2$ using HF is thermodynamically favored, and it is benefited by the use of a reducing agent like $H_2O_2$. The best conditions for the leaching of the sample, with a conversion near 100%, were: temperature of 348 K, stirring speed of 330 rpm, 30 minutes of reaction time, solid-liquid ratio 8 g/L with HF 0.6 M and $H_2O_2$ 0.7 M. In addition, the use of the reducing agent has a double effect. On the one hand, it increases the dissolution of $LiCoO_2$, with extraction values greater than 90%, due to the change of the oxidation state of cobalt, destabilizing the structure of the mixed oxide, favoring its breakage and increasing the dissolution, even at low concentrations and with a weak acid such as HF. On other hand, compared to other investigations, the reaction time and HF concentration are considerably reduced, from 120 to 30 min and 7.5 to 0.6 M, respectively, obtaining similar or higher dissolutions.



Fig. 7. XRD of a) sample without leach and leach residue with: b) HF and c) HF-$H_2O_2$.

Conversely, micrograph in Fig. 6 b) allows us to recognize particles with a high degree of attack and totally disintegrated.

Fig. 7 presents XRD corresponding to: a) sample without leaching, b) solid residue from leaching with HF and c) solid residue from leaching with HF-$H_2O_2$. When comparing the three diffractograms, there is no formation of new crystalline solids evidenced in the diffraction lines, while those corresponding to unreacted $LiCoO_2$ (ICDD 01-077-1370), coincide with those of the sample without leaching.

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