

## Article

# Comparative Study of the Dissolution of LCO in HCl Medium with and without H<sub>2</sub>O<sub>2</sub>

D. Sebastián Drajlín <sup>1</sup>, Daniela S. Suarez <sup>1</sup>, Norman Toro <sup>2</sup>, Edelmira D. Gálvez <sup>3</sup>, Eliana G. Pinna <sup>1,4</sup> and Mario H. Rodríguez <sup>1,\*</sup>

<sup>1</sup> Laboratorio de Metalurgia Extractiva y Síntesis de Materiales (MESiMat), Instituto Interdisciplinario de Ciencias Básicas (ICB)-UNCuyo-CONICET-FCEN, Padre J. Contreras 1300, Parque General San Martín, Mendoza CP M5502JMA, Argentina; dsdrajlin@gmail.com (D.S.D.); dsuarez@fcen.uncu.edu.ar (D.S.S.); epinna@fca.uncu.edu.ar (E.G.P.)

<sup>2</sup> Faculty of Engineering and Architecture, Universidad Arturo Prat, Iquique 1100000, Chile; notoro@unap.cl

<sup>3</sup> Departamento de Ingeniería Metalúrgica y Minas, Universidad Católica del Norte, Antofagasta 1270709, Chile; egalvez@ucn.cl

<sup>4</sup> Facultad de Ciencias Agrarias, Universidad Nacional de Cuyo, Almirante Brown 500, Mendoza CP M5528AHB, Argentina

\* Correspondence: mrodriguez@uncu.edu.ar

**Abstract:** The dissolution of LiCoO<sub>2</sub> (LCO) from spent lithium-ion batteries (LIBs) has been widely studied with organic and inorganic acids. Among these acids, HCl is the one that showed the best results when used at concentrations higher than 4 M. However, its higher cost compared with other acids is disadvantageous. Taking this into account, this work aims to perform a comparative study of the effect of different operational variables such as temperature, reaction time, leaching agent concentration (HCl) and reducing agent concentration (H<sub>2</sub>O<sub>2</sub>) on the dissolution efficiency of LCO for the systems HCl and HCl-H<sub>2</sub>O<sub>2</sub> to determine the optimal parameters to achieve a maximum dissolution in minimum time at low temperatures and reagent concentrations. Increasing temperature, time and concentration of the reagents had a positive effect on the dissolution of LCO. When working with HCl 1.8 M, the highest dissolution for LCO, 91.0% was obtained at 348 K for 60 min. Furthermore, a slightly higher oxide dissolution (93.0%) was obtained in a reducing medium at the same temperature in half the time and with a concentration of HCl more than ten times lower. This will allow us to propose an alternative process to the existing ones with economic and ecological advantages.

**Keywords:** LCO; LiCoO<sub>2</sub>; HCl; LIBs; reducing agent



**Citation:** Drajlín, D.S.; Suarez, D.S.; Toro, N.; Gálvez, E.D.; Pinna, E.G.; Rodríguez, M.H. Comparative Study of the Dissolution of LCO in HCl Medium with and without H<sub>2</sub>O<sub>2</sub>. *Metals* **2022**, *12*, 727. <https://doi.org/10.3390/met12050727>

Academic Editor: Jean François Blais

Received: 27 March 2022

Accepted: 20 April 2022

Published: 24 April 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

In the last years, the rapid growth of the portable device industry, as well as the development of electrical vehicles, has boosted the demand for lithium for lithium-ion batteries (LIB). These are widely used due to their various advantages such as high energy density, high cell voltage, low storage life, low self-discharge rate and wide temperature range of use. However, their short lifespan and frequent replacement due to the emergence of new technologies have led to the generation of enormous amounts of waste; therefore, spent lithium-ion batteries (LIBs) constitute at the same time a risk to the environment and an opportunity for recycling and recovery of valuable metals [1–3].

Inappropriate disposal of LIBs, such as discard in landfills or incineration, may result in the release of heavy metals which accumulate in the environment, polluting soil, air and water streams. Considering the toxicity of the different components and the large volume of waste generated by the high demand and the short lifespan of these batteries, the final disposition of these residues becomes a matter of the utmost importance [4].

Battery recycling is encouraged not only for environmental reasons but also out of concern for the scarcity of raw materials. WEEE (waste of electrical and electronic

equipment) constitutes about 8% of municipal waste and is considered to be one of the fastest-growing waste fractions worldwide [5], posing health risks associated with its hazardous components.

Recycling rates for lithium are less than 1% but are expected to rise significantly to mitigate a part of its future demand [6]. Given that there is no foreseeable substitute for most applications, it is essential to develop methods to recover the lithium present in batteries to ensure long-term supply.

The recovery of valuable metals is typically classified in pyrometallurgical and hydrometallurgical processes. Pyrometallurgy is widely employed in the industry due to its high efficiency. For example, it does not require pretreatment of LIBs since they are directly loaded into the furnace. However, it has significant disadvantages such as loss of materials, release of hazardous gases and high energy consumption.

Alternatively, hydrometallurgy might be used to recover metals from LIBs. These treatments are flexible, environmentally friendly, consume less energy and have acceptable rates of reaction. However, these technologies require pretreatments (crushing) in order to adjust the size of the LIBs and separation steps to isolate all the particular components. Afterward, metals can be recovered by leaching, precipitation, solvent extraction and ion exchange resins.

Different reagents were researched for the acid leaching of  $\text{LiCoO}_2$  (LCO) such as  $\text{H}_2\text{SO}_3$ ,  $\text{NH}_2\text{OH}\cdot\text{HCl}$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HF}$  [7–9]. The best results were obtained when working with  $\text{HCl}$ , probably due to the ability of chloride ions to destabilize the formation of a surface layer [10]. We have found that working with  $\text{HCl}$  at concentrations higher than 4 M results in oxide dissolutions of 92%. Reported leaching efficiencies when working at such concentration are as high as 99% both for Li and Co [9]. Nevertheless, this represents a large consumption of hydrochloric acid, which is more expensive than other acids.

To improve acid leaching performance, many researchers have investigated the process of  $\text{LiCoO}_2$  reductive dissolution with numerous inorganic acids and  $\text{H}_2\text{O}_2$  as the reducing agent. The tested acids were  $\text{H}_2\text{SO}_4$  [11–14],  $\text{HNO}_3$  [15,16],  $\text{H}_3\text{PO}_4$  [17,18] and  $\text{HF}$  [19]. The use of a reducing agent resulted in an increase in the dissolution of  $\text{LiCoO}_2$ , probably due to the weakening of the Co-O bond through the reduction of cobalt.

In a comprehensive literature review, research on the dissolution of  $\text{LiCoO}_2$  obtained from cathodes of LIBs using hydrochloric acid as a leaching agent and  $\text{H}_2\text{O}_2$  as a reducing one is scarce. Mylarappa et al., claim to study operational parameters that affect the process, but show no results to support the obtained conclusions and rather focus on the characterization of the products [20]. Freitas and García used a mixture of  $\text{HCl}$  3 M- $\text{H}_2\text{O}_2$  30% *v/v* in a previous sample preparation step in order to obtain a suitable solution for the electrochemical recycling of cobalt [21]. Recently, Cerrillo-González et al., studied the dissolution kinetics of LCO with  $\text{HCl}$  enhanced by a reducing agent ( $\text{H}_2\text{O}_2$  in concentrations < 0.6% *v/v*), simulating physicochemical models to propose different controls for said reaction [22].

Among all the leaching agents,  $\text{HCl}$  is the one that shows the best results and, in order to achieve similar dissolutions, the other acids (inorganic or organic) need a reducing agent. In view of the above, the purpose of this work is to improve the reductive dissolution of LCO from LIBs using hydrochloric acid and hydrogen peroxide as leaching and reducing agents, respectively, and to study the effect of the operational variables on the dissolution reaction to obtain the necessary knowledge to propose a process with economic and environmental advantages.

## 2. Experimental Procedures

### 2.1. Materials

The reagents used were hydrochloric acid (Sigma-Aldrich, Argentina, ACS reagent, 37%) and hydrogen peroxide (Biopack, Argentina, ACS, 30% *w/v*), both of them of analytical grade. The samples were obtained from LIBs of mobile phones of different brands and models.

### 2.2. Equipment

The dissolution tests were performed in a closed batch reactor (made in Mendoza Argentina) of 500 mL built in PVC 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 (Rigaku, Osaka, Japan). Morphological analysis was performed by SEM in a microscope LEO 1450 VP (Zeiss, Jena, Germany).

### 2.3. Experimental Procedure

#### 2.3.1. Preparation and Characterization of the Sample

The sample was prepared using LIBs of 500 units of mobile phones of different brands and models that were discharged in a saturated solution of NaCl (for 48 h at room temperature) and subsequently disassembled. The components of the LIBs were then separated, isolating the cathodes that were subsequently calcined at 673 K to remove residual adhesives [23]. Then, the sample at room temperature was homogenized for 30 min and divided into three time intervals of 10 min each using a bar mill at 30 rpm. The remaining parts of the batteries were stored for future studies.

Determination of cobalt and lithium content in the LIBs was performed by X-ray fluorescence spectroscopy (XRF) with a Shimadzu EDX 7000 (Shimadzu, Kyoto, Japan) and atomic absorption spectroscopy (AAS) using a Varian SpectrAA 55 spectrometer (Palo Alto, CA, USA) with a hollow cathode lamp (analytical error 1.5%), respectively. The quantitative composition of the sample was 7.1% Li and 54.9% Co, expressed in mass percentage.

In Figure 1, the results of the characterization of the sample by XRD (Figure 1a) and SEM (Figure 1b) are shown. In the diffractogram, the presence of a crystalline structure of lithium cobalt oxide (JCPDS 01-075-0532) is observed and no other crystalline compounds are found. Figure 1b shows the morphology of the sample particles, which are irregular in size and shape and have rounded edges.

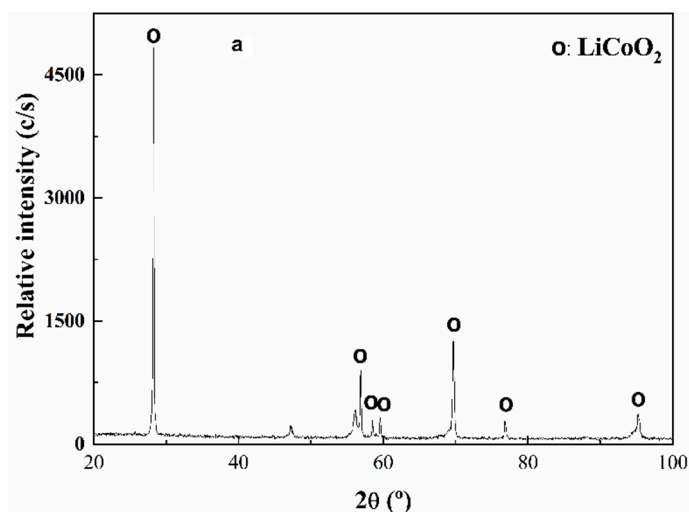
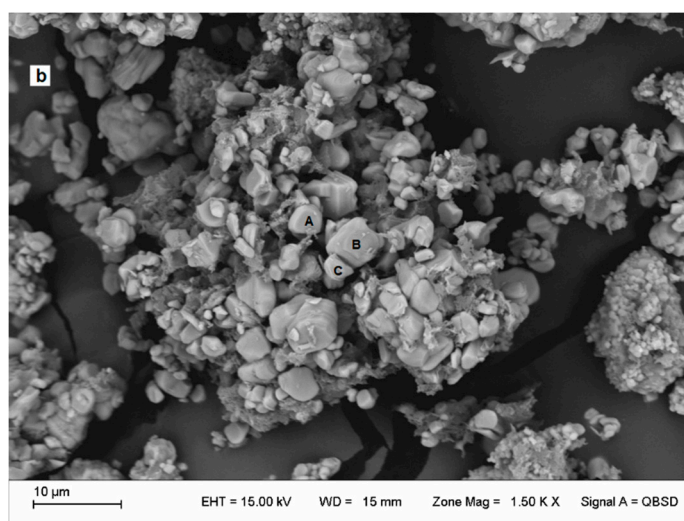


Figure 1. Cont.



**Figure 1.** (a) Diffractogram and (b) SEM micrograph of the sample.

In Table 1 the chemical composition of the particles marked in Figure 1b is presented. The chemical composition obtained for the particles (letters A, B, C) in Table 1 indicates that this particle is composed mainly of cobalt.

**Table 1.** Chemical composition of different particles of the sample in optimal reacting conditions (Figure 1b), in atomic %.

Particle	O (%)	Co (%)	Ni (%)	Mn (%)
A	29.41	70.42	-	0.17
B	14.90	84.47	0.63	-
C	23.87	76.13	-	-

### 2.3.2. Procedure for the Dissolution Tests

To perform each test, calculated amounts of sample and distilled water were placed into the reactor. This mixture was heated with stirring until the working temperature was reached. Then, calculated volumes of HCl and H<sub>2</sub>O<sub>2</sub> were added and, at that moment, reaction time began to be measured. Before characterization by XRD and SEM, the residues from the leaching were washed with distilled water and dried in an oven at 348 K for 2 h. Then, the residue was weighed to carry out the extraction calculations and later some of these residues were separated for their characterization.

The dissolution efficiency was calculated using the expression [8,24]:

$$X\% = [(m^0 - m^f)/m^0] \times 100 \quad (1)$$

where X% is the percent dissolution efficiency, m<sup>0</sup> is the initial mass of the solid reactant and m<sup>f</sup> is the mass that remains unreacted after the reaction.

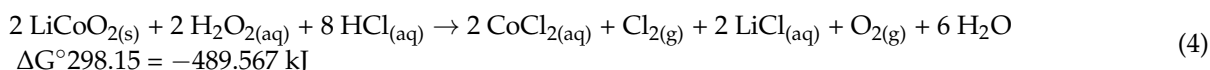
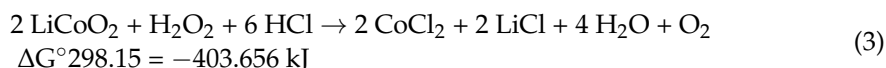
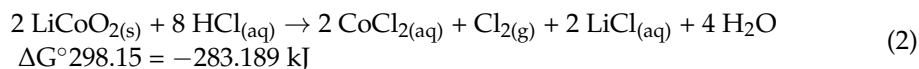
In this research, a univariate analysis of each of the experimental leaching conditions was performed. Studied variables and intervals were as follows: concentration of HCl, 0.12, 0.24, 0.60, 1.20 and 1.80 M; concentration of H<sub>2</sub>O<sub>2</sub>, 2, 5 and 8% v/v; temperature, 298, 323 and 348 K; reaction time, 30, 60 and 120 min. Based on preliminary assays, the stirring speed was kept constant at 330 rpm and the solid–liquid ratio at 5 g/L.

## 3. Results and Discussion

### 3.1. Proposed Reactions

Hydrochloric acid is a monoprotic strong acid, therefore its complete dissociation in an aqueous solution is expected. At the same time, H<sub>2</sub>O<sub>2</sub> is extensively used as a reducing

agent in the recycling of spent LIBs due to its ability to reduce Co(III) to Co(II) [25]. Based on the above, the following reactions are proposed for the leaching of LIBs with HCl (2) or HCl/H<sub>2</sub>O<sub>2</sub> (3) and (4). It is worth noting that (3) and (4) employ the same reactants but the latter uses higher concentrations.

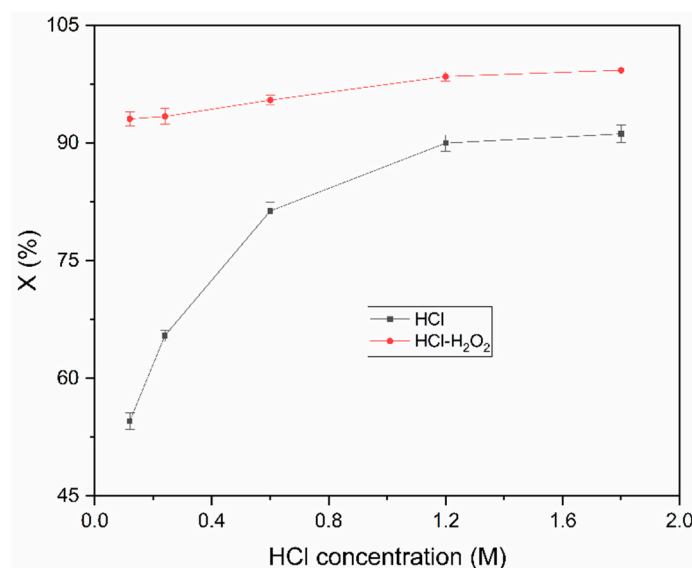


According to these Gibbs energy values, reactions that use H<sub>2</sub>O<sub>2</sub> as a reducing agent would be more thermodynamically favorable than those without it. Furthermore, as we can see in Equations (3) and (4), an increase in the concentration of H<sub>2</sub>O<sub>2</sub> and HCl favors the spontaneity of the leaching reaction.

### 3.2. Dissolution Assays

#### 3.2.1. Effect of Leaching Agent Concentration

The effect of HCl on the reaction dissolution was studied under the following conditions: temperature, 348 K; time, 60 min; stirring speed, 330 rpm; solid–liquid ratio, 5 g/L. HCl concentration ranged between 0.12 and 1.8 M with and without H<sub>2</sub>O<sub>2</sub> 5% *v/v*. The results are shown in Figure 2.

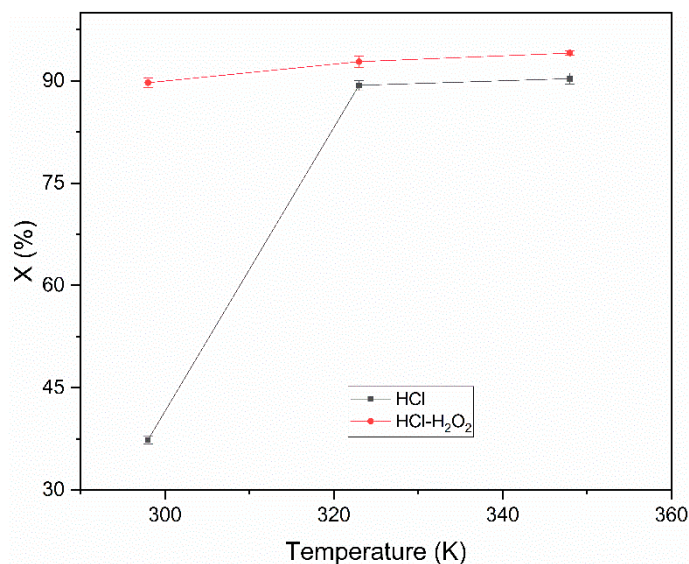


**Figure 2.** Effect of HCl concentration, with and without H<sub>2</sub>O<sub>2</sub>, on the sample dissolution.

Without H<sub>2</sub>O<sub>2</sub>, there is a noticeable increase in the dissolution efficiency as HCl concentration increases with a slight augment between 0.6 M and 1.2 M. However, even for low concentrations of HCl, i.e., 0.12 M and 0.24 M, the dissolutions are over 50%, therefore it is worth trying to improve them with the aid of a reducing agent, maintaining a low expenditure of HCl. Meanwhile, at the same concentrations of HCl, but in the presence of H<sub>2</sub>O<sub>2</sub>, the dissolutions of the sample increase considerably, obtaining dissolutions greater than 90%. At HCl concentrations greater than 1.2 M and in the presence of H<sub>2</sub>O<sub>2</sub> the dissolution of LCO remains almost constant.

### 3.2.2. Effect of Temperature

The effect of temperature on the reaction dissolution was studied under the following conditions: time, 60 min; stirring speed, 330 rpm; solid–liquid ratio, 5 g/L. Two systems were tested: (a) HCl 1.8 M and (b) the mixture HCl 0.24 M-H<sub>2</sub>O<sub>2</sub> 5% *v/v*, in the temperature range 298–348 K. The results are presented in Figure 3.



**Figure 3.** Effect of temperature on the sample dissolution.

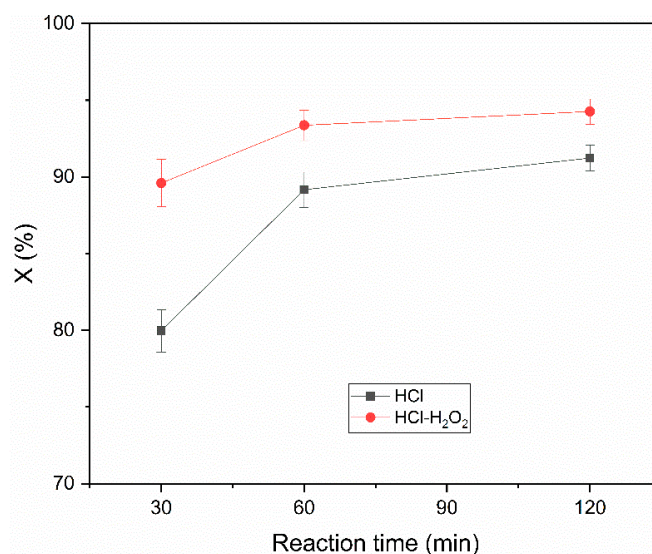
In both systems, an increase in the reaction temperature results in increases in the dissolution of LCO, which agrees with what is expected for a solid–liquid dissolution in which higher temperatures enhance the reactivity of the solids and the solubility of the formed products. Higher dissolutions were achieved for both systems at 348 K, which is why this was selected for further experiments.

### 3.2.3. Effect of Reaction Time

The effect of time on the reaction dissolution was studied under the following conditions: temperature, 348 K; stirring speed, 330 rpm; solid–liquid ratio, 5 g/L. Two systems were tested: (a) HCl 1.8 M and (b) the mixture HCl 0.24 M-H<sub>2</sub>O<sub>2</sub> 5% *v/v*, in the time range 30–120 min. The results are presented in Figure 4.

The results show that time had a clear positive effect on the dissolution efficiency for the HCl system, while it had a slightly positive effect on the HCl-H<sub>2</sub>O<sub>2</sub> system. Since significant dissolutions were obtained even when working for 30 min, and with the aim of optimizing the process, this was selected for further studies of the best operational conditions.

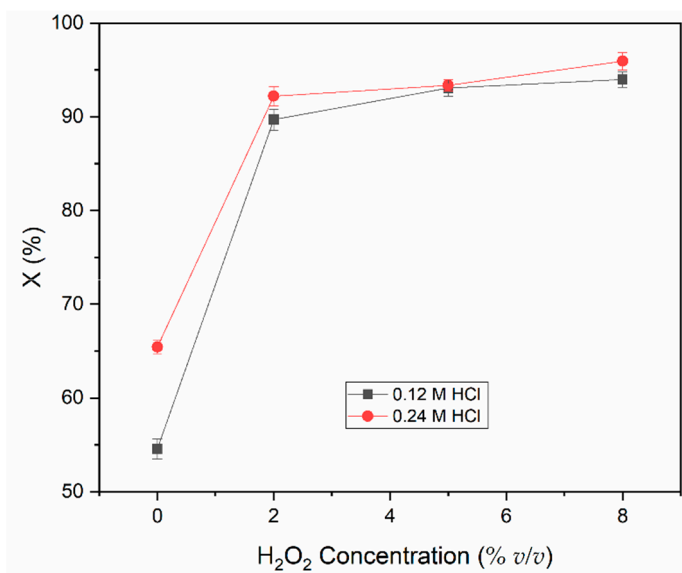




**Figure 4.** Effect of reaction time on the sample dissolution.

### 3.2.4. Effect of Reducing Agent Concentration

The effect of the concentration of the reducing agent on the dissolution of LiCoO<sub>2</sub> was studied under the following conditions: temperature, 348 K; time, 30 min; stirring speed, 330 rpm; solid–liquid ratio, 5 g/L. As mentioned before, lower amounts of HCl were employed: 0.12 and 0.24 M. At the same time, the concentration of H<sub>2</sub>O<sub>2</sub> was set at four levels: 0, 2, 5 and 8% *v/v*. The dissolutions for these combinations are presented in Figure 5.

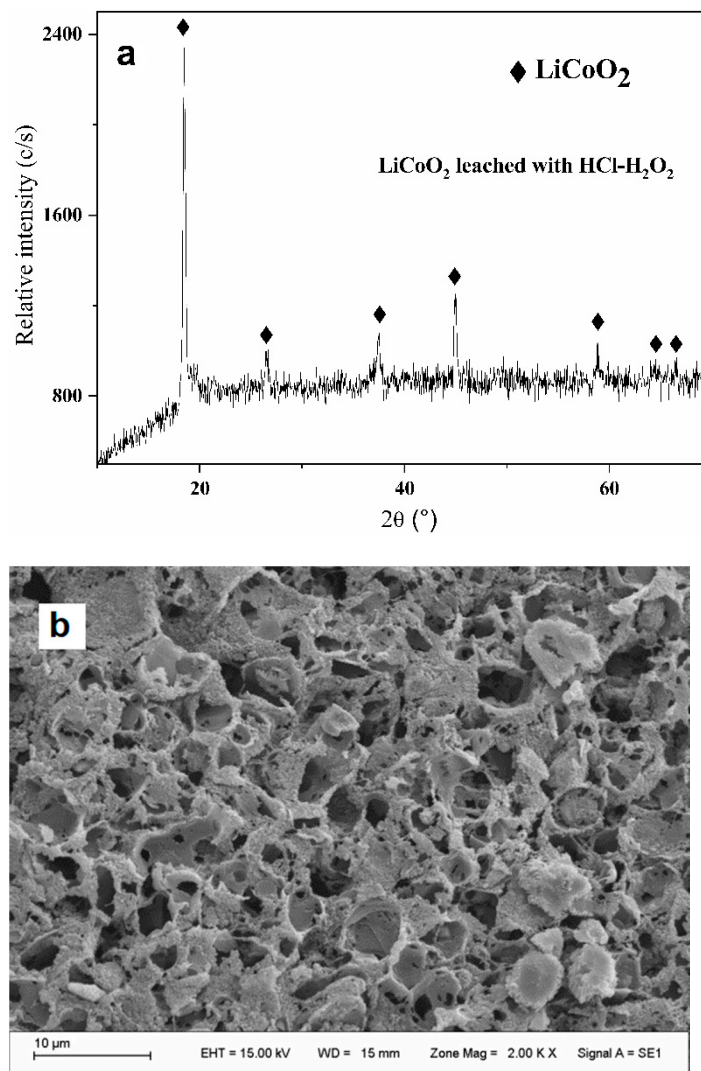


**Figure 5.** Effect of H<sub>2</sub>O<sub>2</sub> concentration on the sample dissolution.

The results show an abrupt increase in the sample dissolution when the reducing agent is added to the mixture and a slight increase in the same when its concentration is increased in the range 2–8% *v/v* [26,27]. This could be attributed to the fact that H<sub>2</sub>O<sub>2</sub> reduces Co in LiCoO<sub>2</sub> from Co<sup>3+</sup> to Co<sup>2+</sup>, destabilizing the crystalline lattice and promoting its breakage and the release of its ions. It is worth noting that for concentrations of H<sub>2</sub>O<sub>2</sub> of 5% *v/v*, dissolution efficiencies are higher than 90%, even with the low amounts of HCl employed.

### 3.3. Characterization of the Residues

The characterization of the residues by XRD and SEM of the samples leached with HCl-H<sub>2</sub>O<sub>2</sub> are presented in Figure 6a,b, respectively.



**Figure 6.** (a) Diffractogram and (b) SEM micrograph of the sample leached with HCl-H<sub>2</sub>O<sub>2</sub>.

In the diffractogram of Figure 6a it is observed that the residue corresponds to LiCoO<sub>2</sub>, whose diffraction lines coincide with those of the unreacted oxide (JCPDS 01-075-0532). In the micrograph of Figure 6b, it can be seen that the particles show a high degree of attack.

## 4. Conclusions

From the experimental results of the acid leaching of LCO in a closed vessel, it is possible to conclude:

- Increased temperature, reaction time and concentrations of leaching and reducing agents favor the LCO dissolution reaction.
- The optimum value of sample dissolution, 93.0%, was obtained working under the following conditions: HCl concentration, 0.12 M; H<sub>2</sub>O<sub>2</sub> concentration, 5% v/v; time, 30 min; temperature, 348 K; stirring speed, 330 rpm; solid–liquid ratio, 5 g/L.
- The use of a reducing agent has a double effect: on the one hand, it reduces reaction time and on the other hand it contributes to significantly decreasing the leaching agent consumption, achieving dissolutions similar to those reported in the literature. This



will allow us to propose an alternative process to the existing ones with economic and ecological advantages.

**Author Contributions:** Conceptualization, D.S.D. and M.H.R.; methodology, D.S.D., D.S.S. and M.H.R.; software, D.S.D. and M.H.R.; validation, D.S.D., D.S.S. and M.H.R.; formal analysis, E.G.P. and D.S.S.; investigation, D.S.D., E.G.P., D.S.S. and M.H.R.; resources, N.T., E.D.G. and M.H.R.; data curation, D.S.D., D.S.S. and M.H.R.; writing—original draft preparation, D.S.D. and M.H.R.; writing—review and editing, D.S.D., E.G.P., D.S.S., N.T., E.D.G. and M.H.R.; visualization, D.S.D., E.G.P., D.S.S., N.T., E.D.G. and M.H.R.; supervision, D.S.S. and M.H.R.; project administration, D.S.S., N.T., E.D.G. and M.H.R.; funding acquisition, N.T., E.D.G. and M.H.R. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The financial support from Universidad Nacional de Cuyo, Secretaria de Investigación, Internacionales y Posgrado, and Consejo Nacional de Investigaciones Científicas y Técnicas is gratefully acknowledged.

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

## References

1. Shaikh, S.; Thomas, K.; Zuhair, S. An exploratory study of e-waste creation and disposal: Upstream considerations. *Resour. Conserv. Recycl.* **2020**, *155*, 1046622. [CrossRef]
2. Lv, W.; Wang, Z.; Cao, H.; Sun, Y.; Zhang, Y.; Sun, Z.H. A Critical Review and Analysis on the Recycling of Spent Lithium-Ion Batteries. *ACS Sustain. Chem. Eng.* **2018**, *6*, 1504–1521. [CrossRef]
3. Zheng, X.; Zhu, Z.; Lin, X.; Zhang, Y.; He, Y.; Cao, H.; Sun, Z. A Mini-Review on Metal Recycling from Spent Lithium Ion Batteries. *Engineering* **2018**, *4*, 361–370. [CrossRef]
4. Li, L.; Ge, J.; Chen, R.; Wu, F.; Chen, S.; Zhang, X. Environmental friendly leaching reagent for cobalt and lithium recovery from spent lithium-ion batteries. *Waste Manag.* **2010**, *30*, 2615–2621. [CrossRef]
5. Widmer, R.; Oswald-krapf, H.; Sinha-khetriwal, D.; Schnellmann, M.; Bo, H. Global perspectives on e-waste. *Environ. Impact Assess. Rev.* **2005**, *25*, 436–458. [CrossRef]
6. United Nations Environment Programme. Metal Recycling Opportunities, Limits, Infrastructure-Summary. 2013. Available online: <https://wedocs.unep.org/20.500.11822/8423> (accessed on 10 March 2022).
7. Sakultung, S.; Pruksathorn, K.; Hunsom, M. Simultaneous recovery of valuable metals from spent mobile phone battery by an acid leaching process. *Korean J. Chem. Eng.* **2007**, *24*, 272–277. [CrossRef]
8. Suarez, D.S.; Pinna, E.G.; Rosales, G.D.; Rodriguez, M.H. Synthesis of lithium fluoride from spent lithium ion batteries. *Minerals* **2017**, *7*, 81. [CrossRef]
9. Zhang, P.; Yokoyama, T.; Itabashi, O.; Suzuki, T.M.; Inoue, K. Hydrometallurgical process for recovery of metal values from spent lithium-ion secondary batteries. *Hydrometallurgy* **1998**, *47*, 259–271. [CrossRef]
10. Joulié, M.; Laucournet, R.; Billy, E. Hydrometallurgical process for the recovery of high value metals from spent lithium nickel cobalt aluminum oxide based lithium-ion batteries. *J. Power Sources* **2014**, *247*, 551–555. [CrossRef]
11. Jha, M.K.; Kumari, A.; Jha, A.K.; Kumar, V.; Hait, J.; Pandey, B.D. Recovery of lithium and cobalt from waste lithium ion batteries of mobile phone. *Waste Manag.* **2013**, *33*, 1890–1897. [CrossRef]
12. Nayl, A.A.; Elkhatab, R.A.; Badawy, S.M.; El-Khateeb, M.A. Acid leaching of mixed spent Li-ion batteries. *Arab. J. Chem.* **2014**, *10*, S3632–S3639. [CrossRef]
13. Zhu, S.G.; He, W.Z.; Li, G.M.; Zhou, X.; Zhang, X.J.; Huang, J.W. Recovery of Co and Li from spent lithium-ion batteries by combination method of acid leaching and chemical precipitation. *Trans. Nonferrous Met. Soc. China* **2012**, *22*, 2274–2281. [CrossRef]
14. Sun, L.; Qiu, K. Vacuum pyrolysis and hydrometallurgical process for the recovery of valuable metals from spent lithiumion batteries. *J. Hazard. Mater.* **2011**, *194*, 378–384. [CrossRef]
15. Lee, C.K.; Rhee, K.I. Reductive leaching of cathodic active materials from lithium ion battery wastes. *Hydrometallurgy* **2003**, *68*, 5–10. [CrossRef]
16. Castillo, S.; Ansart, F.; Laberty-Robert, C.; Portal, J. Advances in the recovery of spent lithium battery compounds. *J. Power Sources* **2002**, *112*, 247–254. [CrossRef]

17. Pinna, E.G.; Ruiz, M.C.; Ojeda, M.W.; Rodriguez, M.H. Cathodes of spent Li-ion batteries: Dissolution with phosphoric acid and recovery of lithium and cobalt from leach liquors. *Hydrometallurgy* **2017**, *167*, 66–71. [[CrossRef](#)]
18. Pinna, E.G.; Drajlín, D.S.; Toro, N.; Rodriguez, M.H. Kinetic modeling of the leaching of LiCoO<sub>2</sub> with phosphoric acid. *J. Mater. Res. Technol.* **2020**, *9*, 14017–14028. [[CrossRef](#)]
19. Pinna, E.G.; Martínez, A.A.; Tunez, F.M.; Drajlín, D.S.; Rodriguez, M.H. Acid leaching of LiCoO<sub>2</sub> from LIBs: Thermodynamic study and reducing agent effect. *Rev. Mex. Ing. Química* **2019**, *18*, 441–449. [[CrossRef](#)]
20. Mylarappa, M.; Venkata Lakshmi, V.; Vishnu Mahesh, K.R.; Nagaswarupa, H.P.; Prashantha, S.C.; Shravana Kumara, K.N.; Siddeswara, D.M.K.; Raghavendra, N. Resource recovery and material characterization of metals from waste li-ion batteries by an eco-friendly leaching agent. *Mater. Today Proc.* **2017**, *4*, 12215–12222. [[CrossRef](#)]
21. Freitas, M.B.J.G.; Garcia, E.M. Electrochemical recycling of cobalt from cathodes of spent lithium-ion batteries. *J. Power Sources* **2007**, *171*, 953–959. [[CrossRef](#)]
22. Cerrillo-Gonzalez, M.M.; Villen-Guzman, M.; Vereda-Alonso, C.; Rodriguez-Maroto, J.M.; Paz-Garcia, J.M. Acid leaching of LiCoO<sub>2</sub> enhanced by reducing agent. Model formulation and validation. *Chemosphere* **2022**, *287*, 1322020. [[CrossRef](#)] [[PubMed](#)]
23. Rodriguez, M.H.; Suarez, D.S.; Pinna, E.G.; Zeballos, C.N. Method for Acid Dissolution of LiCoO<sub>2</sub> Contained in Spent Lithium-Ion Batteries. Patent No. U.S. 20180309174 A1, 25 October 2018.
24. Habashi, F. *Principles of Extractive Metallurgy*; Gordon and Breach Science Publishers: New York, NY, USA, 1986; Volume 3.
25. Golmohammadzadeh, R.; Rashchi, F.; Vahidi, E. Recovery of lithium and cobalt from spent lithium-ion batteries using organic acids: Process optimization and kinetic aspects. *Waste Manag.* **2017**, *64*, 244–254. [[CrossRef](#)] [[PubMed](#)]
26. Li, L.; Qu, W.; Zhang, X.; Lu, J.; Chen, R.; Wu, F. Succinic acid-based leaching system: A sustainable process for recovery of valuable metals from spent Li-ion batteries. *J. Power Sources* **2015**, *282*, 544–551. [[CrossRef](#)]
27. Nayaka, G.P.; Manjanna, J.; Pai, K.V.; Vadavi, R.; Keny, S.J.; Tripathi, V.S. Recovery of valuable metal ions from the spent lithium-ion battery using aqueous mixture of mild organic acids as alternative to mineral acids. *Hydrometallurgy* **2015**, *151*, 73–77. [[CrossRef](#)]