TESIS DOCTORAL
POR COMPENDIO DE PUBLICACIONES

2024

Integrated Hydrometallurgical Approaches for Sustainable Recovery of Metals from Lithium-ion Battery Cathodes

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Programa de doctorado:
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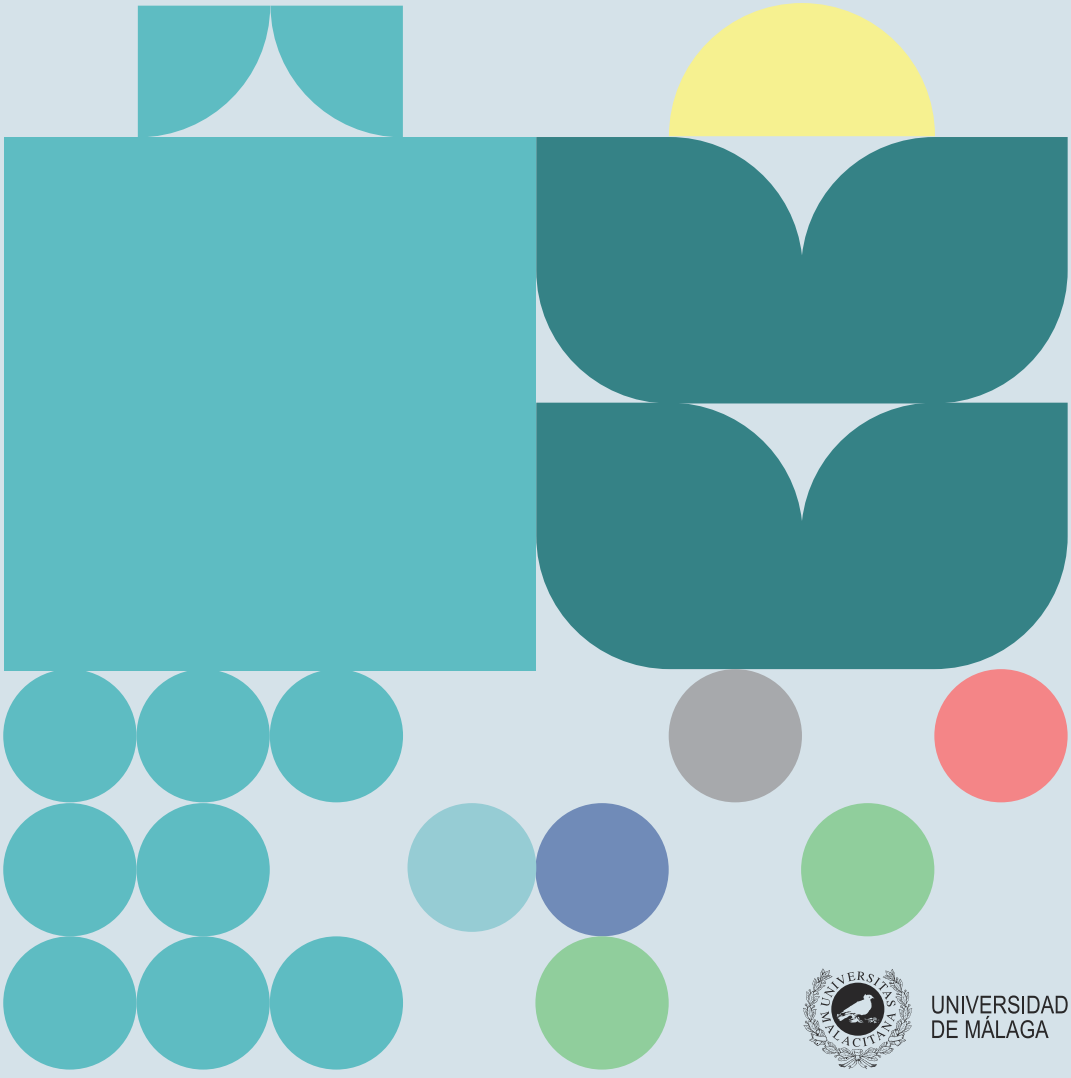

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FACULTAD DE CIENCIAS

DEPARTAMENTO DE INGENIERÍA QUÍMICA

Integrated Hydrometallurgical Approaches for Sustainable Recovery of Metals from Lithium-ion Battery Cathodes

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Doctoral Thesis by Compilation

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Doctoral programe:

QUÍMICA Y TECNOLOGÍAS QUÍMICAS.
MATERIALES Y NANOTECNOLOGÍA

2024

UNIVERSIDAD DE MÁLAGA

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EDITA: Publicaciones y Divulgación Científica. Universidad de Málaga

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Realizada bajo la tutorización y dirección de JOSÉ MIGUEL RODRÍGUEZ MAROTO y dirección de JUAN MANUEL PAZ GARCÍA (si tuviera varios directores deberá hacer constar el nombre de todos)

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El Dr. José Miguel Rodríguez Maroto, Catedrático de Ingeniería Química de la Universidad de Málaga y el Dr. Juan Manuel Paz García, Profesor Titular de Ingeniería Química de la Universidad de Málaga,

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Que la tesis doctoral presentada por compendio de publicaciones, titulada: Integrated *Hydrometallurgical Approaches for Sustainable Recovery of Metals from Lithium-ion Battery Cathodes,* ha sido realizada por Dña. María del Mar Cerrillo González bajo la tutorización y dirección del Dr. José Miguel Rodríguez Maroto, y la dirección del Dr. Juan Manuel Paz García.

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En cumplimiento de la legislación vigente, a su trámite y presentación para la obtención del grado de Doctor en el Programa de Doctorado de la Universidad de Málaga de QUÍMICA Y TECNOLOGÍAS QUÍMICAS. MATERIALES Y NANOTECNOLOGÍA por parte del interesado.

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Preface

This thesis is submitted by María del Mar Cerrillo González, as a fulfilment of the requirements for the international PhD degree at the University of Malaga. This PhD thesis is presented as a collection of publications based on five scientific papers:

- Recovery of Li and Co from $LiCoO_2$ via Hydrometallurgical–Electrodialytic Treatment, *Applied Sciences*. 10 (2020) 2367.
  DOI: 10.3390/app10072367
- Hydrometallurgical Extraction of Li and Co from $LiCoO_2$ Particles–Experimental and Modeling. *Applied Sciences*, 10(18) (2020) 6375.
  DOI: 10.3390/app10186375
- Acid leaching of $LiCoO_2$ enhanced by reducing agent. Model formulation and validation. *Chemosphere*, 287 (2022) 132020.
  DOI: 10.1016/j.chemosphere.2021.132020
- Semi-batch reactor for leaching battery cathodes under low acid concentration. *Hydrometallurgy, (Submitted).*
- Extraction and selective precipitation of metal ions from $LiCoO_2$ cathodes using citric acid. *Journal of Power Sources*, 592 (2024) 233870.
  DOI: 10.1016/j.jpowsour.2023.233870

The thesis has the following structure. Firstly, the topic of the thesis is introduced in Chapter 1, outlining the basic principles and the current state of the art of lithium-ion battery recycling. Additionally, a global overview is provided regarding the objectives and relevance of the publications that constitute the central part of this work. Chapter 2 presents the experimental systems and the methodology employed for the tests. Subsequently, in Chapter 3, a summary of each paper comprising the thesis is provided, discussing the most significant results obtained in this project. Chapter 4 presents the main conclusions of this thesis, and finally, in Chapter 5, the publications that form part of the doctoral thesis are appended.

Most of the experimental results and writing tasks were carried out at the Department of Chemical Engineering of the University of Malaga under the supervision of Dr José Miguel Rodríguez Maroto and Dr Juan Manuel Paz García. This PhD project has been funded through a contract from the Ministry of Universities through a university teacher training program (FPU18/04295), which started in November 2019.

Abstract

Lithium-ion batteries (LIBs) play an important role in our society. Widely used in portable electronics, electric vehicles (EVs), and renewable energy storage, the global demand for LIBs is expected to increase significantly in the next decades. This increase in demand raises concerns about the environmental impact and proper management of the waste generated at the battery's end of life. LIBs contain toxic metals and solvents, which can pose environmental and health risks if they are not correctly managed. Additionally, the manufacturing of LIBs relies on critical raw materials, and most of these resources come from mines outside Europe, creating concerns about supply chain vulnerabilities and ethical issues related to mining practices. To address these challenges, a shift toward a circular economy is proposed, emphasizing battery life extension, design for reuse, and recycling of battery wastes, aiming to decrease the environmental impact of these residues and recover the valuable components contained in these electronic wastes. In other words, LIB wastes would become a secondary source known as urban mining, and recycling can contribute to a sustainable supply chain.

Current LIB recycling methods primarily involve metallurgical processes. These techniques typically submit the batteries to mechanical and thermal pre-treatment to facilitate the dissolution step via acid leaching (hydrometallurgy). However, these processes are usually associated with high energy demand, water and reactants consumption, and the generation of large volumes of wastewater. Therefore, the hydrometallurgical process must be redesigned to become more sustainable. The transition from a linear to a circular hydrometallurgy economy could be a solution to face this challenge.

This thesis summarizes the approaches taken during the author’s doctoral studies towards the leaching process of LIBs cathode to contribute to improving the hydrometallurgical process. In the first work, the electrodialysis technique was proposed to regenerate the acid consumed during the leaching process of LIBs cathode materials as well as to integrate the extraction and recovery step in a single stage. The second and third works studied the reaction mechanisms involved in the extraction of metals from LIB waste. In the fourth work, the kinetic leaching information obtained in the previous works was used to optimize the process's mass and time efficiency, modifying the reactor configuration. Finally, the fifth work was proposed to analyse using citric acid as a benign chemical to dissolve metal oxides from LIBs wastes.

Agradecimientos

Aún me cuesta creer que esta etapa haya llegado a su fin. Después de cuatro años de intenso trabajo, en los que he aprendido muchísimo, no puedo olvidarme de todas aquellas personas que me han acompañado durante este camino. Porque sin su apoyo y ayuda, hoy no estaría escribiendo estas líneas.

En primer lugar, quiero dar las gracias a mis directores, José Miguel Rodríguez Maroto y Juan Manuel Paz García. Gracias por haberme guiado durante estos años, por vuestra dedicación, confianza y apoyo, y no solo a nivel académico sino también a nivel personal. Gracias Maroto, por aceptar aquel día dirigir tu "última tesis doctoral".

Igualmente, quiero dar las gracias a María Villén Guzmán. Me cuesta imaginar esta etapa sin ti. Gracias por tu ayuda todos estos años, por tus consejos, por escucharme y por mostrarme la parte más humana de la academia. Eres toda una referente para mí.

Agradecer también al resto de miembros del equipo de investigación GIGA en el que he desarrollado la Tesis. Gracias a Carlos Vereda Alonso y a César Gómez Lahoz, por estar siempre dispuestos a ayudarme y por haberme introducido en el mundo de la investigación. Gracias también a Brahim Arhoun y a Pedro Díaz por su ayuda en el laboratorio cada vez que la he necesitado. No puedo olvidarme de dar las gracias a todas las personas que han pasado por el laboratorio durante todos estos años. Luis, Joao, Mónica, Eduardo, María, Giulia, Álvaro, Jacobo, Emma y Raffaele, gracias.

Quiero también agradecer la acogida que recibí durante mis estancias de investigación a la profesora Francesca Beolchini y su equipo en la Università Politechnica delle Marche (Italia) y al profesor Akram Alshawabkeh y su equipo en la Northeastern University (EEUU). Ambas estancias han sido muy enriquecedoras. Gracias por haberme hecho sentir una más de vuestros equipos.

Agradecer al Ministerio de Universidades la financiación de esta Tesis mediante el programa de Formación al Profesorado Universitario (FPU18/04295). También agradecer al proyecto europeo e.THROUGH, financiado por la Unión Europea Horizonte 2020 (Marie Sklodowska-Curie grant 77845) , la ayuda para poder realizar las dos estancias de investigación.

En lo personal, doy las gracias a mis amigos y amigas. Compartir con vosotros está etapa ha sido muy especial. Gracias por vuestro cariño y apoyo incondicional. Gracias

por estar, porque como bien dice una canción, puedo saber que sin vosotros duele más.

Y, por último, quiero dar las gracias a mi familia. A mi hermano y mi hermana, por ser mi rayito de luz en esos momentos en los que he podido sentirme más perdida. A mi padre, por enseñarme lo importante que es escucharse a una misma para entenderse y valorarse. A mi madre, por estar presente siempre y por enseñarme a aprovechar y disfrutar de cada momento. Mamá, papá, hermano y hermana, gracias por vuestro cariño y vuestra paciencia, y por apoyarme en todo. Con vosotros a mi lado, todo es mucho más fácil.

María del Mar Cerrillo González

A mi familia, mi refugio

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List of Abbreviations

LIB	Lithium-ion battery
LCO	Lithium Cobalt Oxide
NMC	Lithium Nickel Manganese Cobalt Oxide
NCA	Lithium Nickel Cobalt Aluminium Oxide
LMO	Lithium Manganese Oxide
CRM	Critical Raw Material
CH	Circular Hydrometallurgy
ED	Electrodialysis
EV	Electric vehicle
SDS	Sustainable Development Scenario
S/L	Solid to Liquid ratio
SCM	Shrinking Core Model
USCM	Unreacted Shrinking Core Model

1 Introduction

Lithium-ion batteries (LIBs) are energy storage devices that have become essential in our modern society. These batteries were discovered in the 1970s by the 2019 Nobel laureates (John B. Goodenough, Akira Yoshino, and M. Stanley Whittingham) and were commercialized in the 1990s by Sony [1]. Since then, these batteries have been widely used in the portable electronics sector, thanks to their features, including their high charge voltage and energy density, long lifespan, good safety performance, and low self-discharge rate [2]. Furthermore, their use in the electric vehicle (EV) and renewable energy storage sectors has made them a key component in transitioning towards a decarbonized and clean energy system.

In 2022, the global capacity of the LIB market exceeded 500 GWh. Considering the sustainable development scenario (SDS), this capacity is estimated to reach 6 TWh by 2040 [3]. This increase in demand is directly related to the rise of electric vehicles. In 2020, the number of electric vehicles on the world's roads reached 10 million. According to the International Energy Agency [4], annual sales are estimated to reach 40 million and 80 million vehicles by 2030 and 2040, respectively. This increase in demand for LIBs, coupled with their lifespan, leads to an increase in the generation of LIB waste. The total amount of spent batteries for EV and storage applications is under 2 GWh. However, the volume of batteries reaching the end of their first life will increase modestly to around 100 GWh in 2024, which is expected to reach 1.3 TWh by 2040 [3]. Hence, it is crucial to manage these residues properly to avoid their environmental risk impact and to make them a true enabler of the green transition.

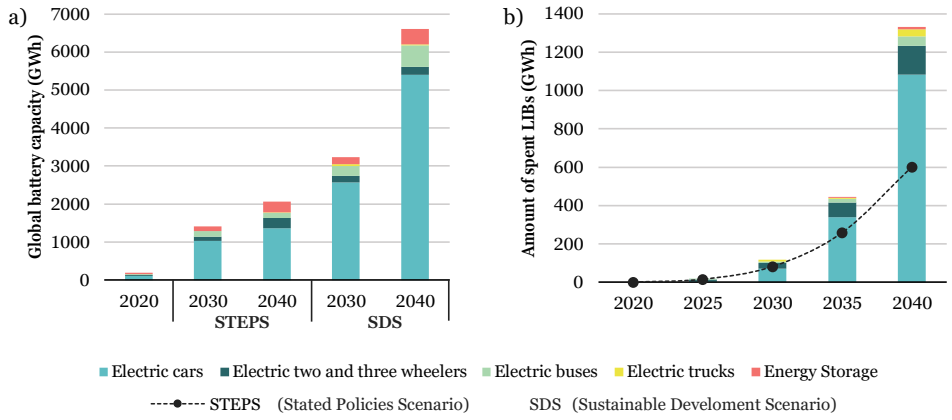

Figure 1 a) Global battery capacity additions in the SDS and STEPS b) Amount of spent LIBs for electric EVs and storage by applications in the SDS

In order to fully comprehend the potential risks associated with an increase in demand and generation of waste from batteries, it is important to analyse their composition. Like other chemical energy storage systems, batteries consist of several components, including an anode, cathode, electrolyte, and separator. **Figure 2** shows a typical diagram of a LIB. The specific characteristics of each battery component are presented below:

- **Cathode**: formed by metallic chalcogens, transition metal oxides, and polyanionic compounds [5], in which structure the lithium is intercalated. Currently, commercial LIBs are named by the material selected in the cathode as it determines their properties. Among the most used materials are lithium cobalt oxide ($LiCoO_2$ or LCO), lithium nickel cobalt manganese oxide ($LiNi_xCo_yMn_{1-x-y}O_2$ or NMC), lithium manganese oxide ($LiMn_2O_4$ or LMO), lithium nickel cobalt aluminium oxide ($LiNiCoAlO_2$ or NCA), and lithium iron phosphate ($LiFePO_4$ or LFP) [2,6,7]. These materials are mixed with conductive black carbon materials to increase their electrical conductivity and the lithium diffusion coefficient through the crystal lattice. To form the electrode, the lithium compound, and black carbon mixture are attached to an aluminium foil, which acts as a current collector, using a binder *(e.g.*, polyvinylidene fluoride) [2].

- **Anode:** usually composed of graphite, a binder, and carbon black. In addition to being abundant and relatively inexpensive materials, they exhibit good mechanical stability and high electrical conductivity thanks to the intercalation of lithium between the graphene layers that make up the graphite [5,8]. As an alternative to graphite anodes, there are titanium and lithium oxide anodes (LTO, $Li_4Ti_5O_{12}$) [2]. Although there is numerous research focused on the development

of new anode materials, such as silicon or metal alloy anodes [8], currently, only the two former types are commercially available [9]. Like the cathode materials, it is adhered to a foil. In this case, the foil material is copper. This foil, along with the aluminium cathode foil, makes up the cell terminals.

- **Electrolyte:** a mixture of lithium salts dissolved in an organic solvent. Lithium hexafluorophosphate ($LiPF_6$) is the most commonly used salt, although lithium perchlorate ($LiClO_4$) and lithium hexafluoro arsenate ($LiAsF_6$) are also used [2]. These salts are dissolved in organic solvents to facilitate the movement of lithium ions. Among the most used solvents are ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylene carbonate (EC), and propylene carbonate (PC) [10]. In the case of polymer LIBs, a precursor gel is added to the electrolyte to allow it to be absorbed into the polymer matrix.
- **Separator:** a safety element placed between the cathode and anode to prevent the contact of both electrodes and, consequently, to avoid short circuits. Therefore, it must be an excellent electrical insulator with a high mechanical and chemical resistance and permeable to lithium ions. The most used materials are polypropylene and polyethylene [2].

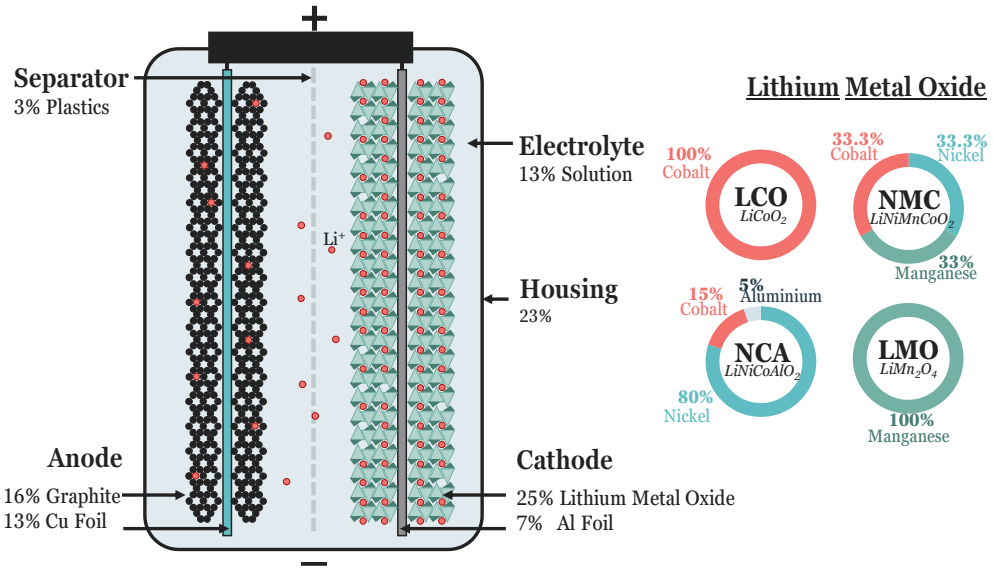

Figure 2 LIB composition (% average mass percentage of 18650 cylindrical cells) and the most used lithium metal oxide cathodes composition (Li is not included in the percentage distribution).

LIB and their waste contain highly toxic metals and organic solvents that threaten the environment and human health [11]. In the case of metals like cobalt and nickel, prolonged exposure to these metals can lead to respiratory problems and dermatitis, and in some cases, even lung cancer and damage to the central nervous system. Additionally, graphite, used in the anode, can react with oxidizing agents like fluorine and produce CO and other toxic gases. The same problems apply to $LiPF_6$ used in the electrolyte, which is highly corrosive and volatile and can form HF, P_2O_5, Li_2O upon contact with air. All these substances can enter the environment directly or indirectly, leading to environmental pollution. Therefore, improper management of these waste materials results in various environmental issues further exacerbated by their severe impacts on ecosystems and human health.

On the other hand, the rise of LIBs technology entails an increased demand for resources for manufacturing. Some of the most used materials in commercial LIB, such as lithium and cobalt, are classified by the European Union as Critical Raw Materials [12]. In the latest update of this list, published in March 2023, new metals have been included, with nickel and manganese standing out due to their importance in the LIBs industry. This classification is based on the current and future assessment of these materials' economic value and supply risk.

Most mines for these materials are located outside of Europe, in particular points of the world, making the European Union highly reliant on these strategic raw materials for industrial and technological development. Currently, approximately 74% of battery materials are supplied by China and a few countries in Africa (e.g., the Democratic Republic of Congo and South Africa) and Latin America (e.g., Chile and Peru) [12]. As a result, natural disasters or political conflicts in these countries can affect the availability of these materials. Moreover, numerous social issues are associated with mining these raw materials [13]. In addition to the environmental impact caused by mining activities (water and soil pollution, ecosystem loss, emissions), the lack of regulation in these countries leads to conflicts between communities and mining companies over land use. Furthermore, inadequate worker safety, human rights abuses (such as child labor), and corruption highlight the necessity of developing new strategies to make these metals more sustainable.

The demand for primary materials for batteries, as well as their criticality, can be decreased by the adoption of circular economy strategies. On the one hand, they are extending the lifespan of batteries and designing batteries to be reused. On the other hand, recycling spent batteries focuses not only on decreasing the environmental impact of these residues but also on recovering the valuable components contained in these electronic wastes. In other words, LIB wastes would become a source of

secondary material, which is known as urban mining. By the year 2040 (**Figure 3**), it is estimated that 51% of cobalt, 42% of nickel, and 23% of manganese consumed for battery production in the European Union could come from recycling. However, it is estimated that only 9% of lithium will come from secondary sources [14].

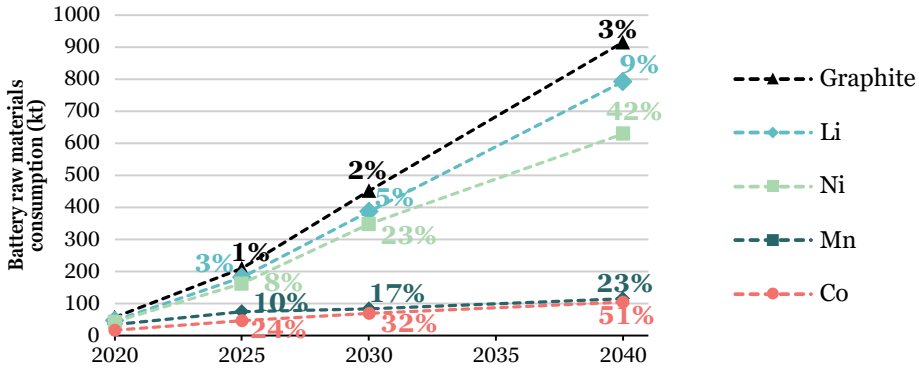

Figure 3 Estimated consumption of battery raw materials and supply potential from secondary sources (%) in the European Union [14].

Key aspects for increasing the volume/quantity of secondary raw materials from battery wastes include traceability and battery identification throughout their life, maximizing the collection of spent batteries, and developing high-quality recycling technologies. In this regard, legislation plays an important role as it sets the target for each stage of the life cycle.

Recently, the European Union has announced new regulations to ensure the sustainability and safety of batteries in the European market. Currently, the recycling of batteries in Europe is regulated by the Batteries Directive (2006/66/EG) [15]. Although this legislation has been updated recently, a new version was required to include measures that Europe must adopt to meet the objectives of the EU Green Deal, the Circular Economy Action Plan, and the New Industrial Strategy. The new regulation will introduce, for the first time, the minimum requirements for collection and recycling efficiency for lithium-based batteries. The collection of waste batteries is a fundamental step in the recovery of valuable materials. The collection targets of portable batteries and electric vehicles are set at 73% and 61%, respectively, by the end of 2031. Regarding to recycling efficiency, targets for lithium-based batteries are set at 65% by the end of 2025 and 70% by the end of 2030. Moreover, all recycling technology shall achieve at least 90% Co, 90% Cu, 50% Li, and 90% Ni for recovery yield [16].

In this context, based on the environmental risk, resource characteristics of spent LIBs, and new battery regulation, the research on the recycling and utilization of LIB wastes has become a global research hotspot. Although various battery recycling technologies based on metallurgical methods are available today, they are still looking for a perfect solution [17]. The key (and most difficult) point of these recycling processes is to recover metals selectively with high purity from the battery wastes due to the variety of cathode chemistries used in commercial LIBs [18]. Many efforts must be made to develop efficient technologies to increase the recycling yield and metal purity and make the process environmentally sustainable and economically viable. In the following section, the state of art of LIBs recycling is presented, as well as the challenges and limitations of the LIBs recycling technologies.

1.1 LIBs Recycling Process

Recycling is the third step in the waste management hierarchy, preferably reducing (designing LIBs with long lifespans) and reusing instead of recycling. However, reducing and reusing postpones recycling, which is the ideal eventual fate for all LIBs. The current LIBs recycling technologies are based on metallurgical processes. Due to the complex structures and the high number of materials in LIBs, a pre-treatment step is required to facilitate recycling [19].

Preliminary treatment comprises three major stages: discharge, dismantling, and separation (if required) [20]. The separation steps consist of physical (flotation), mechanical (shredding and crushing), thermal (organic solvent evaporation), chemical (dissolution of binder or foils) or mechanic-chemical processes [21]. The primary purposes of the pre-treatment step are enriching metallic fraction, lowering crap volumes, enhancing recovery rate, and managing safety issues. Once the battery is pre-treated, it is subjected to pyrometallurgy, hydrometallurgy or direct recycling [19], as shown in **Figure 4**.

Pyrometallurgical processes use high temperatures to recover and purify valuable metals in battery materials. This process usually involves two stages [18]. First, the battery is burned in a smelter under a vacuum or inert atmosphere. The substances of LIBs are heated over their melting points to facilitate the segregation of metallic elements in the liquid phase through reduction and ensuing formations of immiscible molten layers [22]. The main outputs of smelting processing include metal alloys and slag. The metal alloy contains valuable elements such as Co, Ni, and Cu, while the slag fraction usually contains Li, Mn, and Al [23]. In the second stage, metal alloys are further separated to recover pure materials via hydrometallurgical methods. Therefore, pyrometallurgical processes alone are not able to purify the metals and it

aims to transform the metals into favourable phases to facilitate the further leaching process [21].

Pyrometallurgy is a simple and mature recycling technique due to its flexibility. In this method, the sorting and size reduction is unnecessary, as a mixture of batteries can be burned together. Thus, the pre-treatment step is optional. However, several disadvantages limit this technique. Firstly, the generation of toxic gases and the high energy consumption during the smelting process. Secondly, the fact that further processing is required to separate metals from alloys increases the recycling process cost. Moreover, only a few materials from LIBs can be recovered. The process recovers Co and Ni from the cathode and Cu from the anode current collector. However, other materials are lost in the slag (such as lithium and manganese) or evaporated during the process (such as electrolytes and plastics). The technique has been profitable due to the high cobalt content in LIBs. However, the industry is moving toward reducing the cobalt content. Thus, the pyrometallurgy process may not work well for the new low-cobalt-content LIBs [18].

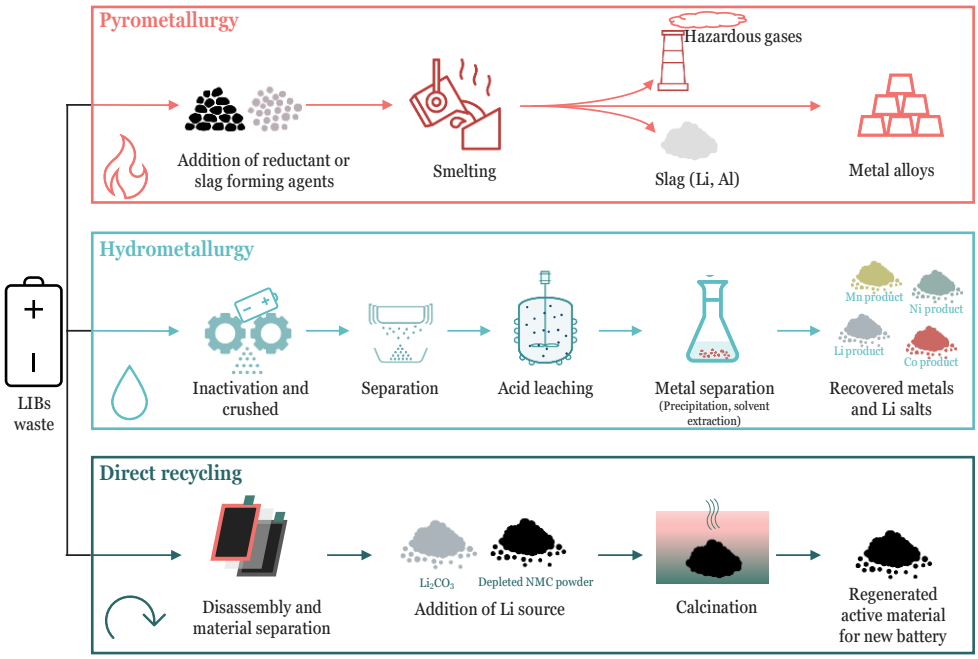

Figure 4 Typical recycling methods for recovery active materials from LIBs.

Hydrometallurgical processes use an aqueous solution to extract and separate metals from LIBs. So, this process involves two main stages: leaching and separation. In the first stage, the pre-treated battery materials are treated using acid and reducing agents to convert metals contained in the solid into soluble metal ions. A wide range of lixiviants have been used to enhance the process, including inorganic (H_2SO_4, HCl, HNO_3) and organic acids (citric acid, tartaric, and oxalic), combined with the use of reductant agents. Once metals are dissolved in the solution, they are selectively separated by chemical precipitation, solvent extraction, ion exchange, or electrodeposition [24].

Compared with the pyrometallurgical process, hydrometallurgy presents relevant advantages, such as lower energy consumption, lower emissions, higher materials recovery (the most constituent of LIB can be recovered), and higher product purity, which makes this method attractive for recycling LIBs. However, this technique also has some drawbacks. One of them is the need for sorting, which requires more storage space and increases the cost and complexity of the overall process. On the other hand, separate selectively metals in solution (such as Co, Ni, Mn, Fe, Cu) become a challenge due to their similarly chemical properties. Moreover, the amount of chemicals and water required in the process and the wastewater treatment increase the cost [18]. In order to improve the profitability and sustainability of battery recycling, it is important to simplify the process, enhance the metal recovery rate, and reduce reactant consumption. More details about recent hydrometallurgical process improvement in recent literature are presented in the section *1.2 Hydrometallurgical Process Improvement*.

Direct recycling is an emerging recovery method that directly recovers the active materials of LIBs to be reconditioned without destroying the original compound structure. In this process, the battery is disassembled, and its constituents are separated by physical separation methods, magnetic separation, and moderate thermal processing to avoid chemical breakdown of the active materials [18]. The purification of active materials involves repairing bulk defects by hydrothermal, solid-phase, electrochemical, and chemical re-lithiation.

This recycling method includes a series of advantages compared with the pyrometallurgical and hydrometallurgical, such as a relatively more straightforward process with lower emissions and less secondary pollution. Moreover, the active materials can be directly reused after regeneration. However, this technique is still limited and only exists at a lab scale [25]. The varieties of cathode chemistry can result in poor recovery efficiency and a challenge to guarantee the high purity and crystal structure required by industrial battery standards. Thus, rigorous sorting and

separation are required for exact material chemistry [26]. Considering the characteristics of different battery wastes (type, chemistry, and condition), it is difficult to think in direct recycling as an industrial method to manage battery wastes. The recent progress is focused on recycling electrode scrap from battery manufacturers due to the chemistry is well-known [18].

Currently, pyrometallurgical and hydrometallurgical processes are widely utilized in industry. Pyrometallurgy methods are used due to their flexibility in battery feedstock, simplicity, and reliability, while hydrometallurgy methods offer less emissions and superior effectiveness. It must be noted that none of the existing recycling methods offers a perfect recovery solution for all LIB components at low energy consumption and low cost and without generating harmful gases and wastewater effluent. Recycling of spent LIBs requires more effort and investment to achieve more effective and greener solutions, to recover not only valuable metals but also to dispose correctly of substances adverse to the ecosystem. In this context, hydrometallurgical advantages make this method one of the most promising in battery recycling. Proof of that is the number of research over the past decade focused on mitigating their disadvantages and increasing their recovery rate and effectiveness [27]. Hence, the hydrometallurgical process needs to develop new strategies to ensure the sustainability of the technique. Since this thesis focuses on the hydrometallurgical process, more details about this technique and its development are presented in the following section.

1.2 Hydrometallurgical Process Improvement

Hydrometallurgy is a chemical metallurgical process that involves the use of an aqueous solution to recover metals from ores. It has been widely used in mining and metallurgical industries, and in the last decades, as aforementioned, its uses have been extended to LIBs recycling sector [28]. The hydrometallurgical process is divided into two main stages: leaching and separation of metals. Several studies are focused on the optimization of parameters controlling these stages to increase the extraction yield and recovery efficiency [24,29] .

Leaching is usually carried out using acids, being the H_2SO_4 the most used at industrial scale [30]. However, other acids, such as HCl and HNO_3, have gained attention because they are much easier to regenerate than H_2SO_4 [31]. The use of organic acids has also been investigated to develop a more sustainable process [32]. In addition to acids, the leaching stage also requires the use of a strong reductant agent to promote the dissolution of metals. Although several reductant agents have been investigated, such as ascorbic acid [33] or current collector scrap [34], H_2O_2 is

the most used in research and on the industrial scale [29]. Despite H_2O_2 is widely known as an oxidizing agent, its use as a reducing agent is justified due to the high reduction potential of Co^{3+}/Co^{2+}. Besides the type and concentration of extractant and reductant agents, other parameters controlling the leaching step are the temperature, the solid-to-liquid ratio (S/L ratio), and the stirring mechanism.

Regarding to the separation stage, different techniques have been studied to separate selectively metals once they are solubilized. The most used at industrial scale is chemical precipitation, which requires the use of alkaline solution to neutralize and precipitate metals [35]. The separation mechanism depends on the solubility of metal compounds under specific conditions of temperature and pH value. The most used precipitant is CO_3^{2-} (as Na_2CO_3 or $CaCO_3$), as it can form insoluble compounds with almost all high-value metals [21]. Other precipitants, such as Na_3PO_4 [36], phosphoric acid [37], and oxalic acid [38], have also been reported. The advantages of this technique are low cost, low equipment requirements, and simple operation. However, the main limitation is the difficulty to selectively separate battery metals due to their properties are so similar, so they precipitate at similar pH values [21]. An effective approach is coprecipitating them and sintering the precursor directly into NMC cathodes [39].

Solvent extraction is another technique to separate metals. In solvent extraction, the driving mechanism is the different solubilities of various metal ions in an organic solvent versus an aqueous liquid. Several efficient solvents employed comprise 5-nonylsacysalicylaldoxime, di-(2-ethylhexyl)phosphoric acid (DEHPA) and Cyanex 272 [18]. This technique has the advantages of short times and high purity of product, but the high cost of solvents and the complexity of the process limit its application. Electrochemical deposition is another method to separate and recover target metals [40]. The principle of this technique is the difference between the metal's redox potential. This technique is mainly focused on the recovery of cobalt [41]. Moreover, the application of ion-exchange membranes and electrodialysis also have been reported as a technique to separate and concentrate metals from LIBs leaching solutions [42]. More details are presented in the section *1.2.3 Electrodialysis*.

As observed, both stages require a large amount of reagents and water, with the subsequent generation of residues and wastewater. It is one of the drawbacks of conventional hydrometallurgy, which can be described as predominantly linear in the sense that reagents consumed are not regenerated for subsequent reuse. It must be noted that many hydrometallurgical processes leave a large carbon footprint because producing hydrometallurgical reagents requires high energy consumption. Nowadays, there is more consciousness-raising of environmental issues, and it has

also reached the extractive metallurgical sector. In this context, the hydrometallurgical process must be redesigned to become more sustainable. The transition from a linear to a circular economy could be a solution to face this challenge.

Circular hydrometallurgy (CH) involves designing of energy-efficient and resource-efficient unit processes that consume the minimum quantities of reagents and produce as minimum waste as possible. The base of the circular approach is the regeneration and reuse of every reagent in the process. It refers not only to the acids and bases used for leaching and pH control, but also the reducing agents, oxidizing agents, and other auxiliary agents employed in the process. Moreover, the circular model should emphasize the decrease of water and energy consumption.

To consolidate the concept of circular hydrometallurgical process, Binnemans and Tom [31] have defined "The 12 Principles of Circular Hydrometallurgy". In this guide, they propose different approaches to set a basis for identifying future research in the field of hydrometallurgy, providing a sustainability benchmark for technological development. The 12 principles are shown in **Figure 5**. Some of these principles are more general, such as regenerating reagents, preventing waste, using benign chemicals, or maximizing mass, energy, time, and space efficiency. Other principles are more specific, such as decreasing the activation energy or electrifying process wherever possible.

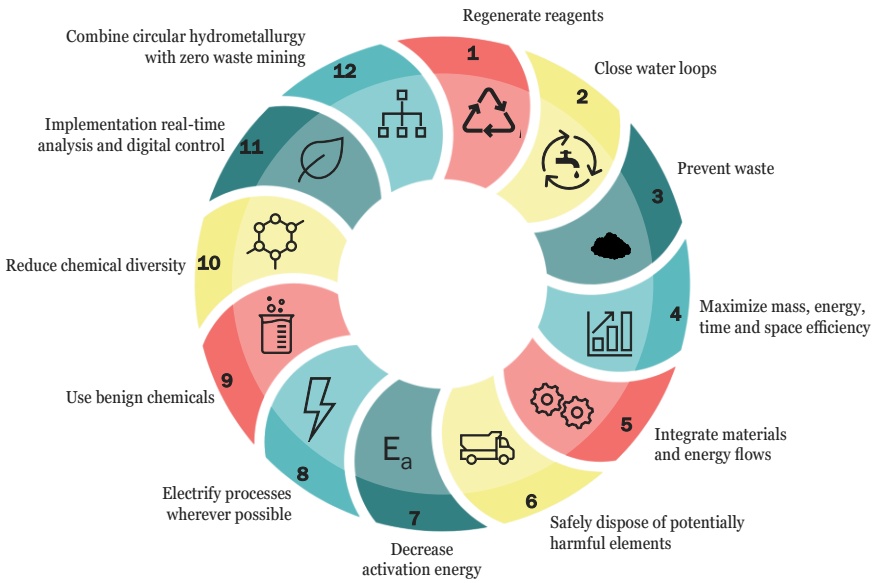

Figure 5 The 12 Principles of Circular Hydrometallurgy [31].

It must be noted that these principles are not independent and can be combined to strengthen the development of a circular hydrometallurgical flowsheet. By far, principle 1 (Regenerate reagents) is the most important because the circular process cannot be designed without regeneration. However, there are synergies between principles. For example, integrating materials and energy flows (Principle 5) results in higher efficiencies (Principle 4). At the same time, a more efficient process with a lower reagent consumption (Principle 4) leads to less requirement for reagent regeneration (Principle 1). Decreasing the activation energy (Principle 7) of hydrometallurgical reactions maximizes the process's mass, energy, space, and time efficiency (Principle 4). But there is also a critical interaction between principles, and optimizing a process focused on one principle could result in a worse performance of the other principles. For example, minimizing the acid consumption decreases the amount of reagent to regenerate. It can be achieved by controlling the pH and adding acid while the reaction consumes it. However, low acid concentration slows down the leaching kinetics, affecting the space and time efficiency [31]. Hence, CH development involves a comprehensive analysis of the different principles and their interactions.

This thesis has been focused on the application of some of the twelve principles of CH in the recycling of LIBs. In the first study (*Recovery of Li and Co from $LiCoO_2$ via Hydrometallurgical-Electrodialytic Treatment)*, the electrodialysis technique has been proposed to regenerate the acid consumed during the leaching process of LIBs cathode materials as well as to integrate the extraction and recovery step in a single stage. The second work (*Hydrometallurgical Extraction of Li and Co from $LiCoO_2$ Particles-Experimental and Modelling)* and third (*Acid leaching of $LiCoO_2$ enhanced by reducing agent. Model formulation and validation)* studied the reaction mechanisms involved in the extraction of metals from LIBs waste. The leaching kinetic information obtained in the previous works was used in the fourth study (*Semi-batch reactor for leaching battery cathodes under low acid concentration*) to optimize the mass and time efficiency of the process, modifying the reactor configuration. Finally, the fifth (*Extraction and selective precipitation of metal ions from $LiCoO_2$ cathodes using citric acid*) study was proposed to analyse the use of citric acid as a benign chemical to dissolve metal oxides from LIBs wastes.

The following subsection contains the literature review presented in the papers that support this thesis.

1.2.1 Hydrometallurgy Leaching Parameters

Leaching is the key factor in the whole hydrometallurgical process since this step determines the technological complexity and the economic viability of the process [43]. This step aims to dissolve and convert metals contained in the solid battery wastes (black mass) into soluble metals ions. At the industrial scale, acid solutions are commonly used to leach LIB wastes, but there are also studies focused on the use of alkaline solutions and bioleaching [44]. Reductant agents are also required to promote the reduction of some target metals (such as Co or Mn) to lower oxidation states, which are more soluble in the leaching solution [45]. Other parameters, such as solid-to-liquid ratio (S/L), temperature, and reaction time, also affect the recovery and reaction rates. **Figure 6** shows the influence level of the leaching parameters, with the order from high to low: acid species and concentration, leaching time, reductant agent species and concentration, S/L ratio, reaction temperature, and stirring speed [46]. Hence, optimizing the process requires the optimization of each of these parameters. **Table 1** summarizes different research results regarding different types of leaching reagents and conditions.

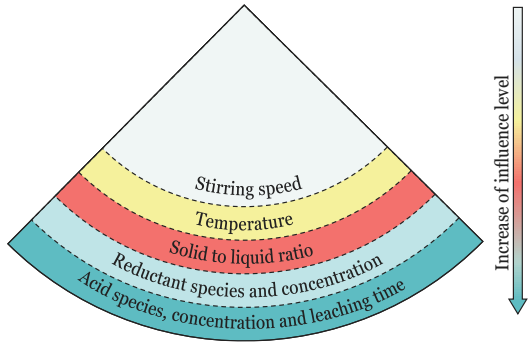

Figure 6 The influence level of leaching parameters on cathode scrap [46].

Acid leaching involves using inorganic acid and organic acid to dissolve the metals in LIBs wastes. Inorganic acid includes using H_2SO_4, HCl, and HNO_3 [24]. They are widely applied during the leaching processes due to the advantages of high leaching efficiency, easy availability, and relatively low price. Although H_2SO_4 is the most used at industrial scale, the use of other inorganic acids such as HCl and HNO_3 has gained attention because they are much easier to regenerate than H_2SO_4 [31]. From **Table 1**, it can be observed that almost all valuable metals can be dissolved from different kinds of waste materials using inorganic acid as extracting agent under relatively high acid concentration, temperatures over 50°C, reaction times more than one hour, and S/L ratio less than 50 g/L.

Table 1 Studies on leaching of LIB waste

LIBs type	Leaching agent	Leaching condition (T, t and S/L)	Efficiency (%)	Ref
NMC	2 M H_2SO_4 4 %v/v H_2O_2	50ºC, 2 h, 50 g/L	Li = 98; Co = 98; Ni = 98; Mn = 98	[47]
LCO	2 M H_2SO_4 2.1 g Cu + 1.06 g/L Fe (II)	30ºC, 2 h, 16 g/L	Co = 95	[48]
NMC	1 M H_2SO_4 0.075 M $NaHSO_3$	90ºC, 4 h, 20 g/L	Li = 96.7; Co = 91.6; Ni = 96.4; Mn = 87.9	[49]
LCO	5 M H_2SO_4 10 %v/v Methanol	90ºC, 2 h, 10 g/L	Li = 99; Co = 99	[50]
Mixture	2 M H_2SO_4 Cu, Al, Fe (present in overflow fractions > 2mm)	80ºC, 1.5 h, 100 g/L Overflow (g) : Underflow (g) = 1:10	Li = 99.9; Co = 99.6	[51]
NMC	1 M H_2SO_4 + 1/1.2 w/w Cu 1 M H_2SO_4 + 1/1.07 w/w Al	30ºC, 1 h, 40 g/L 30ºC, 24 h, 40 g/L	Li = 99; Co = 99; Ni = 99; Mn = 99	[34]
LCO	2 M HCl	80ºC, 90 min, 20 g/L	Li = 99; Co = 90	[52]
NCA	4 M HCl	90ºC, 18 h, 50 g/L	Li = 99; Co = 99; Ni = 99; Al = 99	[53]
LCO	1 M H_2SO_4 1 M HCl 1 M HNO_3	80ºC, 2 h, 20 g/L	Li = 99; Co = 52 Li = 99; Co = 97 Li = 99; Co = 62	[46]
LCO	1 M HNO_3 0.8 %v/v H_2O_2	75ºC, 30 min, 20 g/L	Li = 85; Co = 85	[54]
LCO	1.5 M Malic acid 2 %v/v H_2O_2	90ºC, 40 min, 20 g/L	Li = 100; Co = 90	[55]
LCO	1.25 M Ascorbic acid 1 %v/v H_2O_2	70ºC, 20 min, 25 g/L	Li = 98.5; Co = 94.8	[33]
LCO	1.5 M Sucinic acid 4 %v/v H_2O_2	70ºC, 20 min, 15 g/L	Li = 96; Co = 99	[56]
NMC	1.5 M Lactic acid 0.5 %v/v H_2O_2	70ºC, 20 min, 20 g/L	Li = 97.7; Co = 98.9; Ni = 98.9; Mn = 98.4	[57]
NMC	2 M Acetate acid 1.5 $g/g_{cathode}$ Glucose	175ºC, 2 h, 10 g/L, subcritical leaching	Li = 99.9; Co = 97.5; Ni = 98.7; Mn = 99.3	[58]
LCO	1.25 M Citric acid 1 %v/v H_2O_2	90ºC, 30 min, 20 g/L	Li = 100; Co = 90	[59]
NMC	0.5 M Citric acid 1.5 %v/v H_2O_2	90ºC, 60 min, 20 g/L	Li = 99.1; Co = 99.8; Ni = 98.7; Mn = 95.2	[60]
LCO	1 M citric acid 8 %v/v H_2O_2	70ºC, 70 min, 40 g/L	Co = 99	[61]
LCO	0.1 M Citric acid 0.02 M Ascorbic acid	80ºC, 6 h, 2 g/L	Li = 100; Co = 80	[62]
LCO	1.5 M Citric acid 0.4 g/cathode Tea waste	90ºC, 2 h, 30 g/L	Li = 98; Co = 96	[63]
Mixture	0.5 M citric acid Cu and Al collector scrap	90ºC, 80 min, 80 g/L	Li = 91; Co = 90; Ni = 94; Mn = 89	[64]

One interesting aspect of HCl is that it can also get oxidized; therefore, it may act as a reductant agent during the leaching reactions without adding an extra reductant. Joulie et al. [53] investigated the leaching of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathodes using different inorganic acids solutions of HCl, H_2SO_4, and HNO_3. They observed that the most efficient leaching agent was HCl, obtaining approximately 100% of highly valuable elements under a S/L ratio of 50 g/L, 4 M HCl solution, 18 h, and 90ºC. A similar observation was reported by Gao et al. [46] after dissolving $LiCoO_2$ with different acid species under the same experimental conditions (1 M acid concentration, S/L ratio of 20 g/L and 80ºC). In their experiments, the percentage of Li extracted was almost 99% for H_2SO_4, HCl, and HNO_3, while the percentage of Co only was over 90% for HCl. In the case of H_2SO_4 and HNO_3 the percentage extracted was around 60%. It could be due to the formation of an acid resistant Co_3O_4 crust around the particles, which would stop the reaction [65]. This layer's formation, composed of trivalent and divalent cobalt, emphasizes the use of reductant agents in the leaching process.

Mineral acids show high efficiencies for dissolving all types of cathode materials, allowing more than 99% of all valuable metals to be recovered under the appropriate conditions when adding an external reductant agent. However, their application has several drawbacks. Firstly, the inevitable generation of hazardous gases such as Cl_2, SO_3, and NO_x during leaching poses a significant threat to the environment and human health [66,67]. Secondly, high acid concentrations result in a solution with low pH values even after the leaching, so a large amount of chemicals is needed to neutralize the solution in the recovery step, typically at pH 4-9 [68]. Thirdly, the wastewater generated after the leaching and recovery process needs to be treated to prevent secondary pollution. Consequently, disposing of hazardous gases, acidic leachates, and acidic wastewater demands further attention, incurring additional costs when utilizing inorganic acids as leaching reagents. In this context, organic acids have gained attention to be used as more benign extractant agents for LIBs recycling.

Several organic acids have been used, including tricarboxylic acid (e.g., citric acid), dicarboxylic acids (e.g., succinic acid, ascorbic acid, and oxalic acid), and monocarboxylic acids (e.g., lactic acid, acetic acid, and formic acid). These organic acids offer advantages over inorganic acids, such as recyclability, easy degradation, sufficient acidity for leaching, and reduced secondary emissions. However, some drawbacks still limit their use at the industrial scale. The cost of organic acids is typically higher than the inorganic ones. Additionally, organic acids generally exhibit slower leaching speeds than inorganic acids, and their treatment capacity is lower.

Nevertheless, there are several studies focused on the enhancement of leaching using organic acid.

Li et al. [33,55–57,59,60] reported studies using different organic acids to leach cathode active materials. They found that D-malic acid, citric acid, ascorbic acid, succinic acid, and lactic acid present good performance as lixiviant agent for different cathode materials. According to these studies, the leaching performances with organic acid are succinic>citric acid>malic>lactic. In all the studies, metal percentages higher than 90% were achieved under 1.5 M of acid concentrations, 2 %vol H_2O_2, S/L ratio of 20 g/L, 40 min of reaction, and temperature of 90 ºC. Among of these organic acids, citric acid is the cheapest and most readily available acid, with excellent leaching performance [69].

Citric acid not only presents good leaching performance, but it is also a good chelating agent. It can entail the formation of citrate-metal complexes during the leaching that enhances the dissolution. As a result, after leaching the cathode material with citric acid, metals will be in the solution complexed by different citric acid species. Yu et al. [61] detected the formation of cobalt-citrate complexes during the leaching process of $LiCoO_2$ after drying the leaching solution and characterizing the final solid by Fourier Transform Infrared and UV spectroscopy. They concluded that the final solid was a mixture of citrates and citric acid in coordination with the metals. Therefore, the chelation of metals with citric acid not only plays an important role in improving the leaching efficiency but also in producing precursors to synthetizes new cathode materials for LIBs.

Regarding to the reducing agents, as aforementioned, they are employed to increase the leaching efficiency. The most used reductant agent at the research and industrial scale is H_2O_2, which has the advantage that no additional impurities are added to the solution. Nevertheless, the use of H_2O_2 also has a series of drawbacks. Although its use as a reductant is justified due to its redox potential (O_2/H_2O_2) is lower than Co^{3+}/Co^{2+} and MnO_2/Mn^{2+}, it will act as an oxidant to other metals present in the battery easily oxidizable, such as Cu, Al and Fe, decreasing the selectivity of H_2O_2 to reduce the desired metals [48]. **Table 2** shows the reduction potential in the water of different redox half-reactions of interest in this research.

Moreover, H_2O_2 production process has some drawbacks for the sustainability of the recycling process. The current industrial process to produce H_2O_2, based on the anthraquinone process, is expensive and presents a high-energy demand [70]. Therefore, searching for alternatives to H_2O_2 or optimizing its use is necessary to develop more benign or efficient processes.

Table 2 Standard redox potential

Redox half-reaction	E⁰ (V)	Equation
$N_2 + 2\,H_2O + 4H^+ + 2\,e^- \rightleftarrows 2\,HONH_3^+$	-1.87	(1)
$Al^{3+} + 3e^- \rightleftarrows Al_{(s)}$	-1.66	(2)
$Fe^{2+} + 2e^- \rightleftarrows Fe_{(s)}$	-0.44	(3)
$N_2O + H_2O + 6H^+ + 4\,e^- \rightleftarrows 2\,HONH_3^+$	-0.05	(4)
$Cu^{2+} + 2e^- \rightleftarrows Cu_{(s)}$	+0.34	(5)
$O_2 + 2H^+ + 2e^- \rightleftarrows H_2O_2$	+0.70	(6)
$MnO_2 + 4H^+ + 2e^- \rightleftarrows Mn^{2+} + 2H_2O$	+1.23	(7)
$H_2O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O$	+1.76	(8)
$Co^{3+} + e^- \rightleftarrows Co^{2+}$	+1.93	(9)

Different reductants have been investigated to replace the use of H_2O_2, such as SO_3^-/SO_5^{2-} [49], methanol [50], glucose [58], and ascorbic acid [62] as well as some biomass such as tea waste [63]. Although all these compounds could act as reductants, the addition of extra compounds to the system could involve additional stages to remove them after the leaching process and an increase in chemical consumption. One alternative to avoid the addition of an external reductant for LIBs leaching is the utilization of metallic fragments that already exist in the battery wastes. In a LIB, the anode and the cathode are cast over a layer of Cu and Al foil, respectively, which act as current collectors.

Investigations by Peng et al. [51,71] proved that impurities of copper and aluminium could effectively improve the acid dissolution of target active materials. Joulie et al. [34] studied the reductive capability of these metals separately to dissolve $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$ (NMC) in an acidic media. The results reported an improvement in the leaching efficiencies of Co, Ni, and Mn from 40% to approximately 90% with the addition of metallic Cu to the leaching system. Meng et al. [64] obtained similar results when they studied the leaching of industrial spent LIBs scraps using citric acid. The solid was a mixture of anode, cathode (composed of NMC), electrolyte, and separator. They observed that the presence of Cu and Al in the initial solid promotes the leaching of metals, and about 91% Li, 90% Co, 94% Ni, and 89% Mn were extracted under the optimum leaching conditions (0.5 M citric acid, S/L ratio of 80 g/L, 90ºC, and 80 min). Porvali et al. [48] studied the dissolution of $LiCoO_2$ in a Cu-H_2SO_4 system catalysed by Fe (II)/Fe (III). In this case, Fe (II) was used to reduce Co (III), producing Co (II) and Fe (III), while metallic Cu was used to regenerate Fe (III) to Fe (II). With this system, the 95% of Co was extracted at 30ºC without the

addition of H_2O_2, and with a concentration of 2 M H_2SO_4, 1.06 g/L Fe (II) as catalyst, and 2.1 g of Cu per 6.68 g $LiCoO_2$ (S/L ratio of 16 g/L).

Besides the acid and reductant agent concentration, the S/L ratio is also an important parameter in the leaching process. It determines the concentration of metals in the leach liquor, the metal dissolution rate, and the process's overall efficiency. A higher S/L ratio generally leads to higher metal concentrations in the leach solution. However, it also results in more elevated reactants and energy consumption, and slower leaching rates. Several studies have investigated the effect of S/L ratio on the leaching of metals from LIB wastes. Gao et al. [46] collected the leaching parameters for the $LiCoO_2$ leaching process using different acids (inorganic and organic) to analyse the relationship between S/L ratio and acid concentration of the leaching process (**Figure 7**). They concluded that the leaching process with inorganic acid is mostly concentrated at 3-6 M with S/L ratios higher than 50 g/L, while for the organic leaching process, acid concentrations are generally only at 1-2 M with S/L ratio lower than 50 g/L. In other words, the cathode material treatment capacity per unit volume of inorganic acid solutions is much higher than that of the organic acid solution. From the industry perspective, S/L ratios are typically between 100 and 200 g/L. Currently, H_2SO_4 is the only available acid at industrial scale that can be used to operate at these S/L ratios with a concentration between 2-4 M. However, other acids, such as HCl or Citric acid, can be used to work at S/L ratios between 50 and 100 g/L, so exploring their use at different acid concentrations can be interesting in increasing the material treatment capacity of these acids' solutions.

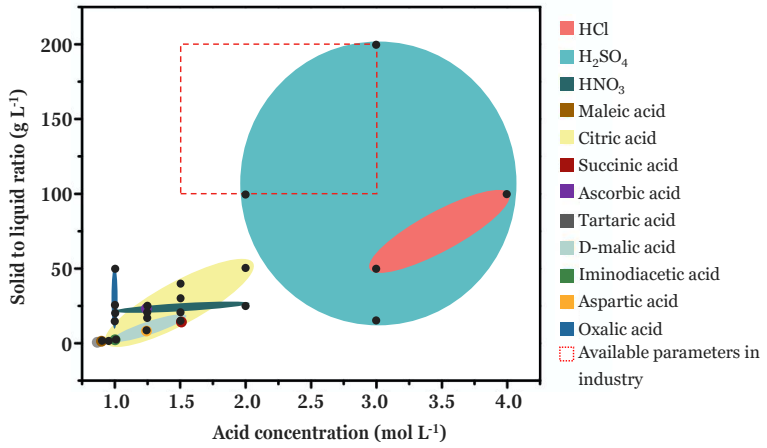

Figure 7 The relationship between S/L ratio and acid concentration of the leaching processes with different acids (Adapted from [46]).

The optimal S/L ratio depends on various factors, such as the type of LIB wastes, acid and reductant agents' concentration, leaching temperature, and time. Generally, a lower S/L ratio achieves a higher metal extraction efficiency within a shorter leaching time. However, excessively low S/L ratios may lead to inadequate contact between the solid material and the leaching solution, resulting in lower metal recovery rates. Furthermore, it is important to note that selecting an appropriate S/L ratio should also consider the process's economic feasibility and environmental impact. Lower S/L ratios may require larger volumes of leaching solution, resulting in increased costs for reagents, water, and waste treatment [31]. Therefore, a balance needs to be struck between the desired leaching efficiency and the economic and environmental aspects of the process.

The temperature is another parameter affecting the leaching process, and its optimization is key for the process efficiency. Temperature has a direct impact on reaction rates. Generally, higher temperatures accelerate chemical reactions, leading to shorter processing times and increased metal recovery [45]. Studies have demonstrated that higher temperatures (between 70-90ºC), combined with appropriate acid concentration and agitation, increase metal extraction rates. This phenomenon is attributed to the improved solubility of metals compounds and the enhanced kinetics of the leaching reactions. However, elevated temperatures involve higher energy consumption, making the process less sustainable. Therefore, energy efficiency van be maximized by processing at room temperature and atmospheric pressure. Several studies are focused on decreasing the activation energy of the leaching process, evaluating the use of catalysts [68], or implementing new stirred systems, such as ultrasound-assisted leaching, to enhance reactions at the solid-liquid interface [72,73].

As can be observed, several parameters influence the leaching process of metals from LIB wastes. The optimization of these parameters, as well as their interaction, is crucial to the development of the hydrometallurgical recycling process. In the last decade, this field has become a very popular research topic, and numerous papers are published weekly related to metals leaching from LIBs. However, there are still many aspects that need to be deeply studied. For example, although the leaching of LIBs cathode materials using different acids and reductant agents have already been studied, there is still a lack of information about the reactions in the process. That information could be used to design new reactor configurations or combine the leaching process with recovery steps, focused not only on maximizing the extraction percentage of metals but also on optimizing the use of reactants.

1.2.2 LIBs Leaching Kinetics

A deep understanding of the different reactions and mechanisms that take place during the leaching step is crucial to optimize the hydrometallurgical process. Particles dissolution involves heterogeneous reactions that only occur at the liquid/solid interface. It can form an insoluble layer around the particle if the work conditions are not appropriate. This crust passivates the particle, slowing the reaction rates and stopping the reaction [31]. In this context, different models have been proposed to describe the dissolution-extraction reactions through solid-liquid interactions. Among them, two of the most widely used are the shrinking core model (SCM) and the unreacted shrinking core model (USCM) [60,74–83].

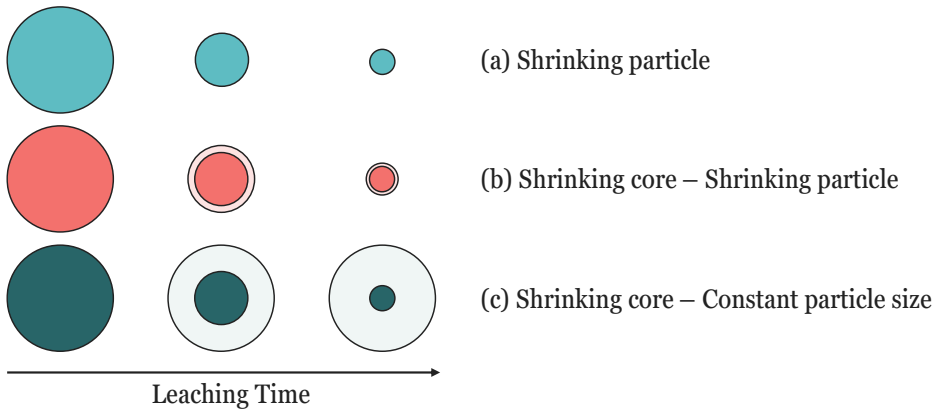

Figure 8 Schematic of different mechanism of leaching.

The SCM considers that the reaction takes place initially at the outer surface of the solid particle and involves the particle size decreasing as the products are formed. That way, the deeper areas of the solid take part in the reaction as they are exposed to the extracting fluid, which involves the constant movement of the reaction zone. The core and the size of the solid particles decrease during the reaction time until they are entirely consumed. These kinds of heterogeneous models consider the rate control mechanisms, from surface chemical reaction control, equation (10), to mass transfer control, equation (11):

$$\frac{t}{t^*} = 1 - (1 - X)^{\frac{1}{3}} \qquad \text{Chemical reaction control} \qquad (10)$$

$$\frac{t}{t^*} = 1 - 3(1 - X)^{\frac{2}{3}} + 2(1 - X) \qquad \text{Film diffusion control} \qquad (11)$$

On the other hand, the unreacted shrinking core model (USCM) considers the conversion of the reactant into another solid phase, which accumulates in the outer part of the particles. In this model, the size of the unreacted core decreases, but the overall particle size remains approximately constant [84]. Several studies have proposed the USCM to evaluate the leaching kinetics of the metals from LIBs [69,77,82,85].

From the comparison of experimental and theoretical results, Zhang et al. [81] concluded that SCM and USCM were not suitable to describe the leaching of metals from the cathode scraps. They also evaluated the kinetics of the leaching processes using the Avrami equation (12), which was initially proposed to describe crystallization kinetics and to give an indication of the crystal growth process.

$$-\ln(1-X) = kt^n \qquad \text{Film diffusion control} \qquad (12)$$

Although these models have been widely applied to study liquid/solid systems as leaching kinetics in hydrometallurgical processes, some assumptions within their formulation could not be valid in the dissolution-extraction of lithium metal oxide particles. For example, SCM and USCM models were developed to describe gas–solid systems assuming a sharp interface between the reactant and the product layer. This condition has been overlooked in models applied to leaching processes since microscopic examination should be required to determine whether there is a diffuse reaction zone or a definite product-reactant interface [86].

The evaluation of solid-liquid reaction kinetics has been carried out through modified models based on the SCM and USCM. Setiawan et al. [82] modified the SCM to include an equilibrium reaction to describe the kinetics of lithium and cobalt recovery from spent LIBs using acetic acid. The mathematical model was formulated based on the kinetic reactions that describe the leaching process. The model predicted well the effect of pH, H_2O_2 concentration, and S/L ratio on the recovery of metals from $LiCoO_2$.

Raschman et al. [87] developed an extended USCM which considers the influence of the S/L ratio, the non-ideal behaviour of concentrates aqueous solution, and the chemical reaction order. Gao et al. [83] studied the role of the reducing agent in the leaching kinetics of LIBs cathode scrap using acetic acid. In their work, the kinetic analysis was carried out using the standard SCM to determine the rate-controlling step in the absence and presence of H_2O_2 during the leaching process. Their results indicated that reducing agents can alter the rate-controlling step from residue layer diffusion to chemical control.

In the same line, Meshram et al. [49,79] studied the effect of the presence of a reducing agent on the leaching efficiency, emphasizing the kinetics aspects. The extractant agent used was H_2SO_4, while the reducing agent was $NaHSO_3$. At the same conditions (1 M H_2SO_4, 368 K, 50 g/L, and 4 hours), the percentage of metals extracted was 93.4% Li, 66.2% Co, 96.3% Ni, and 50.2% Mn in the absence of $NaHSO_3$ while the metal extracted percentage was 96.7% Li, 91.6% Co, 96.5% Ni and 87.9% Mn in the presence of $NaHSO_3$. Moreover, these results were found to follow the logarithmic raw law controlled by the surface layer diffusion of the lixiviant in the absence of a reducing agent, while the controlling step changed to chemical reaction when $NaHSO_3$ was used. It confirms again the need of a reductant agent to alter the rate-controlling step and improved the recovery efficiency.

Although numerous studies are focused on the determination of the rate-limiting step (film diffusion, chemical reaction, or residue layer diffusion) and their respective activation energy, there is a lack of studies that deal with the evaluation of the leaching kinetics of metals [83]. Therefore, the description of models based on the leaching reaction, considering the different parameters involved in the leaching (such as acid concentration, S/L ratio, and reductant concentration), could provide a better understanding of the reaction mechanisms during the process. The works above have motivated the development of a mathematical model in this thesis to determine not only the mechanism control rate but also to describe the different reactions during the leaching process.

Determining the leaching reactions and their kinetics rate could also help design new reactor configurations to avoid parasite reactions take place. Conventionally, the leaching of LIBs is carried out in batch reactors where the active materials are introduced together with the acid solution and reductant agent [30]. In this kind of reactor, controlling the side reactions that take place during the leaching process isn't easy. However, the formation of undesired by-products can be avoided using other reactor configurations, which can increase the selectivity of the desired reactions.

Selectivity quantifies the formation of product. It is defined as a ratio of product (P) formation rate to by-product or undesired product (U) formation rate. The most general form of simultaneous reaction mechanism and their general rate equations are:

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{P} \qquad \frac{d[\mathrm{P}]}{d\mathrm{t}} = k_P[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta} \tag{13}$$

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{U} \qquad \frac{d[\mathrm{U}]}{d\mathrm{t}} = k_U[\mathrm{A}]^{\gamma}[\mathrm{B}]^{\delta} \tag{14}$$

where k_P ($L^{(\alpha+\beta-1)} \cdot mol^{-(\alpha+\beta-1)} \cdot s^{-1}$) and k_U ($L^{(\gamma+\delta-1)} \cdot mol^{-(\gamma+\delta-1)} \cdot s^{-1}$) are the rate constants of product and byproduct reactions, respectively; α and β are the reaction orders for A and B in the product formation reaction, and γ and δ are the reaction orders for A and B in the byproduct formation reaction.

The selectivity of product formation can be described as:

$$S_P = \frac{k_P [A]^{\alpha} [B]^{\beta}}{k_U [A]^{\gamma} [B]^{\delta}} \tag{15}$$

As can be observed, the reaction order values determine the product formation's selectivity. **Table 3** summarizes the different reactor configurations that maximize the product selectivity based on the reaction's orders relation.

Table 3 Relation between reaction orders, selectivity, and reactor configuration [88]

Reaction orders relation	Selectivity expressions	Reactor configurations	Eq.
$\alpha = \beta$ $\gamma = \delta$	$S_P = \frac{k_P}{k_U}$	Batch reactor	(16)
$\alpha > \gamma$ $\beta = \delta$	$S_P = \frac{k_P [A]^{\alpha-\gamma}}{k_U}$	Batch reactor	(17)
$\alpha < \gamma$ $\beta = \delta$	$S_P = \frac{k_P}{k_U [A]^{\gamma-\alpha}}$	Semi-batch reactor	(18)
$\alpha < \gamma$ $\beta < \delta$	$S_P = \frac{k_P}{k_U [A]^{\gamma-\alpha} [B]^{\delta-\beta}}$	CSTR	(19)
$\alpha > \gamma$ $\beta > \delta$	$S_P = \frac{k_P \, [A]^{\alpha-\gamma} [B]^{\beta-\delta}}{k_U}$	Plug Flow	(20)

Batch reactors are used when the selectivity of the desired reaction is independent of all reactants' concentrations or when it is dependent on a high concentration of only one reactant. On the other hand, when there are two reactants (A and B), and the selectivity is maximized maintaining a low concentration of reactant A and a high

concentration of reactant B, the best choice for this process is a semi-batch reactor. In this case, the reactor would be charged with B and the reactant A would be fed at an appropriate rate to obtain a high selectivity. If both reactants must be kept at low concentration to maximize the selectivity, a CSTR would be the best choice. By contrast, if both reactant's concentration must be maintained as high as possible to maximize the selectivity, a plug flow reactor would be chosen instead of a batch or semi-batch reactor [88].

As aforementioned, describing the different reactions and determining their reaction rates is important to select the best reactor configuration, which maximizes the selectivity. Although batch reactors are the most used in hydrometallurgy, some studies have used semi-batch reactors to improve process efficiency and reduce reactant consumption. Larsson et al. [89] studied the effect of controlling the pH on the dissolution of NiMH batteries with the addition of acid (semi-batch) at the same rate as the reactions consume it. They found not only that the metals extraction percentage increased due to a better control of the leaching reactions but also the acid consumption was decreased and only a small exceed of acid was consumed with respect to the stoichiometric demands. It is an important aspect from the point of view of reactant consumption optimization. Semi-batch mode enables to operate at low acid concentrations, with the subsequent advantage that fewer reactants would be necessary to neutralize the solutions in the separation step (traditionally by precipitation). Hence, the controlling acid addition to the system would result in a more effective reactant use in the recycling process. To the best of the author knowledge, although previous studies have evaluated the use of low acid concentrations in the LIBs leaching process [68], the use of a semi-batch reactor has not been studied. This gap motivated the author to evaluate the effect of controlling additions of reactants on the metals leaching from LIBs cathodes.

1.2.3 Electrodialysis

Electrodialysis (ED) is as a membrane separation process in which ions are transferred from one solution to another through selective ion-exchange membranes using an electric field as the driving force [90]. ED is a mature technology in the field of brackish water desalination. In the last decades, the development of new membranes has allowed for extending their application into the food, drug, and chemical process industry, including wastewater treatment [91]. This extension also includes soil remediation and other solid matrices such as sewage sludge ash or marine sediments [92].

The working principle of ED consists of the migrations of cations and anions through cation-exchange membranes (CEMs) and anion-exchange membranes (AEMs), respectively, induced by an applied electric field set between a pair of electrodes. The mass and charge transport in electrolyte solutions and ion-exchange membranes are described with the same equations. Under an electric field, ions are mainly transported by electromigration. Diffusion transport becomes significant at the boundary layers, near the membranes and the electrodes, due to high concentration gradients. The coupling of these transport mechanisms is known as electro-diffusion and can be described by the Nernst-Plank transport equation, which considers the diffusive, electromigration and convective flux [93]. Moreover, the application of an electrical current between the electrodes promotes the dissociation of water at the electrode's surface:

Anode surface $$2H_2O \leftrightarrows 4H^+ + O_{2(g)} + 4e^- \quad (21)$$

Cathode surface $$2H_2O + 2e^- \leftrightarrows 2OH^- + H_{2(g)} \quad (22)$$

In a simple ED cell (**Figure 9**), a pair of membranes is used. The unit cell is formed by an AEM, a CEM, and a channel in between where the concentrated salt solution is fed. Anions migrate towards the anode, and cations towards the cathode, resulting in an overall decrease of the feed stream salt concentration. The two-membrane ED cell produces an acidic and a basic solution from the fed salt. The combination of several unit cells results in a multichannel cell, which produces diluted and concentrated outflows [94].

This technique is gaining attention to be applied in the field of LIBs recycling, specifically to separate and concentrate metals once the solid is dissolved. For this purpose, ED must be considered an emerging green process capable of recovering valuable metals from LIBs waste [95]. The main challenge of ED is the difficulty of

separating metal ions with similar charges due to the low selectivity of ion exchange membranes. To improve the process selectivity, several complexing agents, such as ethylenediaminetetraacetic acid (EDTA), citric acid, malic acid, and lactic acid, are used to form negatively charged complexes which can be separated from the cations. However, there are very few studies on applying ED for metal separation from spent LIBs [96].

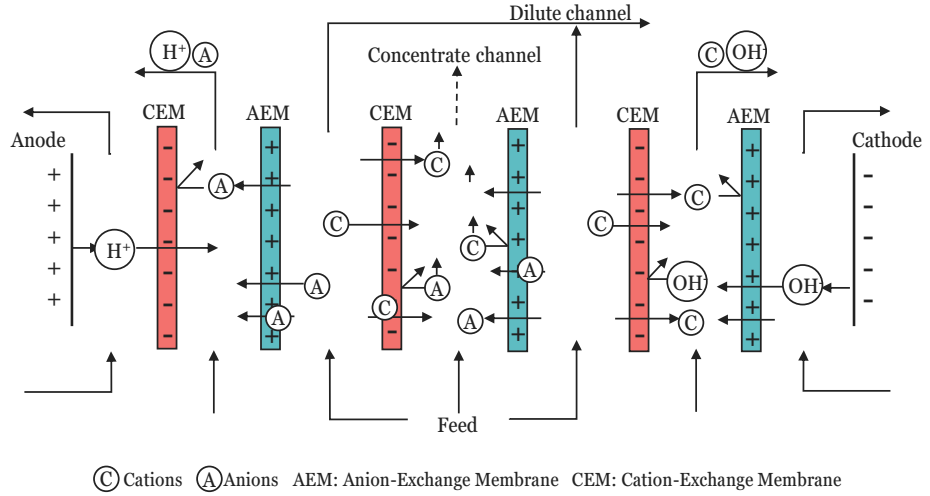

Figure 9 Configuration of a classical electrodialysis stack [94]

Xing et al. [97] and Iizuka et al. [98] proposed the addition of several chelating agents to improve the performance of the ED approach applied to the LIBs leachate solutions. The chelating agent's role depend on the aqueous effluent's transitional metal content. Basically, chelating agent involve creating negative complexes with the metal ions present in the solution, except for lithium ions. Thus, under the effect of the applied current, the lithium ions are separated from the metal complex ions, which recover in another cell compartment. The selectivity for each metal in the recovery cell was about 99%.

In a study conducted by Chan et al. [99], they investigated the separation and recovery of lithium, nickel, manganese, and cobalt from mixtures obtained from spent LIB. The process involved three stages of ED coupled with EDTA using an AEM (PCA PC 400D) and a CEM (Neosepta CMX). Different EDTA-metal complexes were formed in each stage based on the solution pH. Hence, in the first stage, with a solution pH around 2, EDTA formed complexes with Ni, and approximately 99.3% Ni was recovered in the Ni-EDTA compartment, while Co, Mn, and Li were collected at the metal compartment. In the second stage, the pH of the metal outflow from the

first stage was increased to 3, favouring the Co-EDTA complex formation. In this second stage, the 87.3% of Co was separated. Finally, in the third stage, 99% of Li was separated from manganese using a monovalent cation exchange membrane (Neosepta CMS). The study also includes EDTA decomplexation and purification processes to recover the pure metals. All recovered metals' purity were more than 99% pure.

Song and Zhao [100] studied the application of ED to concentrate lithium ions from low lithium and high salt solutions, usually produced in the LIBs recycling process. First, the solution was purified by adjusting the solution pH to 12 to remove the impurity metals. Then, lithium was precipitated by sodium phosphate. The solid obtained was again dissolved in acid as the anolyte, and the Li and PO_4^- were separated by ED with cation-exchange membranes (DuPont NAFION117). The lithium concentration of the catholyte solution was 22.5 g/L, and $NaCO_3$ was added to precipitate the Li as $LiCO_3$ product. This process allows the enrichment of lithium solution to facilitate the obtention of $LiCO_3$.

The development of membrane technologies has allowed new cell configurations, expanding the application of ED [101]. The use of monovalent exchange membranes (*i.e.,* membranes that only allow the passage of ions with one negative or positive charge) was used to selectively separate lithium from the rest of the metals in the leachate solution. Gmar et al. [102] investigated the efficiency of the ED process to recover selectively lithium (I) from cobalt (II), nickel (II), and manganese (II) using monovalent ion exchange membranes.

ED can also be used to generate acid and base solutions from the salt feed. Kang et al. [103] proposed employing ED to generate LiOH and H_2SO_4 from a Li_2SO_4 solution. The feed solution was a by-product of the LIBs hydrometallurgical process, where metals were leached with H_2SO_4 and precipitated using LiOH solution. A three-compartment ED cell was used, with a dilute channel where the Li_2SO_4 solution was introduced and two concentrate channels, one for H_2SO_4 and the other for LiOH solutions. The results indicated a high ions recovery ratio of Li^+ and SO_4^{2-} of 94.3% and 87.5% at a current density of 833 A m^{-2}. This proposal has a huge potential due to the electrogenerated acid and base could be reused in the recycling process, creating a close-loop process.

Although the ED is commonly used to operate with solution, it can also be applied to treat solid matrices or suspensions. The application of this technique to solids began to be studied in 1992 at the Technical University of Denmark (DTU), and it was patented in 1995 (PCT/DK95/00209) to improve the technique of electrokinetic remediation (EKR). Figure 10 (a) schematically illustrates the patented experimental

system. It consists of a three-compartment cell: anodic, central, and cathodic. The solid is placed in the central compartment and separated from the electrolytic compartments by ion exchange membranes. Between the anodic compartment and the central compartment, an anionic exchange membrane (AEM) is used to prevent the passage of cations from the anolyte to the solid matrix or suspension while allowing the passage of anions from the central compartment to the anolyte. Similar behaviour occurs in the cation exchange membrane (CEM) placed between the central and cathodic compartments, which allows the passage of positively charged species to the catholyte and prevents the passage of anions from the catholyte to the solid matrix or suspension.

Figure 10 (b) illustrates another ED cell configuration patented by the DTU (PCT/EP2014/068956). This cell is formed of two compartments, separated by a CEM. The solid suspension is in the anode compartment. This configuration allows the acidification of the compartment due to the water oxidation, promoting the mobilization of metals, and decreasing the amount of acid added to the system.

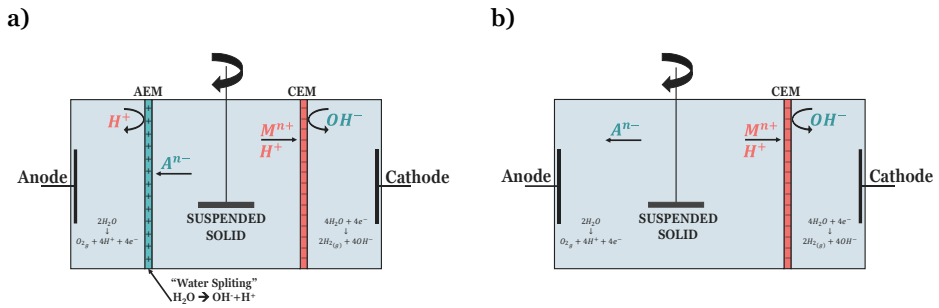

Figure 10 Experimental setup of a (a) 3 compartments and (b) 2 compartments ED cell to remediate solids in suspension.

This technique has been applied in numerous studies for the remediation of soils and solid matrices (*e.g.,* wood, marine sediments, fly ash, and mine tailing) contaminated by inorganic and organic pollutants at a laboratory scale [104–109]. The inorganic pollutants are divided into cationic metals (*e.g.,* lead and cadmium), anionic metals (*e.g.,* arsenic and chromium) and radionuclides (*e.g.,* strontium and uranium). Applying the electric current promotes the electromigration of ions through the soil or solid matrices [110], cleaning the solid matrices. Considering the characteristics of LIB wastes, a solid matrix containing metals, ED could be applied to extract and recover these metals.

Villen et al. [42] reviewed the state of the art of electrodialytic remediation techniques and analysed their potential to be applied in battery recycling. They

propose to connect the extraction step with the separation step to occur in parallel in an ED cell like that represented in Figure 10(b). The LIBs residue, once pretreated and crushed, would be placed in the anolyte compartment, where particles would be dissolved. At the same time, the dissolved metal ions would be continuously removed from the anolyte and sent to the catholyte compartment, where they would be collected. One of the advantages of this technique is the continuous acidification of the extraction medium due to the water oxidation, resulting in a decrease in the acid requirement. In the same study, the authors highlighted the need to optimize the most relevant parameters of this technique, such as the extracting agent, working pH, S/L ratio, energy density, cell configuration, or the type of stirring depending on the waste to be treated and the components to be recovered.

Diaz et al. [111] reported an electrochemical-based method for leaching metals from LIBs active materials. The process was performed in a two-compartment electrochemical cell separated by a bipolar membrane. In the catholyte compartment, the solid was placed with the Fe^{2+}, acting as a reducing agent (Fe^{3+}/Fe^{2+}). This cell configuration decreases the acid requirements since protons are produced electrochemically. On the other hand, the reducing agent Fe^{2+} can be regenerated at the cathode surface to be used again in the leaching medium. A membrane was used to avoid the oxidation of Fe^{2+} to Fe^{3+} at the anode surface. With this design, leaching efficiencies of over 96% for Li, Co, Mn, and Ni were achieved, with a pulp density of 240 g/L and a low concentration of mineral acid. Moreover, the process can reduce the cost of chemicals and energy by 80% compared to peroxide hydrometallurgical leaching.

Electrochemical leaching and ED have the potential to be applied in LIBs recycling processes, not only to enhance the extraction yield but also to decrease the chemical and energy consumption of the process. Nevertheless, optimizing the technique must be addressed to make it competitive at an industrial scale.

1.3 Objectives of this Thesis

This thesis aims to widen the current state of the art on the hydrometallurgical recycling process of LIBs to advance to a more sustainable process. The main objective of this thesis is to investigate and optimise the extraction of metals from LIBs cathodes and contribute to the development of some of the principles of circular hydrometallurgy. After analysing the state of the art, a series of specific objectives were proposed to provide, during the development of this thesis, contributions that would enable overcoming the main objectives. The specific goals defined in this thesis are the following:

- To investigate a combined hydrometallurgical-electrodialytic method for the selective recovery of lithium and cobalt from LIB cathodes, specifically focusing on integrating the extraction and separation in a single step as well as promoting the generation of protons required in the reaction by water electrolysis.
- To develop a physicochemical model to describe the leaching of cobalt and lithium from $LiCoO_2$ cathodes under acidic conditions, evaluating the effect of the particle's passivation on the leaching efficiency.
- To compare the $LiCoO_2$ leaching process in the absence and presence of a reductant agent (H_2O_2), extending the physicochemical model defined previously to understand the controlling mechanisms of the extraction process and predict the metal extraction yield in the absence and presence of the reductant agents.
- To study the effect of the controlled addition of acid and reductant agent to the $LiCoO_2$ leaching system using a semi-batch reactor, focuses on maximizing the selectivity of desired leaching reactions and metals extraction percentage and minimizing the reactant consumption.
- To assess the use of citric acid and copper as benign chemicals for the selective recovery of valuable metals from LIB wastes, evaluating its influence in the leaching process efficiency and their potential to form citrate-metals complexes.

The contributions of this thesis according to these individual objectives are presented in an orderly manner in each of the papers that comprise this thesis.

1.4 Published works.

1.4.1 Appended papers

The results obtained during this PhD project have been collected in the following scientific papers:

- Cerrillo-Gonzalez, M.M. et al. (2020). Recovery of Li and Co from $LiCoO_2$ via Hydrometallurgical–Electrodialytic Treatment. *Applied Sciences*, 10(7), 2367. (Reference [112]).
- Cerrillo-Gonzalez, M.M. et al. (2020). Hydrometallurgical Extraction of Li and Co from $LiCoO_2$ Particles–Experimental and Modeling. *Applied Sciences*, 10(18), 6375. (Reference [113]).
- Cerrillo-Gonzalez, M.M. et al. (2022). Acid leaching of $LiCoO_2$ enhanced by reducing agent. Model formulation and validation. *Chemosphere*, 287, 132020. (Reference [114]).
- Cerrillo-Gonzalez, M.M. et al. (2024). Semi-batch reactor for leaching battery cathodes under low acid concentration. *Hydrometallurgy (submitted)*.
- Cerrillo-Gonzalez, M.M. et al. (2024). Extraction and selective separation of metal ions from $LiCoO_2$ cathodes using citric acid. *Journal of Power Sources*, 592, 233870. (Reference [115]).

1.4.2 Additional paper

During this PhD thesis, an additional paper has been published. Although it is not part of the thesis, it is considered important for a better understanding of electrodialysis technology.

- Cerrillo-Gonzalez, M.M et al. (2023). Metals separation from wastewater using electrodialysis technique. *Metals*, 14, 38. (Reference [116]).

2 Experimental Methods

This chapter describes the common materials and experimental methods used in the different papers that support this thesis, which can be divided into two main groups: extraction and electrodialytic experiments. More details of specific experimental methods can be found in each paper.

2.1 Solid

The solid used in all the papers that support this thesis was a commercial lithium and cobalt oxide (97% $LiCoO_2$, Alfa Aesar), as it is the most widely used material for manufacturing cathodes in LIB and, consequently, one of the most abundant materials in their waste [117]. It was decided to use this commercial solid instead of a real battery waste to reduce the number of metals to be recovered, thus facilitating the study of the leaching process.

$LiCoO_2$ is a crystalline solid with a laminar structure and a molecular weight of 97.52 g/mol, consisting of 60.5 %w/w cobalt (III) and 7.12 %w/w lithium. This compound is insoluble in water, so acids or extracting agents will be needed to dissolve it.

2.2 Metal Extraction Experiments

Extraction experiments were carried out to evaluate the influence of different parameters on metal dissolution from $LiCoO_2$ cathodes. Some parameters studied during this thesis have been the acid and reductant agent concentration, the temperature, and the S/L ratio. In a preliminary step, different inorganic acids such as H_2SO_4, HCl, and HNO_3 were evaluated, being the HCl the acid with the best

extraction yield. Therefore, HCl (37%, analytical grade, PanReac) was selected as the extractant agent for the different studies in the papers 1, 2, 3 and 4. On the other hand, in paper 5, citric acid (1-hydrate, PanReac) was selected to act as extractant agent. Regarding to the reductant agent, H_2O_2 (30%w/v) was chosen in papers 3 and 4, while copper (99% Sigma Aldrich) was used in paper 5. **Table 4** collects the different experimental conditions studies in each paper.

Table 4 Extraction experiment conditions

Paper	Extractant agent	Reductant agent	S/L (g/L)	T (ºC)	Leaching time	Reactor mode
1	0.1 M HCl	-	5	25	6 days	Batch
2	0.1 M HCl	-	5	25	150 h	Batch
	2.5 M HCl		50		1 h	
3	0.5-2.5 M HCl	0-0.25 M H_2O_2	50	25	9 days	Batch
4	0.01-0.2 M HCl	0.25-1 M H_2O_2	50	25	1 h	Semi-batch
5	0.5-2 M H_3Citrate	Cu	50	30-90	24 h	Batch

Most leaching test were performed at 25ºC in a 0.5 L glass reactor equipped with a magnetic stirrer (**Figure 11.a**). Moreover, in paper 4, where the use of a semi-batch reactor was studied, the same glass reactor was sealed with four-necks ground-glass lids containing a pH electrode, an HCl inlet, an H_2O_2 inlet and a sampling port (**Figure 11.b**). Throughout the semi-batch mode tests, the pH was measured and controlled to ensure that solution maintained constant acid concentration. For that, a 3 M HCl solution was continuously fed into the reactor to supply the protons consumed in the leaching process.

On the other hand, in paper 5, the experimental system was changed due to the leaching system needed to be heated (30-90ºC). In that case, the leaching experiments were carried out in 500 mL Erlenmeyer flasks installed inside a shaker bath to keep the suspension mixed and to control the temperature. Erlenmeyer flasks were sealed to avoid mass loss during the reaction (**Figure 12**).

The experimental procedure was the same in the three leaching configurations: a certain mass of $LiCoO_2$ was added to 100 mL of acidic solution. The mass of $LiCoO_2$ depends on the S/L ratio selected. During the leaching time, samples were collected from the reactor at different times to obtain a transient profile to study the leaching rate. All samples were filtered using a 0.6µm glass fiber (Macherey-Nagel GF-3) to remove the solid. At the end of the experiments, the suspension was filtered with a

vacuum filtration assembly (Boeco R-300), and the leached residue was dried at 70ºC for 24h. Regarding the liquid phase, the filtrate was collected to quantify the final volume of the solution.

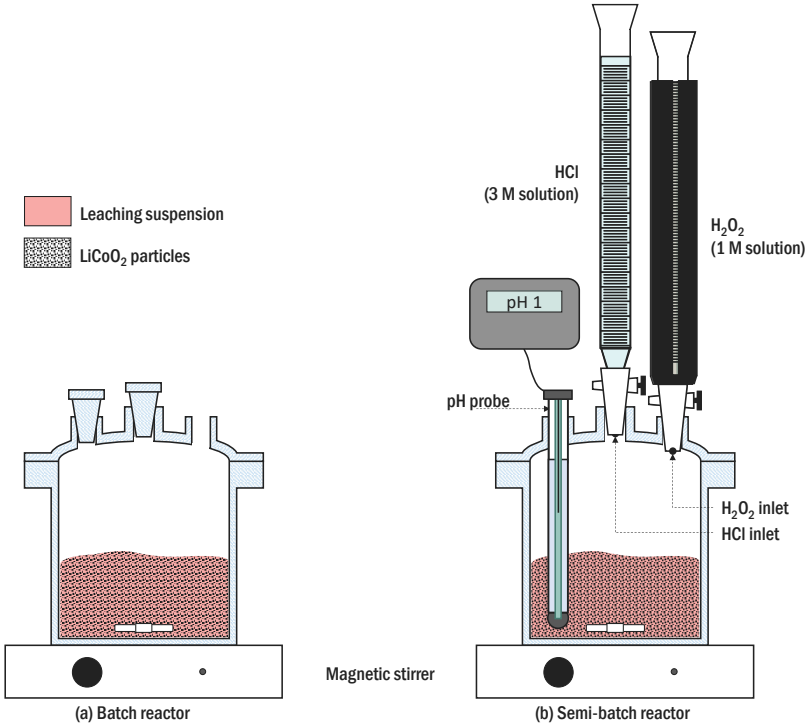

Figure 11 Leaching reactor (a) Batch system (b) Semi-batch system with pH control.

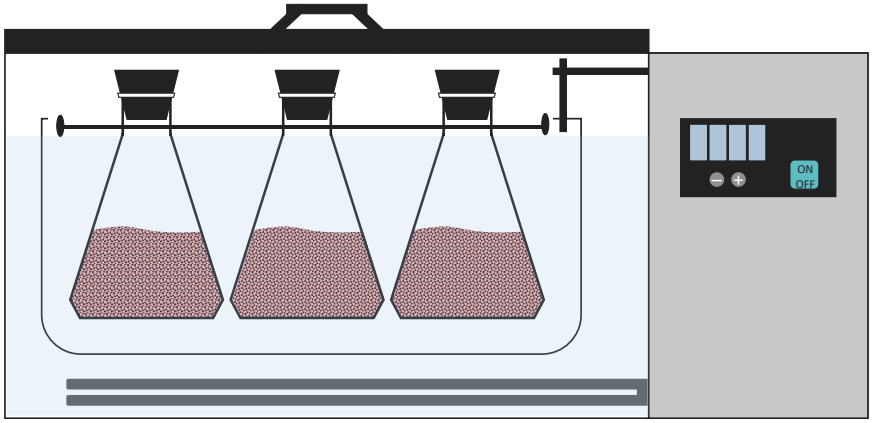

Figure 12 Leaching experiment in a shaker bath with temperature control.

2.3 Electrodialytic experiments

Paper 1 focused on using electrodialysis to combine, in a single step, the extraction and separation of metals from the $LiCoO_2$ cathode. The experimental setup designed is represented in Figure 13, and it consisted of a three-compartment electrodialytic cell using cation exchange membranes (CEMs) to separate the central compartment from both electrode compartments (anode and cathode). Moreover, the central compartment was connected to an external vessel where the solid dissolution was performed. A separatory funnel was introduced between the external vessel and the central cell compartment to ensure that only the liquid was recirculated. The conical shape of the separatory funnel helps the solid particles not to follow the liquid phase containing the extracted metals, preventing the membranes from fouling.

Meanwhile, the liquid with soluble metals (in this case, Co^{2+} and Li^{+}) flowed through the central compartment. Under the influence of the applied electric field, the soluble metals migrated to the cathode compartment, passing through the membrane. Moreover, protons were produced by water electrolysis at the anode surface, which also migrated to the central compartment resulting in a reactant regeneration in the central compartment.

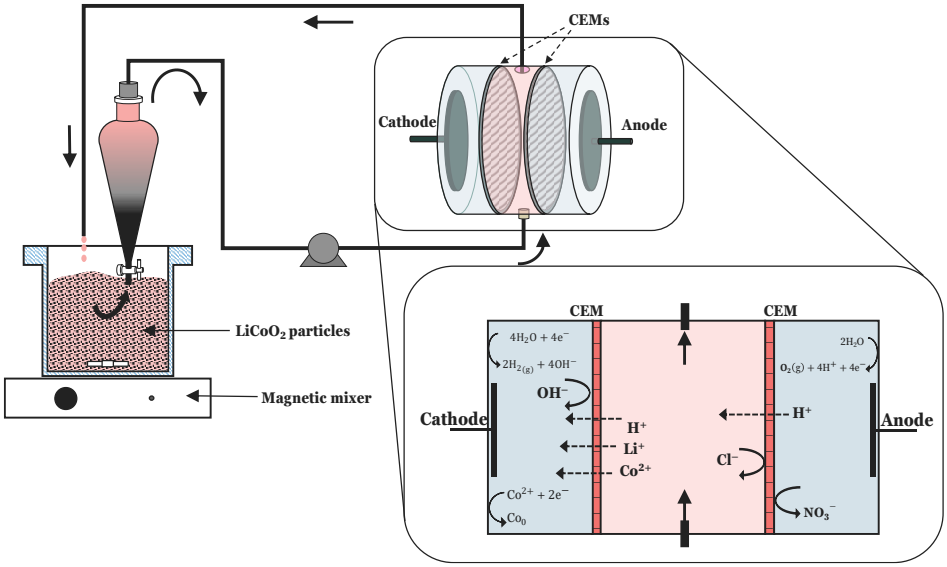

Figure 13 Experimental ED set-up scheme

Each ED cylindrical cell was built using three methacrylate compartments (4 cm length and 8 cm internal diameter). The external vessel was initially charged with 350 mL of 0.1 M HCl solution, and the solution was continuously recirculated to the

central compartment. The flow rate was 0.2 mL s^{-1}, optimized to ensure the undissolved particles' retention in the separatory funnel. The catholyte solution was also 0.1 M HCl, while the anolyte solution was HNO_3 to avoid the oxidation of chloride ions to chlorine gas. Once all the solutions were charged in their respective compartment, 1.75 g of $LiCoO_2$ was added to the external vessel (*i.e.,* the S/L ratio was 5 g/L), and the suspension was stirred. The experiments were performed at a constant current of 50 mA using a DC power supply unit (Genesys RDK Lambda GEN 600-2.6), corresponding to a current density of 1 mA cm^{-2} referred to the internal diameter of the ED cell. During the experimental time (a total of 6 days), liquid samples of 10 mL from the catholyte and central compartment were withdrawn to analyse the metal concentration.

2.4 Analytical methods

Different analytical methods have been employed in this PhD thesis. **Table 5** collects these analytical techniques, indicating the paper where they were employed.

The most used analytical method has been the atomic absorption spectrophotometry (ASS, Agilent 55AA) for metal quantitative analysis in aqueous solutions. Before the analysis, samples obtained during the experiments were filtered using 0.6 μm glass-fiber (Macherey-Nagel (MN) GF-3, Düren). Once metal concentration was determined, the percentage of metal solubilized respect to the initial amount of metal in the solid sample was determined according to Eq. (23):

$$x_{t,i}(\%) = \frac{C_{t,i}V_t}{m_{0,i}}x100 \tag{23}$$

where $x_{t,i}$ (%w/w) is the percentage of metal dissolved, $C_{t,i}$ (mg L^{-1}) is the dissolved metal concentration (analysed by AAS), V_r (L) is the solution volume, and $m_{0,i}$ (mg) is the initial amount of metal in solid sample. All results were obtained considering the volume change due to the sampling and evaporation.

The total content of metal in the solid samples was determined by microwave-assisted acid digestion following the guidelines of the EPA method 3051A: a representative sample of up to 100 mg was dissolved in 9 mL concentrated nitric acid and 3 mL concentrated hydrochloric acid for 10 min using microwave heating.

The pH of samples was measured by a pHmeter (HACH sensION pH 3, Spain). Moreover, in cases where the acid concentration was higher than 1 M, the concentration of hydroniums in the initial and final leaching solution was determined by acid-base titration (Phenolphthalein, NaOH 1 M).

Regarding to the solid characterization, X-ray photoelectron spectroscopy (XPS) was used to study the surface properties of the solid matrix before and after experiments. The XPS measurements were performed with a Physical Electronics PHI 5701 spectrometer with a multi-channel hemispherical electron analyser. Samples of solid before and after extraction were mounted on a sample holder without adhesive tape and kept overnight at a high vacuum in the preparation chamber before being transferred to the analysis chamber for testing.

Another solid analytical technique employed was the CHN technique to quantify the amount of carbon and hydrogen contained in the solid precipitated during some of the leaching experiments of paper 5 (*i.e.,* using citric acid as an extractant agent). Moreover, those solid samples were also characterized by FTIR-ATR (6800FV Jasco, Japan) and UV–Vis analyser (Cary7000 Agilent, Australia) to determine the possible formation of cobalt-citrate complexes.

Table 5 Analytical techniques used in this thesis.

Analytical Technique	Purpose	Paper
Atomic Absorption spectrophotometry	Metals concentration	1,2,3,4,5
pH meter	pH/H^+ concentration	1,2,3,4,5
X-ray photoelectron spectroscopy	Solid surface characterization	1,2,3
CHN	Carbon, Hydrogen, Nitrogen quantification	5
FTIR-ATR	Cobalt-citrate complexes determination	5
UV-Vis	Cobalt-citrate complexes determination	5

3 Global Results and Discussion

This chapter presents the global results and discussions obtained during this PhD project. With the aim of facilitating the discussion of the results, a summary of each paper that supports this thesis is presented in the following subsection. Emphasis is placed in the discussion of the results since the results have already been shown in the published papers listed below:

- Paper 1: Recovery of Li and Co from $LiCoO_2$ via Hydrometallurgical–Electrodialytic Treatment.
- Paper 2: Hydrometallurgical Extraction of Li and Co from $LiCoO_2$ Particles–Experimental and Modelling.
- Paper 3: Acid leaching of $LiCoO_2$ enhanced by reducing agent. Model formulation and validation.
- Paper 4: Semi-batch reactor for leaching battery cathodes under low acid concentration.
- Paper 5: Extraction and selective precipitation of metal ions from $LiCoO_2$ cathodes using citric acid.

3.1 Recovery of Li and Co from $LiCoO_2$ via Hydrometallurgical-Electrodialytic Treatment

In this first work, the combination of hydrometallurgy with the electrodialysis technique was proposed to extract and recover metals from the $LiCoO_2$ particles simultaneously. The experimental setup designed (**Figure 13**) consisted of a three-compartment electrodialytic cell using cation exchange membranes (CEMs) to separate the central compartment from both electrode compartments (anode and cathode). Moreover, the central compartment was connected to an external vessel where the solid dissolution was performed. The suspension was filtered before recirculating into the cell compartment to avoid membrane fouling.

The results obtained in this paper indicated that the combined hydrometallurgical-electrodialytic cell allowed the extraction of lithium and cobalt from the particles and their recovery in the catholyte solution. Once the metals were solubilized in the external vessel (in that case, Li^+ and Co^{2+}) and the solution passes through the central compartment, the soluble metals were transported to the cathode compartment under the influence of the applied electric field. Furthermore, a fraction of cobalt was found to be electrodeposited at the cathode surface, while the lithium remained in the catholyte solution. Therefore, It enables the separation of the metals from the catholyte solution. In addition to the simultaneous extraction and recovery step, this cell configuration also allows the regeneration of the protons consumed during the particle's dissolution, thanks to the water electrolysis. Thus, the protons produced in the anode migrated to the central compartment to be used in the leaching process.

However, the process was limited by the particle's dissolution. After six days of experiments, only 33% of Co and 62% of Li contained in the initial solid were extracted. Moreover, it was found that soluble metals were distributed in the different compartments of the cell. Thus, at the end of the experiment, only 16% of Co and 30% of Li extracted were transported to the catholyte compartment. Increasing the applied current could enhance the electromigration. However, it would also implicate more protons generation at the anode and subsequent transportation from the anode to the central compartment, competing with Li^+ and Co^{2+} to be transported to the catholyte. Hence, before optimizing the applied current, it is necessary to investigate the dissolution of particles to increase the percentage of metals extracted.

Therefore, the kinetic of $LiCoO_2$ particle dissolution was also studied in the first stage of this work. For that, batch extraction experiments used a 0.1 M HCl solution as an extracting agent with a S/L ratio of 5 g/L (the same initial conditions as in the

electrodialytic cell experiments). The kinetics of particle dissolution were found to be moderately slow, and after three days, no more than 30% of Co and 60% of Li were extracted. Like the electrodialytic experiments, a non-equimolar proportion between Li^+ and Co^{2+} was observed, with the concentration of Li^+ approximately twice that of Co^{2+}. Moreover, the low pH of the suspension at the end of the experiment indicated that protons were still in the medium to continue the reaction. These results suggested that there were some limitations in the dissolution steps that stopped the leaching process.

The XPS analysis of the solid particles' surface before and after extraction revealed that the composition of surface particles was consistent with the $LiCoO_2$ stoichiometry before the extraction. In contrast, only cobalt oxides were present at the surface after extraction. These results confirmed the presence of an external passive layer. The decomposition of $LiCoO_2$ involves the reduction of Co^{3+} to soluble Co^{2+}. Without a strong reductant agent, the process is limited by this redox reaction, forming a Co_3O_4 crust around the unreacted core when Li is extracted from the particles. It could explain the non-equimolar proportion between Li^+ and Co^{2+}. Moreover, this passive layer hinders the diffusion of reactants from the solution to the unreacted core, slowing the reaction until it is finally stopped. The use of higher acid concentration and reductant agents could enhance the extraction yield due to the elimination of the passive Co_3O_4 layer.

Overall, this work highlights the potential of the proposed method that combines hydrometallurgical extraction with electrodialytic cells for selective recovery of Li and Co from LIB wastes. However, the techniques must be optimized to be more efficient and yield higher extraction. Considering that the dissolution step was the limited factor of the process, it was decided to continue the research in the direction of studying the reactions involved in this step. The reaction mechanisms of $LiCoO_2$ dissolution in acid media and the absence and presence of a reductant agent are presented in the following papers.

3.2 Hydrometallurgical Extraction of Li and Co from $LiCoO_2$ Particles-Experimental and Modeling

The study of the reaction mechanisms involved in the extraction of metals from battery wastes is essential to optimize the selectivity and efficiency of the process. Different solid-liquid heterogeneous models, such as the shrinking core model (SCM), unreacted shrinking core model (USCM), and Avrami model, have been previously proposed to evaluate the reaction kinetics of these reactions. Although these models can satisfactorily fit the experimental observation, they cannot describe the physicochemical particularities of the process. Moreover, these models do not deal appropriately with the limitations observed in the previous paper (Li:Co extraction in a proportion of 2:1 and limiting Li extraction to around 65%). Hence, in this paper, a physicochemical model was proposed with the aim of increasing the understanding of the leaching process.

The model was described using the stoichiometric reported in the bibliography and considering the formation of an insoluble crust of Co_3O_4 around the unreacted $LiCoO_2$ core, detected through XPS analysis in our previous work. The dissolution reactions of $LiCoO_2$ particles in acid media in the absence of a strong reductant agent can be described following Eq. (24). This reaction considers that the dissolution of $LiCoO_2$ produces Li and Co in a proportion of 2:1 as well as the formation of the outer layer of Co_3O_4 in the external surface of $LiCoO_2$ core.

$$LiCoO_{2(s)} + 2H^+ \rightarrow Li^+ + \frac{1}{2}Co^{2+} + \frac{1}{6}Co_3O_4 + H_2O + \frac{1}{6}O_{2(g)} \quad (24)$$

The proposed model is formulated as a variation of the unreacted shrinking core model, depicted in **Figure 14**. It is assumed that particles are spherics with a core radius decreasing during the reaction time, while the particle's radius remains constant due to the formation of an outer crust around the unreacted core. As the reaction proceeds, the Co_3O_4 crust increases, hindering the diffusion of the protons through the layer. At a certain thickness of the crust, the process reaches a point in which the rate of proton diffusion is lower than the chemical kinetic consumption. Therefore, the model considers the switch in the controlling reaction mechanism from chemical kinetics to mass transfer. The Li^+ and Co^{2+} production rate and H^+ consumption is determined based on the protons concentration and the unreacted $LiCoO_2$ core radius. Moreover, another expression is proposed to calculate the reaction rate when the rate is controlled by the diffusion.

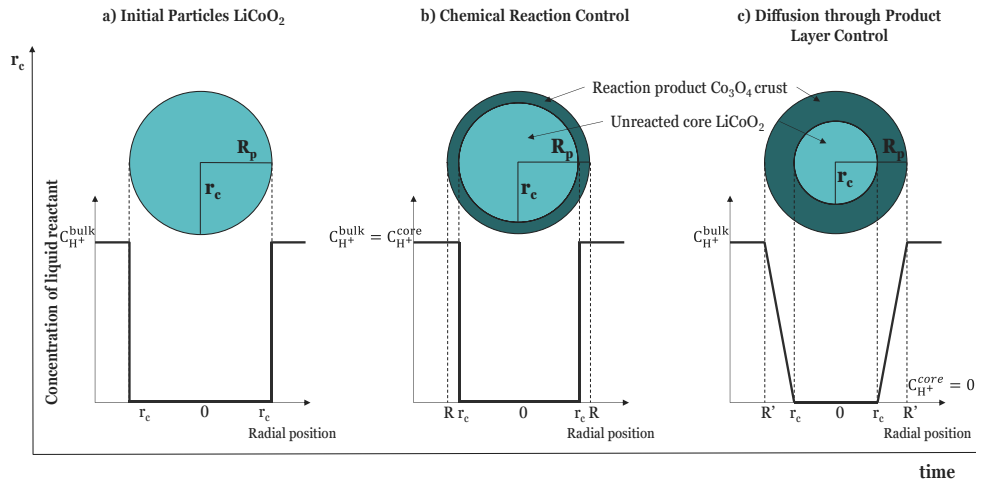

Figure 14 Time transition of $LiCoO_2$ particles radius core (a) Initial particle (b) Process rate controlled by chemical kinetics and (c) Process rate controlled by the diffusion through the outer layer.

Two set of experiments at different conditions were carried out to validate the model results. The first one with a 0.1 M HCl solution and a S/L ratio of 5 g/L, and the second one, with a solution of 2.5 M HCl and a S/L ratio of 50 g/L. It was obtained that the model satisfactorily reproduces the experimental observations. Moreover, the model accurately predicts the non-equimolar proportion between Li^+ and Co^{2+} extracted and the maximum extraction limitation associated with the formation of the Co_3O_4. In both experiments, the maximum percentage of Li^+ and Co^{2+} extracted were around 65-70% and 31-35%, respectively. The model also predicts the switch of process rate control from chemical kinetics to mass transfer as proton diffusion resistance increases with the crust's thickness. It can be confirmed that the process is limited by the formation of a layer around the unreacted core that slows down the reaction until it is stopped.

In summary, the model provides a good understanding of the leaching process and predicts the limitations of the hydrometallurgical treatment of $LiCoO_2$ cathodes from LIBs. Although the model is focused on $LiCoO_2$ cathodes, it can be extended to other cathode chemistries and extracting agents. Nevertheless, other parameters influencing the leaching process, such as the use of reductant agents and temperature, need to be included in the model with the aim of optimizing the hydrometallurgical process.

3.3 Acid leaching of $LiCoO_2$ enhanced by reducing agent. Model formulation and validation

This work extends the physicochemical model formulated in the previous study. Since the $LiCoO_2$ leaching process involves the reduction of Co^{3+} to soluble Co^{2+}, the presence of a strong reductant agent can improve the leaching yield, avoiding the formation of the Co_3O_4 outer crust. Accordingly, this study evaluates the effect of adding an external reductant agent on the leaching reactions. The reductant agent selected was H_2O_2, one of the most used in hydrometallurgy because it does not introduce additional ions to the system. Although H_2O_2 is widely known as an oxidizing agent, the high reduction potential of Co^{3+} justified its use as a reductant agent in that case.

The model was based on the same assumptions that in the previous work: spheric particles with a decreasing unreacted core; the formation of a Co_3O_4 crust around the core which increases the resistance to the diffusion of the species; and the switch from chemical kinetics to diffusion transport controlling mechanisms. The chemical reactions used to formulate the model were the following:

$$r_1 \qquad LiCoO_{2(s)} + 2H^+ \rightarrow Li^+ + \frac{1}{2}Co^{2+} + \frac{1}{6}Co_3O_4 + H_2O + \frac{1}{6}O_{2(g)} \qquad (25)$$

$$r_2 \qquad Co_3O_{4(s)} + 6H^+ \rightarrow 3Co^{2+} + 3H_2O + \frac{1}{2}O_{2(g)} \qquad (26)$$

$$r_3 \qquad LiCoO_{2(s)} + 3H^+ + \frac{1}{2}H_2O_2 \rightarrow Li^+ + Co^{2+} + 2H_2O + \frac{1}{2}O_{2(g)} \qquad (27)$$

$$r_4 \qquad Co_3O_{4(s)} + 6H^+ + H_2O_2 \rightarrow 3Co^{2+} + 4H_2O + O_{2(g)} \qquad (28)$$

where the dissolution of $LiCoO_2$ particles was described by the reaction (25) and (27). In the presence of H_2O_2, both reactions take place simultaneously. The use of H_2O_2 not only enhances the dissolution of $LiCoO_2$, avoiding the formation of the Co_3O_4 layer but also promotes the dissolution of the crust formed during the leaching. Therefore, the reactions (26) and (28) were also considered in the model to describe the dissolution of the Co_3O_4 crust.

To validate the model and estimate the model parameters, a set of 12 extraction experiments were carried out, varying the concentration of acid (0.5-2.5 M HCl) and H_2O_2 (0-0.6 %v/v). Experimental results showed that the model can predict the extraction percentage of Co^{2+} and Li^+ for a wide range of conditions, as well as they

are aligned with the assumptions of the model. The presence of H_2O_2 seems to decrease the effect of the formation of the Co_3O_4 crust. It is reflected in the extraction percentage proportion of Li and Co. In the absence of H_2O_2, it was near 2:1, while in the presence of H_2O_2, it was 1:1. Moreover, the change in the tendency of the extraction rate associated with the change of control mechanism was observed before in the experiments without H_2O_2 than in the experiments with H_2O_2.

The addition of H_2O_2 to the leaching process not only accelerates the reaction rates, promoting higher extraction yields but also influences the controlling reaction mechanism. The previous paper discussed that the leaching reaction mechanism can switch from kinetics to mass transfer depending on the thickness of the outer Co_3O_4 crust. The leaching process is initially controlled by the chemical kinetics, being the reaction rates determine by the reactions rate constant and reactants concentration. As the leaching proceeds and the crust Co_3O_4 forms, the diffusion of reactants through this crust becomes the rate-limiting step. Therefore, the use of reductant agent enhances the leaching process because it does not react only with the $LiCoO_2$, but also with the Co_3O_4 crust, which decreases its thickness. In other words, the use of H_2O_2 promotes that the chemical kinetic rate controls the process.

The extended model presented in this paper can be used to optimize the extraction process of $LiCoO_2$ due to it enables to predict the extraction yields under different experimental conditions. Different scenarios can be simulated to identify the optimal conditions for maximizing the extraction of Li and Co from $LiCoO_2$ particles, helping to design efficient and sustainable recycling processes for LIBs. Although the model was focused only on the dissolution of $LiCoO_2$, the model can be extended to study the dissolution of different materials using different extractant and reductant agents, which will be addressed in future works.

3.4 Semi-batch reactor for leaching battery cathodes under low acid concentration

In this study, the use of a semi-bath reactor was proposed to enhance the leaching process of $LiCoO_2$ particles. Traditionally, the leaching of LIBs has been carried out in batch reactors where the active materials and reactants are introduced together and mixed until the leaching yield is reached. However, in this kind of reactor, controlling the side reactions involved in the process is not easy.

Based on our previous work, where the $LiCoO_2$ leaching mechanism was studied, it was demonstrated that different reactions took place simultaneously during the particle's dissolution in the presence of H_2O_2. One of the reactions resulted in the formation of an insoluble crust of Co_3O_4 that limited the process. In terms of efficiency and productivity, the system would be ideal if only the reaction that totally dissolves the particles *(i.e.* r_3 Eq.(27)) took place due to subproduct Co_3O_4 would not appear. Considering the reaction rates proposed in the previous work, the selectivity coefficient between the two main reactions (r_3 and r_1) could be defined as follows:

$$S = \frac{r_3}{r_1} = \frac{k_3}{k_1} \cdot \frac{\left(\frac{n_p 4\pi r_c^2}{V_r}\right)[H^+_{core}]^{1/3}\,[H_2O_2]^2}{\left(\frac{n_p 4\pi r_c^2}{V_r}\right)[H^+_{core}]} = \frac{k_3}{k_1} \cdot \frac{[H_2O_2]^2}{[H^+_{core}]^{2/3}} \qquad (29)$$

where k_1 and k_3 are the reaction constant of r_1 (Eq.(25)) and r_3 (Eq.(27); r_c is the unreacted core radius (m); n_p is the number of particles (-); V_r is the reaction volume (m^3); $[H_2O_2]$ is the hydrogen peroxide concentration (mol m^{-3}) and $[H^+]$ is the protons concentrations (mol m^{-3}). Thus, according to this expression, selectivity will be maximized by maintaining high H_2O_2 concentration and low H^+ concentration. However, operating at low acid concentration in a batch reactor is difficult due to the high number of protons required to dissolve the particles.

In order to enhance the selectivity of the process, a semi-batch reactor was suggested to carry out the leaching of $LiCoO_2$. In this kind of reactor, the reactants are intermittently or continuously fed to the system. Therefore, this configuration could allow to operate at low acid concentrations due to protons are supplied to the system based on its consumption.

With the aim of optimizing the $LiCoO_2$ leaching process in semi-batch mode, several experiments were performed varying the initial acid and H_2O_2 concentration, the most influential parameters in the process selectivity. In all the experiments, the

pH was maintained constant by adding the protons consumed in the leaching process.

The hypothesis proposed to maximize the selectivity coefficient was confirmed based on the experimental results. On one hand, it was found that H_2O_2 concentration plays an important role in the leaching process selectivity: the higher the H_2O_2 concentration, the faster the reaction rate and the higher the percentage of metal extracted. It aligns with the selectivity expression and reaction rate of r_3, both depended on H_2O_2 concentration at the square.

On the other hand, comparing a batch and a semi-bath process under the same experimental conditions demonstrated that low acid concentration enhances the leaching yield (from 50% to 70%). The only difference between both experiments was the protons feeding to the system. The batch reactor was loaded with an initial 1.5 M HCl solution, while the semi-bath was charged with an initial 0.2 M HCl solution, which remained constant by adding the required protons. Hence, the semi-batch reactor can operate at low acid concentrations thanks to the control addition of protons to the system. This results in an improvement of the process not only in terms of extraction yield, but also, optimizing the use of reactants.

Semi-batch mode has a huge potential to be used in the leaching process of LIBs, and several advantages of this reactor have been probed with the results obtained in this study. One of the most interesting advantages is the option to operate at low acid concentrations. It not only increases the selectivity coefficient and conversion but also minimizes the use of reactants. Semi-bath mode allows reducing the consumption of reactants not only during the leaching step but also in the neutralization stage following the leaching. Once leaching is finished, soluble metals are usually separated by precipitation. This technique requires using of an alkaline solution to neutralize the leaching solution until metals precipitate. In the traditional process, the solution still contains residual acid after the process due to the high initial acid concentration. It involves the use of a high amount of reactant to increase the pH solution before the recovery step of metals. On the other hand, implementing this reactor configuration in the actual hydrometallurgical industry process could be carried out without high additional investment cost due to the reactor would be the same as in the batch system.

This study highlights the importance of studying the leaching kinetic mechanism and the change in the solid surface during the process to optimize the operational conditions. Semi-batch mode achieves better results than the batch reactors due to it enables better control of particle dissolution.

3.5 Extraction and selective separation of metal ions from $LiCoO_2$ cathodes using citric acid.

This study aimed to evaluate the role of citric acid and copper as extracting and reducing agents in the leaching process of cobalt and lithium from $LiCoO_2$ cathodes. Citric acid was selected as lixiviant because it is a green solvent with good leaching performance and one of the cheapest organic acids available in the market. Citric acid is a weak acid and an excellent chelating agent with metal ions, which can enhance the metal's solubilization. On the other hand, copper was selected due to it is already present in battery wastes (anode material foil). In this case, copper can act as a reducing agent due to the high reduction potential of Co (III). Experiments were designed to optimize the leaching conditions, varying the temperature (30-90 ºC), citric acid concentration (0.5 M-2 M) and copper dosage.

According to the experimental results, temperature is the critical factor in the leaching process using citric acid due to the endothermicity of the metal leaching process. It could explain the low percentage of metals extracted at 30 ºC. Although the same concentration of protons (the initial pH was 1.5) was available in the medium for all the temperature studies, the activation energy was insufficient to start the reaction under low-temperature conditions. Hence, temperatures above 70 ºC are required when citric acid is used as an extractant agent.

Citric acid concentration and reaction time also determine the leaching efficiency of metals extracted. During the first two hours of experiments, it was observed that the Li and Co extraction did not take place with a ratio of 1:1 due to the formation of the Co_3O_4 crust around the particle, aforementioned in the previous works. However, over a longer time, the percentages of metals extracted increased and were similar for both metals. The consumption of protons by the reaction and the formation of citrate-soluble metals complex entails a shift of the dissociation equilibrium of citric acid. This phenomenon leads to a higher availability of protons in the aqueous solution, being released from the H_3Citrate molecule to the medium during the reaction time, promoting the slow dissolution of the formed crust.

Additionally, using copper as a reductant agent with citric acid enhanced the extraction of lithium and cobalt. Copper acts as a reductant agent in front of the cobalt, where each atom of copper can donate two electrons to two cobalt atoms. The spontaneous redox potential between cobalt and copper promotes the dissolution of $LiCoO_2$ in a 1:1 proportion, avoiding the formation of the passivated layer around the particles. The most interesting aspect of copper is its presence in the battery wastes. The synergy to recover copper and valuable metals from the active electrode materials

simultaneously without adding external reductant agents results in an improvement from the point of view of the efficiency and sustainability of the leaching process.

Nevertheless, one of the most interesting aspects found in this study was the formation of a precipitate during the leaching process, which drastically decreased the cobalt concentration in the leaching solution. This precipitate appeared both in the absence and presence of copper when the citric acid solution was 2 M. The only difference was the formation time: 8 h in the presence of copper instead of 24 h only with citric acid. In both cases, metals in the precipitate were first extracted from $LiCoO_2$. Once the medium was saturated with cobaltous ions and the pH reached the value of 2.36, the precipitate formation was favoured. The result: a liquid phase contained 79% and 10% of the initial Li and Co, and a solid phase contained 18% of the initial Li and 71% of cobalt. Hence, citric acid not only can extract the metals but also the citrate species could complex the cobaltous ions, precipitating as CoHCitrate or $Co_3Citrate_2$ salts when the medium reaches the saturation point.

Different analyses were conducted to identify the species precipitated. First, the presence of carbon and hydrogen in the precipitated was confirmed by an elemental CHN analysis. The C and H precipitate compositions were similar to those of the two cobalt citrate salts available: CoHCitrate and $Co_3Citrate_2$. Moreover, FTIR and UV-visible analysis confirmed the presence of metal-citrate complexes in the precipitate.

Finally, the cobalt solubility test in citric acid was studied to measure the solubility of Co (II) in citric acid at different pH values. This test provided valuable information on the concentration of soluble cobalt under varying pH conditions, which was essential for understanding the behaviour of cobalt in citric acid leaching processes. The results of the solubility test contributed to the evaluation of the distribution of citrate and cobalt-citrate complex species, as well as the possible formation of citrate-cobalt salts, providing insights into the solubility products of these salts. Additionally, the cobalt solubility test can help understand the behaviour of cobalt species precipitation under controlled conditions using citric acid, which is relevant for recovering metals from the cathode materials of LIBs wastes.

In conclusion, although using citric acid for leaching valuable metals of LIB cathodes has some limitations (*e.g.,* high-temperature leaching), their use has considerable potential. The fact that citric acid not only acts as an extractant agent but also promotes the formation of cobalt-citrate solid species makes it a promising way to recover metals from spent LIBs selectively.

4 Conclusions and Future Works

This chapter summarizes of the key findings and conclusions of the thesis. Section 4.1 outlines the conclusions drawn from the preceding discussions, while Section 4.2 describes the future lines of work that we plan to explore.

4.1 Conclusions

The integrated hydrometallurgical approaches presented in this thesis offer promising routes for improving the recovery of metals from LIB cathodes. The $LiCoO_2$ solid was selected as the cathode material in the different studies, and the leaching process was employed to dissolve metals in acidic solutions. Firstly, the combination of electrodialysis with the extraction process to dissolve and separate the metals in the same step has been studied. Secondly, in the absence and presence of an external reductant agent, a deep study of the reactions involved in the leaching process was carried out to determine the reaction mechanism control and optimize the extraction process. The information obtained from the kinetic model was used to evaluate the effect of the reactor configuration on the extraction efficiency. Finally, using citric acid and copper as an alternative acid and reductant agents was investigated. The main conclusions obtained from the results of this thesis are listed below:

- The experimental setup designed to combine hydrometallurgy with electrodialysis enables the simultaneous extraction of lithium and cobalt from the particles and their recovery in the catholyte solution. Moreover, electrodialysis allows the regeneration of the protons consumed during the leaching reaction due to the water oxidation in the anode surface. However, the

hydrometallurgical-electrodialytic treatment is limited by the particle's dissolution.

- Without the addition of a stronger reductant agent, lithium and cobalt are not extracted in the same proportion, and the percentage of lithium dissolved is not over 60%. It was found that leaching reactions were slowed down due to the formation of an insoluble crust of Co_3O_4 around the core particles, limiting the diffusion of reactants from the bulk to the $LiCoO_2$ core.
- The developed physicochemical model accurately predicts the behaviour of leaching of $LiCoO_2$ under different conditions. The model also considers the formation of a diffusion limiting crust and the controlling mechanisms of the extraction process.
- The leaching process is firstly controlled by the chemical reaction, and in a second step, is controlled by the mass transfer due to the formation of the crust around the core. The use of an external reductant agent promotes that the process is mainly controlled by the chemical kinetic rate.
- Cobalt in the $LiCoO_2$ particles is in the stable form of Co (III) and requires reduction to Co (II) for its dissolution. Due to the high reduction potential of Co (III), H_2O_2 acts as a reducing agent against it, generally through oxygen evolution, with the advantage of not introducing additional ions to the medium.
- The concentration of H_2O_2 plays a crucial role in the leaching process in terms of selectivity and reaction rate, and maintaining low acid and high H_2O_2 concentrations enhances the selectivity of the desired reactions and conversion.
- Using a semi-batch leaching system improves metal mass extraction from LIB cathodes compared to batch processes due to the possibility of operating at low acid concentrations. The semi-batch reactor with controlled acid and H_2O_2 addition results in faster dissolution rates and a higher extraction percentage of lithium and cobalt. Semi-batch optimizes not only the percentage of metal extracted but also promotes a more effective use of the reactants.
- Optimizing acid and reductant concentrations in a semi-batch leaching process can improve extraction efficiency and minimize environmental impact, offering potential advantages for the industrial-scale recycling of LIB.
- Citric acid shows promising potential as a sustainable lixiviant for the selective recovery of cobalt and lithium from spent LIBs. However, its use is hindered by

the endothermicity of metal extraction, which involves operating at elevated temperatures.

- The formation of cobalt-citrate complexes during leaching experiments promotes the recovery of cobalt via precipitation, which could simplify the precipitation process and decrease the cost of reactants in battery recycling.

4.2 Future works

This thesis has studied the extraction process of metals from $LiCoO_2$ cathodes in more detail. From the results obtained in the different papers, the following aspects have been proposed to continue the research line in the future:

- Expanding the physicochemical model to study the dissolution of different LIB cathodes such as NMC or LMO, using different extractant agents and reductants agents.
- Leaching experiments with real battery waste, taking account the whole battery cell (*i.e*, study not only the recovery of components from cathode but also from the anode).
- Evaluating the use of semi-batch reactor to treat real LIB wastes.
- Scaling-up the semi-batch leaching reactor to evaluate the economic and environmental potential in the LIB recycling field.
- Applying electrodialysis to produce acid and base solution (i.e. HCl and LiOH) from LIBs leaching solution.

5 Appended Publications

This chapter collects copies of papers published during the PhD. Specifically, five papers have been published in journals indexed in the Journal of Citation Reports (JCR):

- Paper 1: Cerrillo-Gonzalez, M.M. et al. (2020). Recovery of Li and Co from $LiCoO_2$ via Hydrometallurgical–Electrodialytic Treatment. *Applied Sciences*, 10(7), 2367.
- Paper 2: Cerrillo-Gonzalez, M.M. et al. (2020). Hydrometallurgical Extraction of Li and Co from $LiCoO_2$ Particles–Experimental and Modeling. *Applied Sciences*, 10(18), 6375.
- Paper 3: Cerrillo-Gonzalez, M.M. et al. (2022). Acid leaching of $LiCoO_2$ enhanced by reducing agent. Model formulation and validation. *Chemosphere*, 287, 132020.
- Paper 4: Cerrillo-Gonzalez, M.M. et al. (2024). Semi-batch reactor for leaching battery cathodes under low acid concentration. *Hydrometallurgy* (submitted).
- Paper 5: Cerrillo-Gonzalez, M.M. et al. (2024). Extraction and selective separation of metal ions from $LiCoO_2$ cathodes using citric acid. *Journal of Power Sources*, 592, 233870.

Table 6 collects the information and quality indicators of journals where the results of this thesis were published. Two of them (papers 3 and 5) are in the first quartile in their respective category in the JCR, while two of them (papers 1 and 2) are in the second quartile. Therefore, they add up to 3.5 points according to ANECA criteria. It satisfies the requirement of the doctoral program to present the thesis as a

collection of publications (a minimum of 4 papers with a total sum of 2 points according to ANECA criteria).

Table 6 Journals information

Paper	Journal Identification and Quality indicators
1	**Tittle:** Recovery of Li and Co from $LiCoO_2$ via Hydrometallurgical-Electrodialysis Treatment **DOI:**10.3390/app10072367 **Journal:** Applied Sciences **Date of publications:** 2020 **Quartile and position in its category:** 38/90 (Q2) - Engineering, multidisciplinary
2	**Tittle:** Hydrometallurgical Extraction of Li and Co from $LiCoO_2$ Particles-Experimental and Modelling **DOI:** 10.3390/APP10186375 **Journal:** Applied Sciences **Date of publications:** 2020 **Quartile and position in its category:** 38/90 (Q2) - Engineering, multidisciplinary
3	**Tittle:** Acid leaching of $LiCoO_2$ enhanced by reducing agent. Model formulation and validation **DOI:** 10.1016/j.chemosphere.2021.132020 **Journal:** Chemosphere **Date of publications:** 2022 **Quartile and position in its category:** 30/274 (Q1) – Environmental science
4	**Tittle:** Semi-batch reactor for leaching battery cathodes under low acid concentration **DOI: -** **Journal:** Hydrometallurgy (submitted) **Date of publications: -** **Quartile and position in its category:** 12/79 (Q1) Metallurgy & Metallurgical Engineering
5	**Tittle:** Extraction and selective separation of metal ions from $LiCoO_2$ cathodes using citric acid **DOI:** 10.1016/j.jpowsour.2023.233870 **Journal:** Journal of Power Sources **Date of publications:** 2024 **Quartile and position in its category:** 59/344 (Q1) Materials Science, multidisciplinary

5.1 Paper 1

"Recovery of Li and Co from $LiCoO_2$ via Hydrometallurgical-Electrodialysis Treatment"

María del Mar Cerrillo-González, María Villén-Guzmán, Carlos Vereda-Alonso, César Gómez-Lahoz, José Miguel Rodríguez-Maroto and Juan Manuel Paz-García

Published in: Applied Sciences, 2020

Reference: M.M. Cerrillo-Gonzalez, M. Villen-Guzman, C. Vereda-Alonso, C. Gomez-Lahoz, J.M. Rodriguez-Maroto, J.M. Paz-Garcia (2020). Recovery of Li and Co from $LiCoO_2$ via Hydrometallurgical–Electrodialytic Treatment, *Applied Sciences*. 10, 2367.

DOI: 10.3390/app10072367

applied sciences

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Article

Recovery of Li and Co from $LiCoO_2$ via Hydrometallurgical–Electrodialytic Treatment

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Received: 4 March 2020; Accepted: 27 March 2020; Published: 30 March 2020

Abstract: Lithium-ion batteries play an important role in our modern society as the main option to power portable electronic devices and electric vehicles. The growing demand for these batteries encourages the development of more efficient recycling processes, aiming to decrease the environmental impact of the spent batteries and recover their valuable components. In this paper, a combined hydrometallurgical-electrodialytic method is proposed for processing battery waste. In the combined technique, the amount of leaching solution is reduced as acid is generated via electrolysis. At the same time, the use of ion-exchange membranes and the possibility of electroplating allows for a selective separation of the target metals. Experiments were performed using $LiCoO_2$, which is one of the most used cathodes in lithium-ion batteries. First, 0.1 M HCl solution was used in batch extractions to study the kinetics of $LiCoO_2$ dissolution, reaching an extraction of 30% and 69% of cobalt and lithium, respectively. Secondly, hydrometallurgical extraction experiments were carried out in three-compartment electrodialytic cells, enhanced with cation-exchange membranes. Experiments yielded to a selective recovery in the catholyte of 62% of lithium and 33% of cobalt, 80% of the latter electrodeposited at the cathode.

Keywords: $LiCoO_2$; critical raw materials; lithium-ion battery recycling; electrodialysis

1. Introduction

Nowadays, lithium-ion batteries (LIBs) are the most consumed energy storage and supply devices for portable electronics. Their characteristics (high energy density, long cycle life, high roundtrip efficiency, wide range of operating temperature, high reliability, safety, fast recharge and low self-discharge rate) make them the best option for numerous applications. LIBs play a vital role in the development of electric vehicles and in the storage of energy from renewable sources [1,2], which will contribute to decreasing the global carbon emissions. The increasing demand for LIBs from the sectors of portable electronics and transportation comes together with an increasing interest for recycling of spent batteries [2–4].

The main limitations for the implementation of proper recycling procedures are the lack of standards for the physical formats and the frequent appearance of new batteries with different chemistries [1]. There are normally three different shapes: prismatic, pouch (or polymer) and cylindrical cells. With respect to the chemical composition, LIBs consist of a cathode, an anode, an organic electrolyte and a separator. In most of the LIBs currently commercialized, the anode is made of graphite cast over copper foil. Nowadays, alternative anodes are under study, such as $Li_4Ti_5O_{12}$, graphite nanotubes or nanoparticles, or compounds of Si and Sn. The cathode, supported on an aluminum foil, is usually built from transition metal oxides, such as $LiMn_2O_4$ (LCO), $LiFePO_4$ (LFP),

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5.2 Paper 2

"Hydrometallurgical Extraction of Li and Co from $LiCoO_2$ Particles - Experimental and Modelling"

María del Mar Cerrillo-González, María Villén-Guzmán, Luis Acedo-Bueno, José Miguel Rodríguez-Maroto and Juan Manuel Paz-García

Published in: Applied Sciences, 2020

Reference: M.M. Cerrillo-Gonzalez, M. Villen-Guzman, L.F. Acedo-Bueno, J.M. Rodriguez-Maroto, J.M. Paz-Garcia (2020). Hydrometallurgical Extraction of Li and Co from $LiCoO_2$ Particles–Experimental and Modeling, *Applied Sciences*, 10, 6375.

DOI: 10.3390/APP10186375

applied sciences

MDPI

Article

Hydrometallurgical Extraction of Li and Co from $LiCoO_2$ Particles–Experimental and Modeling

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Received: 12 August 2020; Accepted: 9 September 2020; Published: 13 September 2020

Featured Application: The physicochemical model described in this work will be useful for the optimization of hydrometallurgical and combined electrochemical–hydrometallurgical recycling processes for spent lithium-ion batteries.

Abstract: The use of lithium-ion batteries as energy storage in portable electronics and electric vehicles is increasing rapidly, which involves the consequent increase of battery waste. Hence, the development of reusing and recycling techniques is important to minimize the environmental impact of these residues and favor the circular economy goal. This paper presents experimental and modeling results for the hydrometallurgical treatment for recycling $LiCoO_2$ cathodes from lithium-ion batteries. Previous experimental results for hydrometallurgical extraction showed that acidic leaching of $LiCoO_2$ particles produced a non-stoichiometric extraction of lithium and cobalt. Furthermore, the maximum lithium extraction obtained experimentally seemed to be limited, reaching values of approximately 65–70%. In this paper, a physicochemical model is presented aiming to increase the understanding of the leaching process and the aforementioned limitations. The model describes the heterogeneous solid–liquid extraction mechanism and kinetics of $LiCoO_2$ particles under a weakly reducing environment. The model presented here sets the basis for a more general theoretical framework that would describe the process under different acidic and reducing conditions. The model is validated with two sets of experiments at different conditions of acid concentration (0.1 and 2.5 M HCl) and solid to liquid ratio (5 and 50 g L^{-1}). The COMSOL Multiphysics program was used to adjust the parameters in the kinetic model with the experimental results.

Keywords: battery recycling; COMSOL; unreacted shrinking core model

1. Introduction

In the last three decades, lithium-ion batteries (LIBs) have prevailed over the other types of secondary batteries due to their advantageous properties, such as high energy density or low self-discharge [1]. The growing use of LIBs encourages the development of reusing and recycling techniques aiming to minimize the environmental impact of the LIB technology and to favor the circular economy goal [2,3].

Different technologies for LIBs recycling have been developed [2]. Among them, pyro- and hydrometallurgical methods are the most commonly used today. Biometallurgical and combined bio-electro-pyro-hydrometallurgical methods are also being developed [4–6]. Pyrometallurgical methods are based on the treatment of LIBs at high temperatures to produce pyrolysis, metal reduction, and subsequent gas incineration. Despite the easiness of the procedure and the optimal technology

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5.3 Paper 3

"Acid leaching of $LiCoO_2$ enhanced by reducing agent. Model formulation and validation"

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Published in: Chemosphere, 2022

Reference: M.M. Cerrillo-Gonzalez, M. Villen-Guzman, C. Vereda-Alonso, J.M. Rodriguez-Maroto, J.M. Paz-Garcia (2022). Acid leaching of $LiCoO_2$ enhanced by reducing agent. Model formulation and validation. *Chemosphere*, 287, 132020.

DOI:10.1016/j.chemosphere.2021.132020

Chemosphere 287 (2022) 132020

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Acid leaching of $LiCoO_2$ enhanced by reducing agent. Model formulation and validation

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HIGHLIGHTS

- A model to describe the acidic-reductive leaching of $LiCoO_2$ is presented.
- H_2O_2 is selected as reducing agent to enhance the extraction yields.
- The model is based on the formation of a Co_3O_4 insoluble crust around the particle.
- The model predicts the switch of controlling mechanisms from kinetics to mass transfer.
- The model has been validated with a set of 12 experiments at different conditions.

ARTICLE INFO

Handling Editor: Y Yeomin Yoon

Keywords:
Lithium-ion batteries recycling
Reductive leaching
H_2O_2
Shrinking core

ABSTRACT

In this work, a model has been formulated to describe the complex process of $LiCoO_2$ leaching through the participation of competing reactions in acid media including the effect of H_2O_2 as reducing agent. The model presented here describes the extraction of Li and Co in the presence and absence of H_2O_2, and it takes into account the different phenomena affecting the controlling mechanisms. In this context, the model predicts the swift from kinetic control to diffusion control. The model has been implemented and solved to simulate the leaching process. To validate the model and to estimate the model parameters, a set of 12 (in triplicate) extraction experiments were carried out varying the concentration of hydrochloric acid (within the range of 0.5–2.5 M) and hydrogen peroxide (range 0–0.6%v/v). The simulation results match fairly well with the experimental data for a wide range of conditions. Furthermore, the model can be used to predict results with different solid-liquid ratios as well as different acid and oxygen peroxide concentrations. This model could be used to design or optimize a $LiCoO_2$ extraction process facilitating the corresponding economical balance of the treatment.

1. Introduction

Lithium-ion batteries (LIBs) play an important role in the ecological transition towards a global decarbonized energy scheme. Until recently, LIBs were only used in portable electronic devices, but their technical features have made them attractive for electric transport and stationary energy storage (Velázquez-Martínez et al., 2019). It is estimated that the global demand for batteries will increase 14 fold by 2030 (compared to 2018 market), and electric vehicles are projected to require the 90% of that amount (Tsiropoulos et al., 2018). Such exponential growth of LIBs' use comes together with an increase of the demand of raw materials as well as an increase of the environmental impact associated with the manufacture of the batteries and their waste management.

The European Commission identifies the list of Critical Raw Materials (CRMs) to promote circular economy and to reduce the dependency on strategic raw materials (European Commission, 2008). This classification is based on the current and future evaluation of both the supply risk and the economic importance. As new information on the environmental impact of materials and technological advances appears, it is necessary to revise the CRMs list. The most recent list (2020) includes some of the most common raw materials used in LIBs such as cobalt, phosphorous, magnesium, natural graphite, and lithium (Amato et al.,

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https://doi.org/10.1016/j.chemosphere.2021.132020
Received 6 July 2021; Received in revised form 21 August 2021; Accepted 23 August 2021
Available online 25 August 2021

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5.4 Paper 4

"Semi-batch reactor for leaching battery cathodes under low acid concentration"

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Submitted to: Hydrometallurgy

Reference: **M**.M. Cerrillo-Gonzalez, M. Villen-Guzman, A. Rivas-Bascon, J.M. Rodriguez-Maroto, J.M Paz-Garcia (2024). Semi-batch reactor for leaching battery cathodes under low acid concentration. *Hydrometallurgy*.

DOI: -

Semi-batch reactor for leaching battery cathodes under low acid concentration

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Abstract

Recovery of cobalt and lithium from Li-ion batteries wastes has been evaluated in a semi-batch leaching system. In this study, HCl and H_2O_2 were used as extractant and reductant agents, respectively. The comparison of batch and semi-batch processes was carried out, obtaining an improvement from 40% to 70% in the metal mass extracted (*i.e.* Co and Li) for semi-batch experiments under the same experimental conditions. Effects of the initial concentration of reductant and leaching agents were evaluated for a semi-batch system in which the acid was continuously fed to maintain constant the pH value. From experimental results, it was found that the concentration of H_2O_2 plays an important role in the leaching process in terms of selectivity. For the experiments carried out using 0.1 M of HCl and 1 M of H_2O_2, the percentage of Li and Co extracted was 90% for a leaching time of 30 minutes. The double-controlled addition of HCl and H_2O_2 to the semi-batch system allows the reduction of the H_2O_2 concentration to 0.5 M. The optimization of reactants entails not only the decrease of their consumption but also maximize the selectivity of the reactions desired, which represents promising results for the environmental sustainability of the process.

Keywords: Lithium-ion batteries, recycling, semi-batch reactor, leaching.

1 Introduction

Hydrometallurgy is a chemical metallurgy process that involves the use of aqueous solutions to recover metals from ores. It has been widely used in mining and metallurgical industries. In the last decades, its use has been extended to the sector of lithium-ion battery (LIBs) recycling due to the characteristics of these wastes (Raj et al., 2022). LIBs contain valuable metals such as lithium, cobalt, nickel, and manganese, whose recovery is necessary to promote the circular economy in the batteries industry (Mishra et al., 2022). Therefore, hydrometallurgical processes have some attractive advantages such as a high product purity, low energy consumption and minimal gas emission that make it one of the most promising methods for the recycling of LIBs wastes (Yao et al., 2018).

The hydrometallurgical process generally includes two main stages: (i) leaching of the solid, and (ii) separation of the valuable compounds. Although the two steps are crucial, leaching is the key factor in the whole process since this step determines the technological complexity and the economic viability of the process (Lv et al., 2018). Leaching of battery cathodes is usually carried out using acids and reducing agents to convert metals contained in the solid into soluble metal ions. Although a wide range of lixiviants have been investigated to enhance the process, including mineral (H_2SO_4, HCl, HNO_3) (Song et al., 2022) and organic acids (citric acid, tartaric acid, maleic acid) (Nayaka et al., 2019), only few acids, such as H_2SO_4 and HCl, remain currently viable in terms of industrial production (Baum et al., 2022). Nevertheless, high concentration of acids is normally required to achieve great yields of metals. This is an issue from process perspective due to the high consumption of reagents, not only during the leaching but also in the following stages. The use of high acid concentrations results in a solution with low pH values even after the leaching, so a large amount of chemicals is needed to neutralize the solution in the recovery step which typically occurs at the pH 4-9 (Porvali et al., 2020b). Therefore, reducing the reactive consumption without decreasing the extraction yield is vital to improve the process economically and environmentally.

To optimize the hydrometallurgical process, it is important to understand the different reactions and mechanism that takes places during the leaching steps. In a previous work (Cerrillo-Gonzalez et al., 2020), a mathematical model was developed to describe the mechanism of $LiCoO_2$ dissolution in acid media. Basically, the leaching of $LiCoO_2$ involves the reduction of Co^{3+} to soluble Co^{2+}. In the absence of a stronger reductant agent, water oxidation transfers the electrons

required to complete the reaction (Porvali et al., 2020a). In that case, the reaction takes place very slowly and Li^+ and Co^{2+} are extracted from the $LiCoO_2$ particles leaving a residue of $Co_3O_{4(s)}$ around the $LiCoO_2$ core (Eq (1)). The formation of this insoluble crust reduces the leaching reaction rate due to the limited diffusion of the reactant from the aqueous solution to the surface of the unreacted core. This phenomenon emphasizes the use of reductant agent in the leaching process (Ferreira et al., 2009). Although several reductant agents, such as ascorbic acid(Li et al., 2012) and current collector scrap (Chernyaev et al., 2021; Joulié et al., 2017) have been investigated to be used in acid leaching of LIBs, H_2O_2 is still the most common reductant agent in research and the industrial scale (Baum et al., 2022). Its use as a reductant agent has the advantage of introducing no additional ions to the system. H_2O_2 is well known as a strong oxidizing agent (H_2O_2/H_2O; $E^0 = 1.776$ V). However, cobalt in the $LiCoO_2$ particles is in the stable form of Co (III) and requires reduction to Co (II) for its dissolution (Co^{3+}/Co^{2+}; $E^0 = 1.93$ V). Due to the high reduction potential of Co (III), H_2O_2 acts as a reducing agent against it, generally through oxygen evolution (O_2/H_2O_2, $E^0 = 0.695$ V). Its role in the leaching mechanism of $LiCoO_2$ was also studied in an extension of the aforementioned model (Cerrillo-Gonzalez et al., 2022), in which it was assumed that the following reactions occur simultaneously:

$$LiCoO_2 + 2H^+ \rightarrow Li^+ + \frac{1}{2}Co^{2+} + \frac{1}{6}Co_3O_{4\,(s)} + H_2O + \frac{1}{6}O_2 \qquad k_1 = 2.17\cdot10^{-8}\ (m\ s^{-1}) \qquad (1)$$

$$Co_3O_4 + 6H^+ \rightarrow 3Co^{2+} + 3H_2O + \frac{1}{2}O_2 \qquad k_2 = 8.33\cdot10^{-9}\ (m^2mol^{-2/3}\ s^{-1}) \qquad (2)$$

$$LiCoO_2 + 3H^+ + \frac{1}{2}H_2O_2 \rightarrow Li^+ + Co^{2+} + 2H_2O + \frac{1}{2}O_2 \qquad k_3 = 6.67\cdot10^{-11}\ (m^5mol^{-4/3}\ s^{-1}) \qquad (3)$$

$$Co_3O_4 + 6H^+ + H_2O_2 \rightarrow 3Co^{2+} + 4H_2O + O_2 \qquad k_4 = 1.67\cdot10^{-12}\ (m^8mol^{-8/3}\ s^{-1}) \qquad (4)$$

In terms of efficiency and productivity, the leaching system would be ideal in the case that only reaction (3) takes place (*i.e.* subproduct Co_3O_4 would not appear). However, the four reactions take place simultaneously during the leaching process. Therefore, the experimental conditions need to be optimized to promote the generation of the desired products. Conventionally, the leaching of LIBs is carried out in batch reactors where the solid is introduced together with the acid solution and reductant agent (Brückner et al., 2020). Then, the suspension is mixed until the leaching yield is reached. In this kind of reactor, it is difficult to control the side-reactions that take place during

the leaching process. However, the formation of undesired by-products can be decreased with the use of the reactor in a semi-batch mode (Worstell, 2015). For this configuration, one or more reactants are intermittently or continuously feeding to the reactor. Controlling the reactant concentration can enhance the conversion and selectivity of the desired reactions, which results in a higher yield with a more effective use of the reactants.

Considering the reaction rates proposed in a previous work (Cerrillo-Gonzalez et al., 2022), for the reaction (1) and (3), the selectivity coefficient, *S*, could be defined with the following expression:

$$S = \frac{r_3}{r_1} = \frac{k_3}{k_1} \cdot \frac{\left(\frac{n_p 4\pi r_c^2}{V_r}\right)[H^+_{core}]^{1/3}\,[H_2O_2]^2}{\left(\frac{n_p 4\pi r_c^2}{V_r}\right)[H^+_{core}]} = \frac{k_3}{k_1} \cdot \frac{[H_2O_2]^2}{[H^+_{core}]^{2/3}} \quad (5)$$

where k_1 and k_3 are the reaction rate constant of reaction (1) and (3), respectively; r_c is the unreacted core radius (m); n_p is the number of particles (-); V_r is the reaction volume (m^3), $[H_2O_2]$ is the hydrogen peroxide concentration (mol m^{-3}) and $[H^+_{core}]$ is the protons concentration (mol m^{-3}). According to this expression, the selectivity coefficient increases with the H_2O_2 concentration while it decreases with the proton concentration. Thus, selectivity will be maximized when the ratio between H_2O_2 and protons concentration is high.

This work focused on the application on a semi-batch reactor to recover lithium and cobalt from spent LIBs. The initial concentration of extractant (HCl) and reductant agent (H_2O_2) were evaluated to maximize the process selectivity. The novelty of this paper is the use of a semi-batch reactor which allows to carry out leaching experiments under low acid concentrations compared with batch reactor.

2 Methodology

Leaching experiments were carried out in a 0.25 L glass reactor equipped with a magnetic stirrer at 25ºC. The reactor was sealed with a four-necks ground-glass lids for containing a pH electrode, a HCl inlet, a H_2O_2 inlet and sampling. The experimental system is schematically illustrated in **Fig. 1**. For all experiments, 100 mL of leaching solution was added to 5 g of $LiCoO_2$ (97% Alfa easer). The leaching solution was prepared using HCl (35% Panreac) and H_2O_2 (30% Panreac), which were selected to act as the extractant and reductant agent, respectively. Their initial

concentration for each experiment is detailed in Table 1. During the experiments, except for test B1 and B2, the pH was measured (pH meter HACH sensION pH 3) and controlled to ensure that the acid concentration was maintained constant in the reactor. For that, a 3 M HCl solution was continuously fed into the reactor to supply the protons consumed in the leaching process.

The experiments B1 and B2 (Batch), and S1 (Semi-batch) were focused on evaluating the effect of control the acid feed on the leaching reaction. The influence of H_2O_2 concentration on the $LiCoO_2$ leaching reaction rates was examined in the experiments S1-S4. On the other hand, the effect of the fixed HCl concentration was studied in the experiments S4-S6. Finally, the study of the doble addition of reactants, both HCl and H_2O_2, into the reactor was performed in the experiments S7-S9. To determine the amount of H_2O_2 required by the reactions, it was assumed that the H_2O_2 was consumed following the stoichiometry of reaction (3): 1 mol H_2O_2/6 mol H^+. Thus, the H_2O_2 was fed based on the acid added to the system, using a 1 M H_2O_2 solution (*i.e* 1 mL of 1 M H_2O_2 per 2 mL of 3 M HCl solution). It should be noted that the H_2O_2 solution was prepared and isolated in a dark container to avoid its photodegradation. All the experiments were carried out in duplicate to ensure their reproducibility.

Table 1: Experimental conditions used in metal extraction experiments.

Test code	S/L ratio (g L^{-1})	T (ºC)	Time (min)	Initial HCl (M)	Initial H_2O_2 (M)	HCl addition	H_2O_2 addition	Reactor mode
B1	50	25	120	1.5	0.5	No	No	Batch
B2	50	25	120	1	0.5	No	No	Batch
S1	50	25	120	0.2	0.5	Yes	No	Simple Semi-batch
S2	50	25	120	0.2	0	Yes	No	Simple Semi-batch
S3	50	25	120	0.2	0.25	Yes	No	Simple Semi-batch
S4	50	25	120	0.2	1.0	Yes	No	Simple Semi-batch
S5	50	25	120	0.1	1.0	Yes	No	Simple Semi-batch
S6	50	25	120	0.01	1.0	Yes	No	Simple Semi-batch
S7	50	25	120	0.1	1.0	Yes	Yes	Double Semi-batch
S8	50	25	120	0.1	0.5	Yes	Yes	Double Semi-batch
S9	50	25	120	0.1	0.25	Yes	Yes	Double Semi-batch

Total leaching time was 2 hours for all the experiments, and samples were collected from the reactor at 3, 6, 10, 15, 20, 30, 60, 90 and 120 min. All samples were filtered using a 0.6 µm glass-

fiber (Macherey-Nagel GF-3) and analyzed via Atomic Absorption Spectrophotometry (Agilent 55AA) to quantify the amount of lithium and cobalt extracted. At the end of the experiments, the suspension was filtered with a vacuum filtration assembly (Boeco R-300) and the leachate residue was dried at 70 ºC for 24 h. Regarding the liquid phase, the filtrate was collected to quantify the final volume of the solution.

The percentage of metal extracted, both lithium and cobalt, was calculated according to the following expression:

$$x_{t,i}(\%w/w) = \frac{C_{t,i}V_t}{m_{0,i}}x100 \quad (6)$$

where $x_{t,i}$ is the percentage of metal extracted (%w/w), $C_{t,i}$ is the dissolved metal concentration (mg L^{-1}), V_t is the solution volume at each time (L) and $m_{0,i}$ is the initial amount of metal in the solid sample (mg). The total content of cobalt and lithium in the solid samples was determined by microwave-assisted acid digestion (EPA method 3051A). All results were calculated considering the volume change caused by the addition of reactants as well as the sampling.

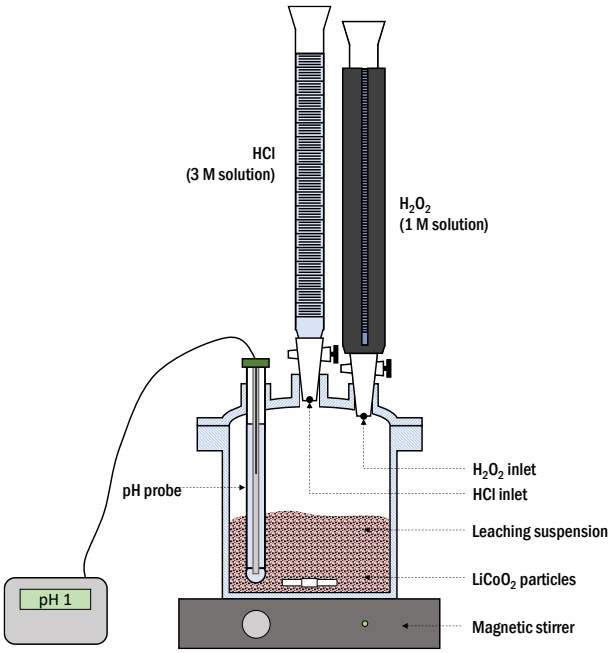

Fig. 1: Schematic illustration of semi-batch leaching reactor

3 Results and Discussion

3.1 Batch vs Semi-Batch reactor

Leaching of $LiCoO_2$ was studied in batch (B1 and B2) and a semi-batch reactor (S1) to evaluate the effect of acid feeding mechanism on the metal extraction. The three experiments were conducted under the following conditions: S/L ratio of 50 g/L, 25 ºC and 0.5 M H_2O_2. Regarding to the acid, 100 mL of 1.5 M HCl (*i.e*, a total of 150 mmol H^+) and 1M HCl solution (*i.e*, a total of 100 mmol H^+) was loaded to the batch reactor at the initial time in the test B1 and B2, respectively. The semi-batch reactor was initially charged with 100 mL of 0.2 M HCl solution (S1), and the initial pH value of the solution (pH = 0.88) was kept constant adding to the system the acid consumed during the leaching reaction.

Fig. 2a-b show the transient percentage of lithium and cobalt extracted in the three experiments. It can be observed that the dissolution rate was faster in the semi-batch than in the batch mode, resulting in a higher percentage of metal extracted. Thus, after 60 min of the experiment, 84.3% of Li and 85.7 % Co were extracted in the S1 test (semi-batch) while 70 % of Li and 60 % of Co were dissolved in the B1 test (1.5 M HCl batch). It must be noted that the proton consumption in both experiments was similar: 150 mmol in B1 and 140 mmol in S1 (the initial 20 mmol plus 120 mmol of H^+ added to the system during the reaction time). The mole ratio Co/Li extracted is presented in **Fig. 2d** to evaluate the selectivity of reactions. As can be observed, this ratio was close to 1 in the S1 test, while it was between 0.8-0.9 in the B1 test. These results confirm that low acid concentration in the leaching medium can enhance the selectivity of the reaction (3).

In the B2 test (batch reactor at 1 M HCl), the selectivity was enhanced compared to the B1 test due to the initial acid concentration was lower. However, the conversion was lower in the B2 than in the B1 test. It is basically due to the depletion of protons in the system, as observed in the pH profile (**Fig. 2**c). After 30 min, the reactions were slowed down in the test B2, achieving a plateau of Co and Li extracted. Therefore, it is not possible to enhance the selectivity and conversion at the same time in the batch reactor due to high acid concentration involves higher conversion but lower selectivity. In comparison, low acid concentration achieves higher selectivity but lower conversion. From these results, the use of semi-batch reactor enables the enhancement of both the selectivity and conversion of the leaching reactions. Therefore, the controlled addition of protons to the system not only increases the extraction yield but also optimizes the use of the reactants.

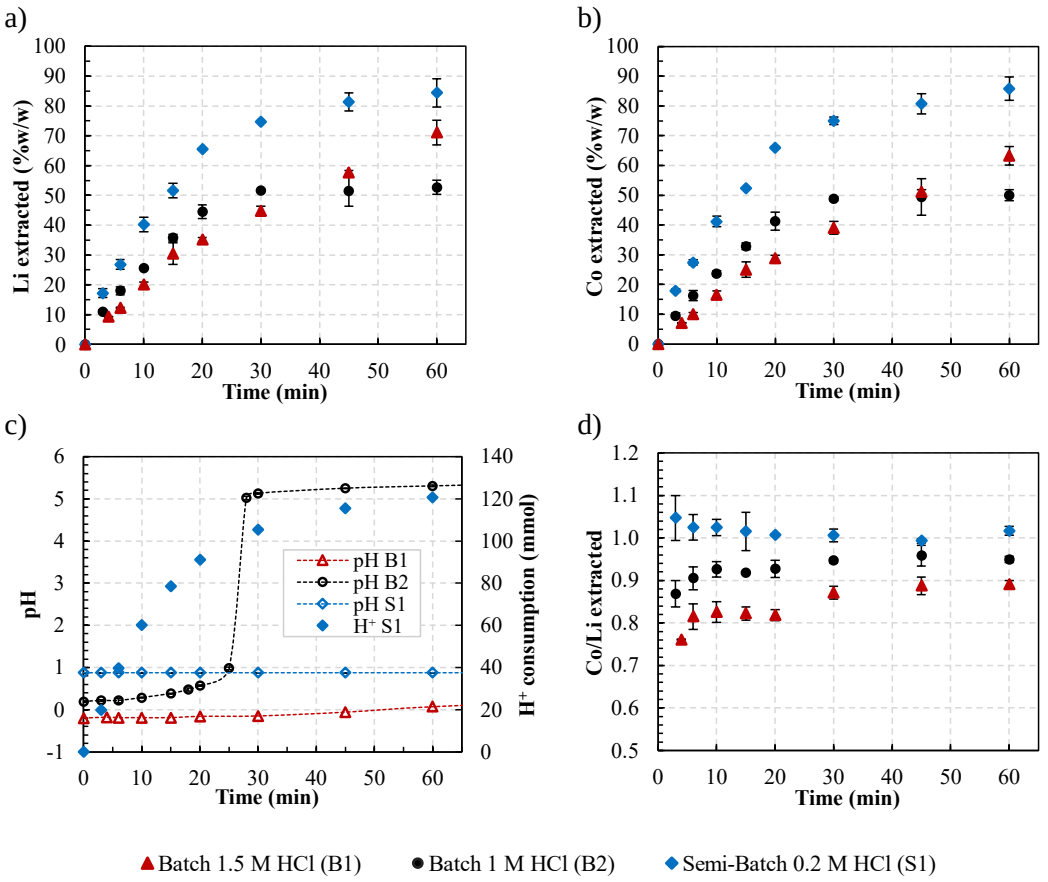

Fig. 2: Effect of acid feeding mechanism on the leaching of (a) lithium and (b) cobalt; (c) pH profile and protons consumption and (d) mole ratio of Co/Li extracted (Conditions: S/L ratio 50 g/L; 0.5 M H_2O_2; 25 ºC)

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3.2 Simple Semi-batch system

In this section, the influence of initial H_2O_2 and HCl concentration on the $LiCoO_2$ dissolution was studied in a semi-batch reactor, in which the acid was continuously added to the system to keep the pH value of the solution constant.

3.2.1 Effect of initial H_2O_2 concentration

The effect of initial H_2O_2 concentration on $LiCoO_2$ leaching rate and reaction selectivity was investigated varying H_2O_2 concentration from 0 to 1 M in a semi-batch reactor (S1-S4). Initially, the reactor was charged with the solid and a 0.2 M HCl solution with the selected H_2O_2 concentration. While the H_2O_2 was consumed during the reaction, the initial pH (pH = 0.88) was remained constant by the controlled acid addition to the system based on its consumption. Experimental results are presented in **Fig. 3**. The leaching efficiencies for lithium and cobalt are shown in **Fig. 3a-b**. The acid consumed in each experiment and the mole ratio of H^+ consumed per Co^{2+} extracted are shown in **Fig. 3c** and **Fig. 3d**.

From the extracted metal results, it can be observed that $LiCoO_2$ dissolution rate is highly dependent on the H_2O_2 concentration. In absence of H_2O_2 (S2), only 27% Li^+ and 14% Co^{2+} were extracted at 2 hours. In this case, only the reaction (1) and (2) took places, which would explain that the mole ratio of H^+/Co^{2+} was around 4 (stoichiometric ratio reaction (1)) as well as the extraction proportion of Li and Co was near 2:1. It is known that the acidic leaching of lithium cobalt oxides is limited by the extremely strong chemical bond between cobalt and oxygen (Jiang et al., 2018).

The presence of H_2O_2 can effectively enhance the leaching process due to its capacity to reduce Co^{3+} to soluble Co^{2+} (He et al., 2017). It was found that an increase of H_2O_2 concentration not only results in an improvement of metal extracted, but also in an acceleration of the leaching reaction. For the experiments at 0.25 M H_2O_2 (S3), the percentage of Li and Co extracted was 58% and 56% at 2 hours, respectively, while the 93% of Li and Co was dissolved at 1 hour when a 1 M H_2O_2 solution (S4) was used. Moreover, H_2O_2 concentration plays an important role in terms of the selectivity, as it was described in Eq (5), in which a high H_2O_2 concentration maximizes the selectivity of the desired reaction. It agrees with H^+ consumed/Co^{2+} extracted mol/mol ratio. In the case of 1 M H_2O_2 (S4), this ratio was close to 3, corresponding with the stoichiometric ratio of reaction (3). However, when the reductant concentration was lower, this ratio increased, which

197 would indicate that parallel reactions take places in the system. These results highlight the
198 importance of optimizing the reductant concentration not only to maximizes the selectivity of the
199 reactions but also to minimize the reactive consumption which have a direct effect on the
200 environmental and economical sustainability of the process.

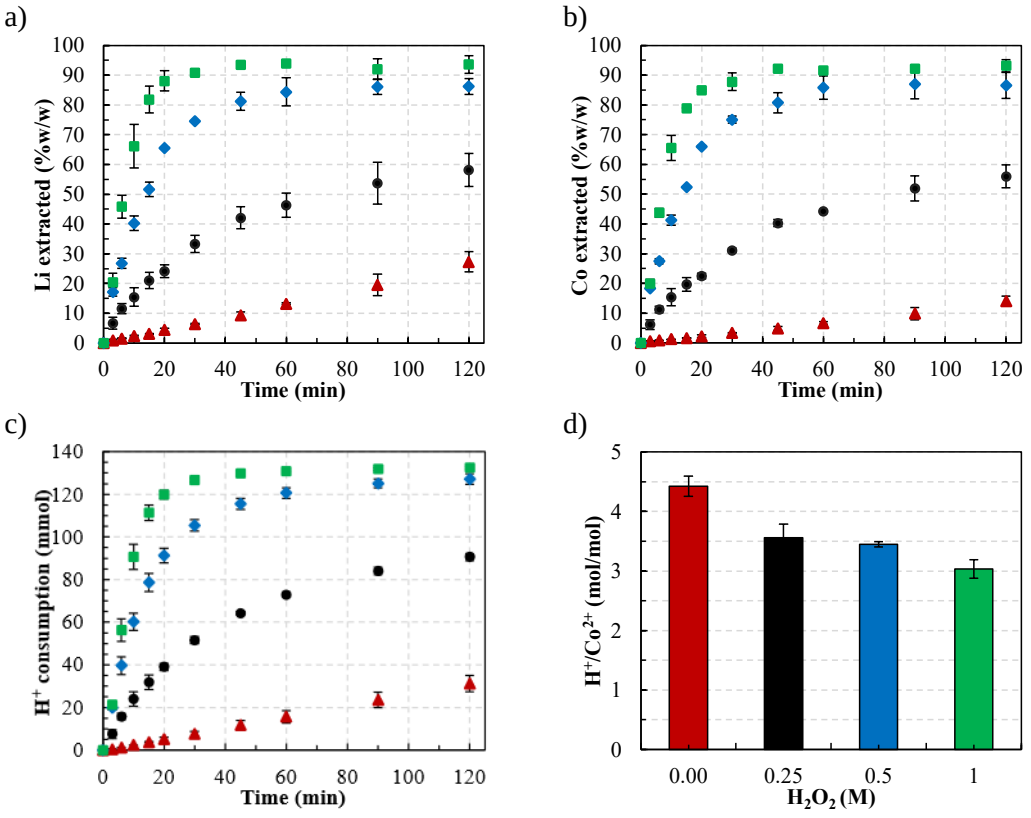

Fig. 3: Effect of initial H_2O_2 concentration in a semi-batch reactor on leaching of (a) lithium and (b) cobalt; (c) protons consumption and (d) mole ratio of H^+/Co^{2+} at 2 hours. (Conditions: S/L ratio 50 g/L; 0.2 M HCl; 25 ºC, 2 hours)

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3.2.2 Effect of initial HCl concentration

Acid concentration is another parameter affecting not only the selectivity but also the leaching reaction rate. It was demonstrated previously that low acid concentration enhanced the extraction yield when a semi-batch reactor was used. However, if the acid concentration were too low, it could affect the reaction rate and even result in the reaction would not take place (Takacova et al., 2016). In this section, the influence of the fixed HCl concentration on the $LiCoO_2$ leaching was studied to optimize the extraction yield and leaching rate. Experiments were carried out in a semi-batch reactor where $LiCoO_2$ (50 g L^{-1}) and 1 M H_2O_2 were initially charged together with the initial amount of HCl, from 0.2 to 0.01 M (S4-S6). During experiments, the acid required was added intermittently to the system to keep constant the initial pH (target pH values were 0.88, 1.15 and 2.09 for experiments S4, S5 and S6, respectively).

According to the experimental results, shown in **Fig. 4**, not significantly differences were observed when the HCl concentration was reduced from 0.2 to 0.1 M. In both cases, the percentage of Li and Co extracted was around 90% after 30 min. Moreover, the leaching rate was almost identical for both acid concentrations during the reaction time. A reduction of 10 times the acid concentration
(0.01 M) resulted in a deceleration of the leaching rate, although the final percentage of Li and Co extracted was close to the percentage extracted with higher HCl concentrations. Once again, it was concluded that remaining low acid concentration enhances the selectivity of the desired reaction (Eq. (3)), as reflected in the mole ratio of H^+/Co^{2+} (**Fig. 4**d) which was close to 3 in all cases.

From LIB recycling process point of view, leaching at low acid concentration is positive from an operational and economic perspective. Firstly, low acid concentration improves the selectivity resulting in higher percentage of metal extracted at lower operational times. Moreover, the consumption of reactants is reduced in the leaching process as well as in the subsequent neutralization stage. The controlled addition of acid enables to keep a low acid concentration due to the protons consumed in the reaction are constantly added to the system. On the other hand, once the leaching is finished, soluble metals are usually separated by precipitation (Yang et al., 2020a). This technique requires the use of an alkaline solution to increase the pH solution until the metal precipitation occurs. Considering the high initial acid concentration used in the traditional leaching systems (ranging from 2 to 4 M (Yao et al., 2018)) to achieve appreciable leaching rates and yields, the final solution contains residual acid. Consequently, high amount of reactants would be needed to neutralize the leaching solution. To the best of our knowledge, although previous studies have

evaluated the use of low acid concentration in leaching processes (Porvali et al., 2020b), the experimental conditions proposed in this work (*i.e.* rate solid to liquid, acid concentration) has not been previously assessed.

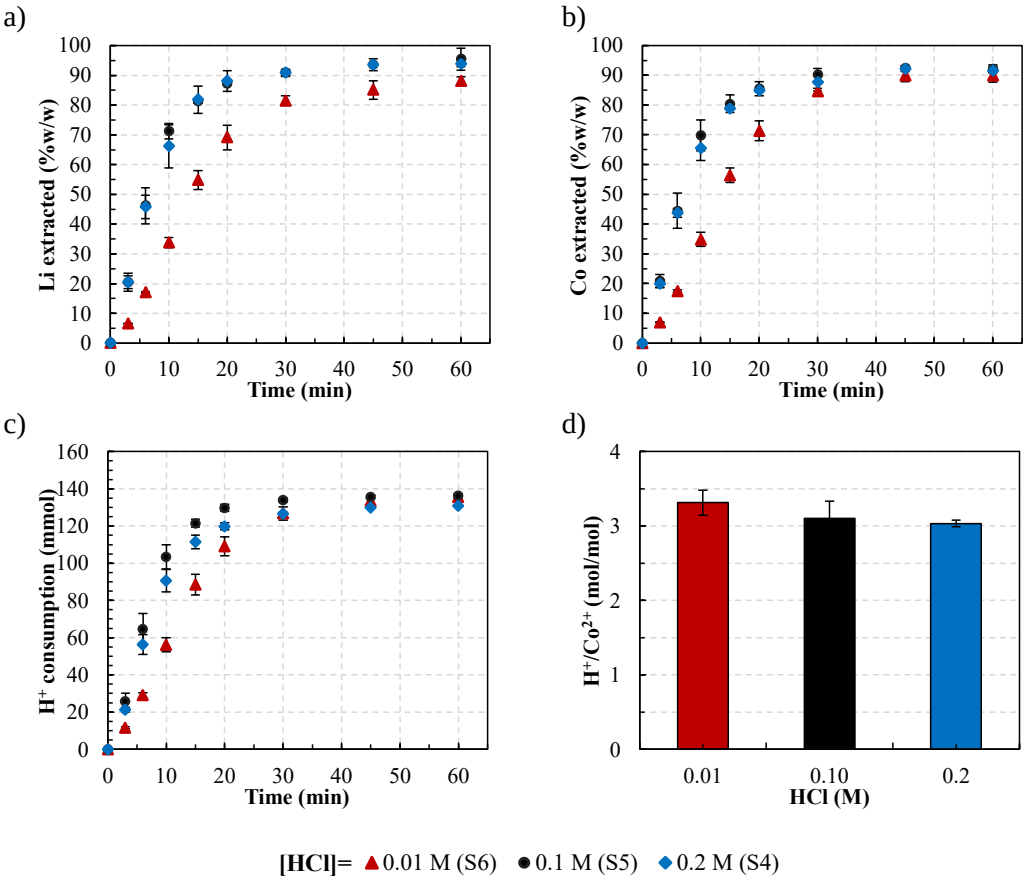

Fig. 4: Effect of fixed HCl concentration in a semi-batch reactor on leaching of (a) lithium and (b) cobalt; (c) protons consumption and (d) mole ratio of H^+/Co^{2+} at 2 hours (Conditions: S/L ratio 50 g/L; 1 M H_2O_2; 25 ºC, 1 hour)

3.3 Double Semi-batch system

In the previous sections, it was demonstrated that maintaining low acid and high H_2O_2 concentrations enhanced the selectivity and therefore, the extraction yield. However, the optimal concentration of H_2O_2 (1 M) was much higher than that was required to dissolve the solid sample according to the reaction stoichiometry. The double controlled addition of HCl and H_2O_2 was evaluated to optimize the initial H_2O_2 concentration. Previously, in the simple semi-batch reactor, only the acid was continuously fed to the reactor while H_2O_2 was loaded at the initial time. Thus, H_2O_2 concentration decreased during the reaction time. In the double semi-batch system, the concentration of H_2O_2 also remained constant with the continuous addition of this reactant. Experiments were conducted by fixing the initial HCl concentration at 0.1 M (*i.e.*, the pH was kept constant at 1.15) and varying the initial H_2O_2 concentration from 1 to 0.25 M (S7-S9). Experimental results are shown in **Fig. 5**

According to the percentage of lithium and cobalt extracted (**Fig. 5 a-b**), both the leaching rate and extraction yield were improved when the initial H_2O_2 concentration was increased from 0.25 to 1 M. The total solid dissolution was achieved in less than 30 min when 1 M H_2O_2 (S7) initial concentration was used, while the same results were obtained for 0.5 M H_2O_2 (S8) at 60 min. In the case of 0.25 M H_2O_2 (S9), 81% of Li and Co was dissolved after 2 hours of experiment. However, the curve trend indicates that the complete dissolution of the solid could be achieved if longer leaching times had been applied. These results are in line with the fact that H_2O_2 concentration influences the leaching rate.

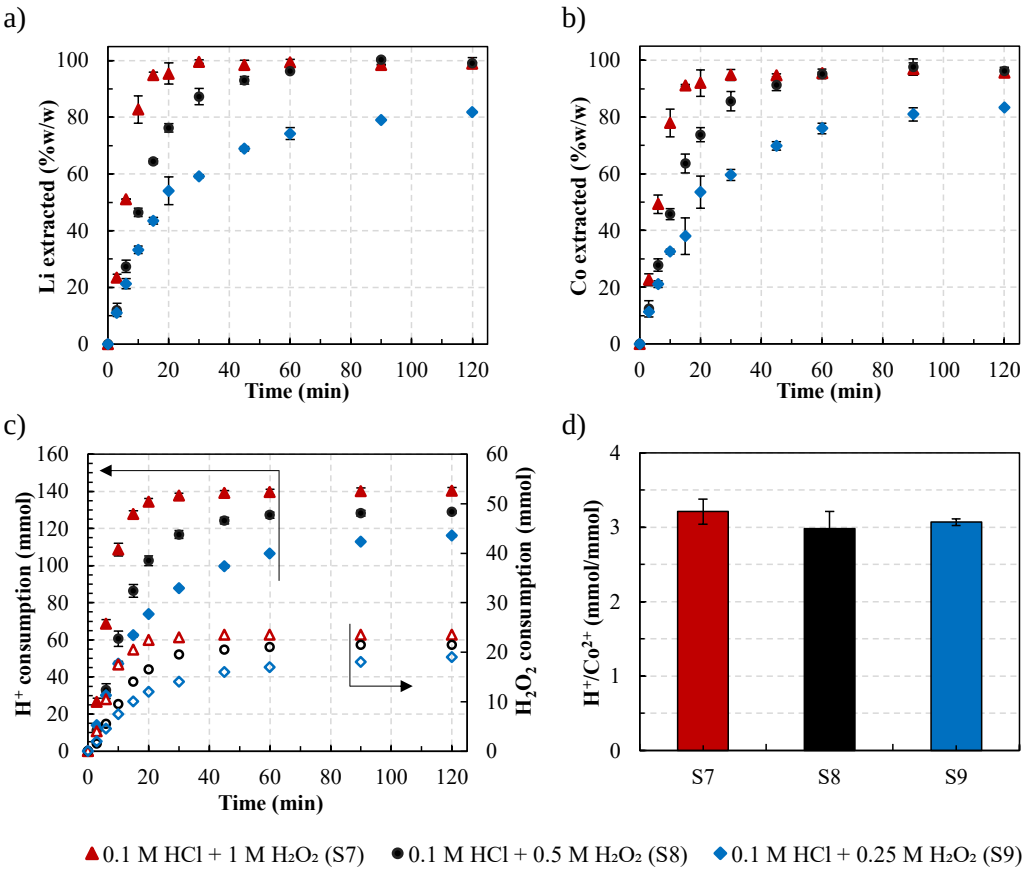

Fig. 5: Effect of doble addition of HCl and H_2O_2 in a semi-batch reactor on leaching of (a) lithium and (b) cobalt; (c) protons and H_2O_2 consumption and (d) mole ratio of H^+/Co^{2+} at 2 hours (Conditions: S/L ratio 50 g/L; 25 ºC, 2 hours)

Fig. 6 shows a comparison, according to the reactor mode (batch, simple or double semi-batch), for the HCl and H_2O_2 consumed after 30 min of reaction and the percentage of Li and Co extracted. It can be observed that the semi-batch mode shows not only a significant improvement in the metal extracted, but also a more effective use of the reactants. For the same initial H_2O_2 concentration (0.5 M), the percentage of Li and Co extracted enhanced from 40% (B1) to 75% (S1) when the simple semi-batch mode was used, while the percentage increased to 86% (S8) in the double semi-batch mode. Moreover, it must be noted that semi-batch leaching not only increase the percentage of metal extracted but also decrease the consumption of acid. In test S1 and S8 (semi-batch mode), the total protons consumed after 30 min was around 125 mmol, while in the batch reactor, the protons consumed was 150 mmol. The double semi-batch experiments (S8) allowed obtaining the

similar percentage of metals extracted than in simple semi-batch mode (S5) for a leaching time of 30 minutes with the advantage of a decrease of reactant consumption (30% H_2O_2 and 13% of HCl).

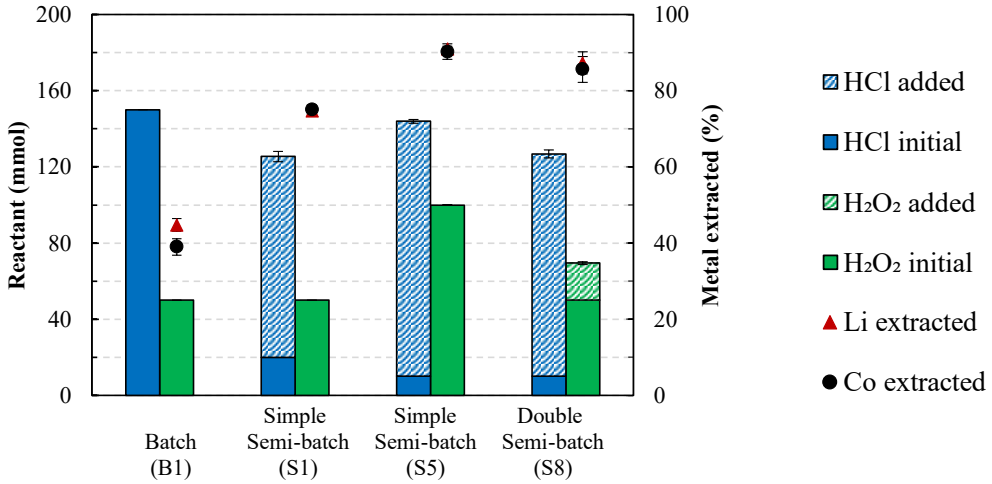

Fig. 6: Reactant consumption and metal percentage extracted based on the reactor mode at 30 min**.**

3.4 Advantages of semi-batch mode

According to experimental results, semi-batch mode has a high potential to be used in the leaching process of LIBs. Several advantages of this reactor configuration have been probed according to the results previously discussed. First, the semi-batch mode enables better control of solid dissolution, avoiding the surface structural reorganization, which improves of the extraction yield. These results highlight the importance of studying the leaching kinetic mechanism and understanding the solid surface structure changes during the process to optimize the operational conditions (Cerrillo-Gonzalez et al., 2022; Porvali et al., 2020b). The controlled addition of reactants optimized its consumption as can be seen from the ratio of mmol H^+ consumed per mmol of Co^{2+} extracted in test B1 and S1 (7.7 and 3.7 for experiments B1 (batch) and S1 (semi-batch), respectively). Reducing acid consumption also has advantages in the neutralization stage, which usually follows the leaching process. In conventional processes, the solution after leaching still contains residual acid because of the high initial acid concentration required to extract metals (the final pH in the leaching test B1 was close to 0). It involves using a high concentration of reactants to neutralize the solution before recovering the metals (Yang et al., 2020b).

The implementation of the proposal described in the current industrial hydrometallurgical process could be carried out without high additional investment costs because the reactor would be the same as in the batch system. Only the feeding of reactants would change with respect to the batch mode.

4 Conclusion

The optimization of the $LiCoO_2$ leaching process in semi-batch mode has been performed through the evaluation of the more influential parameters in the process (*i.e.*, initial concentration of H_2O_2 and HCl as reductant and leaching agents). The results indicated that maintaining low acid and high reductant concentrations (0.1 M HCl and 1M H_2O_2) enhances the selectivity and extraction yield of the leaching process (93% Li and 91% Co). The controlled addition of acid as an extractant agent enables to operate at low acid concentrations. The semi-batch process controlling the double addition of HCl and H_2O_2 to the system was also evaluated to optimize the initial H_2O_2 concentration. According to the results, the semi-batch mode allows not only to maximize the selectivity of the reactions but also to minimize the consumption of the reactants. The promising results obtained demonstrate that the optimization of semi-batch processes to extract metals from LIBs should be further studied to be implemented for different LIBs materials at an industrial scale.

Acknowledgments

Authors acknowledge the funding from the University of Malaga (B1-2021_35). Cerrillo-Gonzalez acknowledges the FPU2018/04295 grant obtained from the Spanish Ministry of Universities.

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5.5 Paper 5

"Extraction and selective separation of metal ions from $LiCoO_2$ cathodes using citric acid"

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Published in: Journal of Power Sources, 2024

Reference: **M**.M. Cerrillo-Gonzalez, J.M. Paz-Garcia, M. Muñoz-Espinosa, J.M. Rodriguez-Maroto, M. Villen-Guzman (2024). Extraction and selective precipitation of metal ions from $LiCoO_2$ cathodes using citric acid. Journal of Power Sources, 592, 233870.

DOI: 10.1016/j.jpowsour.2023.233870

Journal of Power Sources 592 (2024) 233870

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Extraction and selective precipitation of metal ions from $LiCoO_2$ cathodes using citric acid

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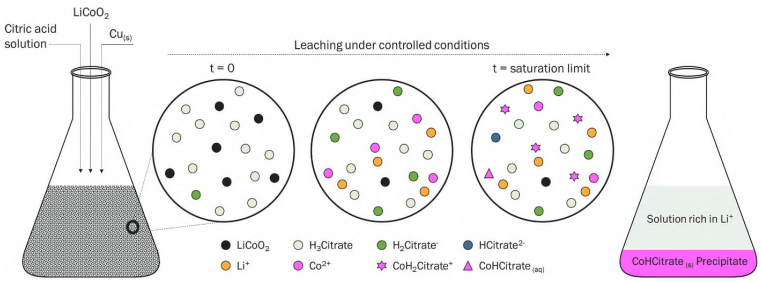
HIGHLIGHTS

- Evaluation of citric acid leaching to dissolved $LiCoO_2$ is presented.
- The addition of Cu as efficient and sustainable reductant agent has been explored.
- The 97 % Li and 81 % Co was extracted under the optimal experimental conditions.
- Cobalt was selectively recovered by formation of citrate complexes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Lithium-ion batteries
Recycling
Leaching
Citric acid
Copper
Citrate-cobalt complexes

ABSTRACT

The most common methods for recycling Lithium-Ion Batteries use strong mineral acids and hydrogen peroxide. Alternative acids and reducing agents are currently being studied to reduce the environmental impact of these batteries recycling processes. This research provides a practical pathway for recycling batteries using citric acid as a sustainable lixiviant. The combination of citric acid and copper as extractant and reductant agents, respectively, to selectively recover lithium and cobalt from $LiCoO_2$ has been studied. Leaching with 2 M citric acid and 70 °C in the presence of copper resulted in a recovery of nearly 100 % Li and around 81 % Co, contained in the liquid phase and the solid precipitate formed during the experiments. Cobalt solubility experiments and solid characterization were performed to understand further the formation of cobalt-citrate solid species detected. Experimental and theoretical results suggest that the precipitate could be identified as CoHCitrate, associated with the selective recovery of cobalt from $LiCoO_2$. Results obtained in this work indicate that citric acid could be used not only as an extractant agent but also as a precursor to precipitate metals from LIBs, improving the efficiency and selectivity of recycling processes.

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https://doi.org/10.1016/j.jpowsour.2023.233870
Received 5 October 2023; Received in revised form 14 November 2023; Accepted 15 November 2023
Available online 12 December 2023

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6 Resumen en español

La batería de ion de litio ha sido uno de los avances tecnológicos de mayor impacto en la sociedad actual. Desde su puesta en el mercado en los años 90, han ido desplazando al resto de baterías recargables en prácticamente todos los aparatos electrónicos portátiles (teléfonos móviles, ordenadores, electrodomésticos y herramientas). Además, su uso en el sector de los vehículos eléctricos y en el del almacenamiento de energías procedentes de fuentes renovables la convierten en un componente clave en la transición hacia un sistema energético descarbonizado y limpio.

Sin embargo, un aumento en la demanda de estas baterías lleva asociadas algunas consecuencias que podrían poner en duda su papel en un sistema de energías limpias. La primera de ellas es que un aumento en la producción trae consigo un aumento en la generación de residuos de baterías, que, en caso de no ser tratadas de forma adecuada, supondría un gran impacto para el medio ambiente. Por otro lado, el auge de esta tecnología conlleva una mayor demanda de algunas materias primas, entre las que se encuentran el litio, cobalto, fósforo o grafito natural, clasificados por la Unión Europea como "materias primas críticas" debido a su alto valor económico y a su baja disponibilidad. Para abordar la problemática relacionada con el aumento de la demanda de LIBs, es crucial el cambio hacia una economía circular en el sector. Diseñar baterías con una mayor vida útil y pensadas para poder ser reutilizadas y recicladas al final de su vida útil, supondrían no solo una disminución del impacto ambiental de las mismas, sino que, además, se convertirían en una fuente secundaria de recursos.

Los métodos actuales de reciclaje de LIBs están basados principalmente en los procesos metalúrgicos. En estos procesos, las baterías son sometidas a un

pretratamiento mecánico y térmico para facilitar la etapa de disolución mediante lixiviación ácida (hidrometalurgia). Tras la etapa de extracción, los metales son separados mediante precipitación, extracción líquida o electrodeposición. Sin embargo, estos procesos normalmente llevan asociados una alta demanda energética, un gran consumo de agua y reactivos, así como la generación de grandes volúmenes de aguas residuales. Por lo tanto, es necesario rediseñar el proceso hidrometalúrgico para hacerlo más sostenible. La transición de una economía hidrometalúrgica lineal hacía una circular podría ser una solución para enfrentar este reto.

Esta tesis doctoral, que se presenta como un compendio de cinco publicaciones, se centra en el proceso de extracción de la etapa hidrometalúrgica. El **objetivo principal** de la misma es la optimización y mejora del proceso de disolución de los metales presentes en los cátodos de las LIBs. Una vez analizado el estado del arte, se propusieron una serie de objetivos específicos para proporcionar, durante el desarrollo de esta tesis, resultados que contribuyeran a superar el objetivo principal de la misma. Los **objetivos específicos** definidos en esta tesis han sido los siguientes:

- Investigar la combinación del método hidrometalúrgico y electrodialítico para la recuperación selectiva de Li y Co de cátodos LIB, centrándose específicamente en integrar la extracción y separación en un solo paso, así como en promover la generación de los protones requeridos en la reacción por la electrólisis del agua.
- Desarrollar un modelo fisicoquímico que permita describir el proceso de extracción de Co y Li de cátodos de $LiCoO_2$ en condiciones ácidas, y evaluar el efecto de la pasivación de las partículas en la eficiencia del proceso.
- Comparar el proceso de lixiviación de $LiCoO_2$ en ausencia y presencia de un agente reductor, extendiendo el modelo fisicoquímico definido previamente para entender los mecanismos de reacción que controlan el proceso y predecir la conversión en ausencia y presencia de agentes reductores.
- Estudiar el efecto de la adición controlada de ácido y agente reductor en el sistema de lixiviación de $LiCoO_2$ utilizando un reactor semi-batch, enfocado en maximizar la selectividad de las reacciones deseadas y el porcentaje de extracción de metales y en minimizar el consumo de reactivo.
- Evaluar el uso de ácido cítrico y cobre como agentes extractante y reductor para la recuperación de metales de cátodos de LIBs, determinando su influencia en el proceso de extracción y el potencial de los iones citratos para formar complejos con los metales solubilizados.

Los resultados obtenidos para alcanzar cada uno de los objetivos específicos planteados en esta tesis ha dado lugar a la publicación de cinco artículos científicos. En todos los trabajos se ha utilizado un sólido comercial de $LiCoO_2$. Se decidió utilizar un sólido comercial en lugar de un residuo real de LIBs para facilitar el estudio del proceso de extracción.

En el primer trabajo, titulado "**Recovery of Li and Co from $LiCoO_2$ via Hydrometallurgical-Electrodialytic Treatment**" (Recuperación de Li y Co de las partículas de $LiCoO_2$ mediante técnica hidrometalúrgica-electrodialítica), se propuso la combinación de la hidrometalurgia con la técnica de electrodiálisis para extraer y recuperar metales de las partículas de $LiCoO_2$ simultáneamente. El diseño experimental consistió en una celda electrodialítica de tres compartimentos, separados por membranas de intercambio catiónico (CEMs). Además, el compartimento central estaba conectado a un recipiente externo donde se llevaba a cabo la disolución de las partículas.

Los resultados mostraron que la celda diseñada permite llevar a cabo simultáneamente la extracción de Li y Co de las partículas y su recuperación en la solución del catolito. El funcionamiento de la celda era el siguiente: los metales se solubilizaron en el recipiente externo y la disolución se recirculó por el compartimento central, donde los metales solubles fueron transportados hacia el compartimento del cátodo bajo la influencia del campo eléctrico aplicado. Una vez en el catolito, el Co se electrodepositó en la superficie del cátodo, mientras que el litio se mantuvo en la disolución. Sin embargo, el proceso estuvo limitado por la disolución de las partículas. Después de seis días de experimentos, solo se consiguió extraer el 33% de Co y el 62% de Li contenidos en el sólido inicial.

Es por ello, que se llevó a cabo un estudio de la cinética de disolución de las partículas de $LiCoO_2$. Tras realizar un análisis XPS a la superficie del sólido antes y después del proceso de extracción, se encontró que, tras la extracción, la superficie solo contenía oxido de cobalto. Estos resultados confirmaron la presencia de una capa externa insoluble (Co_3O_4) que pasiva las partículas de $LiCoO_2$, y, por tanto, que limita el proceso de extracción. Esta capa pasiva dificulta la difusión de los reactivos desde la solución hasta el núcleo no reaccionado, ralentizando la reacción hasta que finalmente se detiene. El uso de una mayor concentración de ácido y agentes reductores podría mejorar el rendimiento de la extracción debido a la eliminación de la capa pasiva de Co_3O_4.

En general, este trabajo destaca el potencial del método propuesto que combina la extracción hidrometalúrgica con las celdas electrodialíticas para la recuperación selectiva de Li y Co de los residuos de LIB. Sin embargo, la técnica debe optimizarse

para ser más eficientes. Considerando la disolución de las partículas como el factor limitante del proceso, se decidió continuar la investigación en la dirección de estudiar las reacciones involucradas en el proceso de extracción.

El segundo estudio, titulado **"Hydrometallurgical Extraction of Li and Co from $LiCoO_2$ Particles-Experimental and Modeling"** (Extracción hidrometalúrgica de Li y Co de las partículas de $LiCoO_2$ – experimental y modelo), se centra en el estudio de los mecanismos de reacción que tienen lugar durante el proceso de extracción. En bibliografía se puede encontrar que se han utilizado diferentes modelos, como el de núcleo decreciente (SCM) o el modelo de núcleo sin reaccionar (USCM) para evaluar la cinética de las reacciones de lixiviación de LIBs. Aunque estos modelos pueden ajustarse a las observaciones experimentales, no describen las particularidades fisicoquímicas del proceso. Es por ello por lo que, en este trabajo, se propuso un modelo físicoquímico, basado en las reacciones encontradas en bibliografía, para describir el proceso de extracción de los metales.

El modelo propuesto se presenta como una variación del modelo de núcleo sin reaccionar. En él, se asume que las partículas son esféricas, con un núcleo cuyo radio disminuye durante el tiempo de reacción mientras que el radio de la partícula permanece constante debido a la formación de una costra externa alrededor del núcleo. A medida que avanza la reacción, el espesor de la costra de Co_3O_4 va aumentando, lo que dificulta la difusión de los protones a través de la costra. Esto provoca que, para un cierto espesor de la costra, la velocidad de difusión de los protones llegue a ser menor que la velocidad de reacción de los protones con el núcleo sin reaccionar. Para poder describir este fenómeno, se han planteado diferentes ecuaciones de velocidades de reacción en función del mecanismo controlante de la reacción (difusión o reacción química).

Para validar el modelo, se llevaron a cabo una serie de experimentos en diferentes condiciones. El primero con una solución de 0.1M HCl y una relación S/L de 5 g/L, y el segundo, con una solución de 2.5M HCl y una relación S/L de 50 g/L. Además de reproducir satisfactoriamente los resultados experimentales, el modelo fue capaz de predecir la proporción no equimolar entre Li^+ y Co^{2+} extraídos, así como la limitación de la cantidad máxima extraída asociada con la formación del Co_3O_4. En ambos experimentos, el porcentaje máximo de Li^+ y Co^{2+} extraídos fue alrededor del 65-70% y del 31-35%, respectivamente. Se puede confirmar que el proceso está limitado por la formación de una capa alrededor del núcleo no reaccionado que ralentiza la reacción hasta que se detiene.

En resumen, el modelo permite estudiar y entender mejor el proceso de lixiviación y predice las limitaciones del proceso de lixiviación de los cátodos de $LiCoO_2$.

Además, confirma que una de las principales limitaciones del proceso es la formación de una capa alrededor del núcleo, que pasiva la partícula, y que ralentiza la reacción hasta que acaba por detenerse. Aunque el modelo se centra en los cátodos de $LiCoO_2$, podría extenderse a otras químicas de cátodos. Además, sería recomendable incluir en el modelo más parámetros que influyen en el proceso de extracción, como sería el uso de agentes reductores o la temperatura de trabajo.

Con el objetivo de ampliar el modelo planteado en el estudio anterior, se decidió evaluar cómo afecta a los mecanismos de reacción del $LiCoO_2$ el uso de un agente reductor. Este estudio se recoge en el tercer trabajo presentado en esta tesis, titulado "**Acid leaching of $LiCoO_2$ enhanced by reducing agent. Model formulation and validation**" (Lixiviación ácida del $LiCoO_2$ mejorada por un agente reductor. Formulación de modelo y validación). En este trabajo, el modelo fisicoquímico planteado fue una extensión del modelo anterior, y, por lo tanto, partía de las mismas suposiciones: partículas esféricas con un núcleo sin reaccionar, formación de una costra de Co_3O_4 alrededor del núcleo y cambio en los mecanismos que controlan la velocidad de reacción (de la reacción química a la difusión de los reactivos).

El agente reductor seleccionado fue el H_2O_2, uno de los más utilizados en el proceso hidrometalúrgico a escala industrial. Aunque es más conocido por su poder como agente oxidante, en este caso se puede utilizar como agente reductor debido al alto potencial de reducción del Co^{3+}/Co^{2+}. Para poder estudiar el efecto de este agente reductor en los mecanismos de la reacción, se plantearon nuevas reacciones químicas que, por un lado, tienen en cuenta la reacción del H_2O_2 con las partículas de $LiCoO_2$ en medio ácido y, por otro lado, la interacción en medio ácido entre el H_2O_2 con la costra de Co_3O_4 formada durante la reacción.

Para validar el modelo, se realizaron una serie de experimentos de extracción variando la concentración de HCl y H_2O_2. Los resultados experimentales mostraron que el modelo es capaz de predecir el porcentaje de Co^{2+} y Li^{+} extraído para un amplio rango de condiciones experimentales. Además, se confirmó que la presencia de H_2O_2 no solo mejora los porcentajes de metal extraído, sino que además influye en los mecanismos que controlan la reacción. Se observó como a altas concentraciones de H_2O_2, la reacción estuvo controlada la mayor parte del tiempo por la reacción química, mientras que, en ausencia de este, se observó que la reacción estuvo controlada por la difusión. Por lo tanto, el uso del agente reductor mejora el proceso de extracción porque no solo reacciona con las partículas de $LiCoO_2$, sino también con la costra de Co_3O_4 que se haya podido formar durante el tiempo de reacción.

La información obtenida en los estudios anteriores sobre la cinética de la reacción de disolución de $LiCoO_2$ en medio ácido y en presencia de agente reductor se utilizó

para optimizar el porcentaje de extracción y la eficiencia del proceso, modificando la configuración del reactor. En el cuarto trabajo, titulado, "**Semi-batch reactor for leaching battery cathodes under low acid concentration**" (Reactor semi-batch para disolver cátodos de baterías a bajas concentraciones de ácido), se propone estudiar el efecto que tiene sobre la eficiencia del proceso el uso de un reactor semi-bacth. Tradicionalmente, el proceso de lixiviación de las LIBs se lleva a cabo en reactores tipo batch, donde el material activo se introduce en el reactor junto con los reactivos y se mantiene en agitación hasta que se alcanza una determinada conversión. Sin embargo, en estos reactores es muy difícil controlar las reacciones paralelas que ocurren durante el proceso.

Del estudio cinético anterior se ha observado que tienen lugar reacciones paralelas, y que, en términos de eficiencia y productividad, el sistema sería ideal si solo tuviera lugar la reacción que disuelve completamente la partícula de $LiCoO_2$ (es decir, sin que se forme la costra de Co_3O_4). Teniendo en cuenta las velocidades de cada una de las reacciones propuestas en los trabajos anteriores, la selectividad de la reacción deseada (coeficiente selectividad definido en la Eq.(29)) podría maximizarse si se mantiene en el medio de reacción una alta concentración de H_2O_2 y una baja concentración de protones. Sin embargo, en un reactor tipo batch, operar a bajas concentraciones de ácido afecta negativamente a la conversión.

Con el objetivo de mejorar la selectividad del proceso, se planteó la posibilidad de llevar a cabo el proceso de extracción utilizando un reactor semi-batch. En este tipo de reactores, los reactivos son alimentados al sistema intermitentemente o de forma continua. Por lo tanto, en este reactor sería posible operar a bajas concentraciones de ácido, ya que los protones consumidos durante la reacción se suministrarían al sistema en base a su consumo. Para poder confirmar esta hipótesis, se llevaron a cabo una serie de experimentos donde se modificó la concentración inicial de ácido y H_2O_2, Hay que destacar que, en todos los ensayos, el pH de la disolución se mantuvo constante debido a que los protones consumidos durante la reacción se alimentaron al sistema de forma intermitente. Es decir, la concentración inicial de ácido se mantuvo constante durante todo el tiempo que duro la reacción.

Los resultados confirmaron la hipótesis planteada sobre la mejora en la selectividad y la conversión de $LiCoO_2$ al utilizar un reactor semi-batch. Por un lado, se observó que la concentración inicial de H_2O_2 juega un papel fundamental en la selectividad el proceso: cuanto mayor es la concentración inicial, mayor es la velocidad de reacción y la conversión. Esto está en línea con la ecuación de la selectividad y la velocidad de la reacción deseada, ambas dependientes de la concentración de H_2O_2 al cuadrado.

Por otro lado, comparando el sistema semi-batch con el batch bajo las mismas condiciones experimentales, se demostró que mantener bajas concentraciones de ácido en el medio de reacción mejoraba el rendimiento del proceso (de un 50% metal extraído a un 70%). La única diferencia entre los dos sistemas experimentales fue la forma en la que los protones fueron añadidos. En el reactor batch, se alimentó una disolución inicial de HCl con una concentración de 1.5M mientras que el semi-batch se introdujo una disolución de 0.2 M HCl, concentración que se mantuvo constante por la adición de ácido al sistema. Por lo tanto, podemos confirmar que el reactor semi-batch tiene la ventaja de que se puede operar a bajas concentraciones de ácido. Esto supone una mejora no solo en términos de rendimientos del proceso de extracción, sino también en una optimización de los reactivos utilizados, tanto en el proceso de extracción como en las siguientes etapas de recuperación.

Este estudio resalta la importancia de estudiar las cinéticas de las reacciones que tienen lugar durante el proceso de lixiviación para optimizar las condiciones operativas. Además, confirma que el uso de reactores semi-batch permiten mejorar la eficiencia del proceso, al poder tener un mayor control en el proceso de disolución de las partículas.

En el último trabajo, titulado "**Extraction and selective separation of metal ions from $LiCoO_2$ cathodes using citric acid**" (Extracción y separación selectiva de los iones metálicos de los cátodos de $LiCoO_2$ usando ácido cítrico), se evaluó el uso del ácido cítrico y el cobre como agente extractante y reductor, respectivamente, en el proceso de lixiviación de cobalto y litio de los cátodos $LiCoO_2$. El ácido cítrico fue seleccionado como agente lixiviante por ser un solvente orgánico que presenta buenos rendimientos de extracción y además, por ser unos de los ácidos orgánicos más baratos disponibles en el mercado. Se decidió estudiar el efecto del cobre como agente reductor porque es un componente ya presente en los residuos de baterías (lámina del ánodo).

Para estudiar el efecto de ambos agentes en el proceso de extracción, se realizaron una serie de experimentos, variando la temperatura de la reacción, la concentración de ácido y la dosis de cobre. En base a los resultados obtenidos, se llegó a la conclusión de que la temperatura es el factor crítico del proceso de lixiviación debido a la endotermicidad de la rección. Por lo tanto, para trabajar con ácido cítrico como agente extractante, se requieren temperaturas superiores a 70ºC. Por otro lado, la concentración de ácido cítrico y el tiempo de reacción también influyen en la eficiencia de la extracción de los metales.

Uno de los aspectos más interesantes encontrados en este estudio fue la formación de un precipitado durante el proceso de lixiviación. Este precipitado apareció tanto

en ausencia como en presencia de cobre cuando la solución de ácido cítrico era 2 M. La única diferencia fue el tiempo de formación: 8 h en presencia de cobre en lugar de 24 h solo con ácido cítrico. En ambos casos, los metales en el precipitado fueron extraídos en una primera etapa del $LiCoO_2$. Una vez que el medio se saturó de iones Co, y se alcanzó el pH de 2.36, se favoreció la formación del precipitado. El resultado: una fase líquida con el 79% y el 10% del Li y Co inicial, y una fase sólida con el 71% del Co inicial. Tras analizar el sólido formado, mediante las técnicas FT-IR, UV-Vis y CHN, se obtuvo que el precipitado formado correspondía a una sal de CoHCitrato. Por lo tanto, aunque el uso del ácido cítrico como agente extractante presenta algunas limitaciones, como puede ser el tener que operar a temperaturas altas, su uso tiene un gran potencial debido a que no solo actúa como agente extractante, sino que también favorece la formación de especies sólidas de citratos de cobalto, permitiendo llevar a cabo la extracción y recuperación en una misma etapa.

Los diferentes enfoques hidrometalúrgicos estudiados en esta tesis ofrecen aspectos prometedores para mejorar la eficiencia del proceso de extracción. Una de las conclusiones obtenidas es la importancia del estudio cinético desde el punto de vista de la optimización del proceso. Conocer las reacciones que tienen lugar y los fenómenos de pasivación de las partículas permiten poder configurar el proceso para maximizar la selectividad de las reacciones deseadas. Por otro lado, el uso de la electrodiálisis se presenta como una técnica con un gran potencial para ser utilizada en el área del reciclaje de baterías, ya que permite separar selectivamente los metales y, además, generar el ácido necesario en la etapa de extracción. En relación a la sostenibilidad del proceso, el uso del ácido orgánico como agente extractante y el cobre como agente reductor presentan un gran potencial. No obstante, se requiere seguir optimizando el proceso de extracción para poder escalar las mejoras observadas en esta tesis.

Además, hay que tener en cuenta que esta tesis se ha centrado en el sólido $LiCoO_2$, uno de los materiales utilizados para fabricar los cátodos de baterías. Para futuros trabajos, se ha propuesto ampliar el modelo físico químico propuesto para estudiar la disolución de diferentes cátodos de LIBs, como NMC o LMO utilizando diferentes agentes extractantes y reductores. También, se planea continuar estudiando el proceso de extracción, tanto en reactores batch como semi-batch, utilizando residuos reales de baterías. Con respecto a la electrodiálisis, se plantea estudiar su uso no solo para separar los metales del medio de lixiviación, sino también, para producir las disoluciones ácidas y básicas requeridas a partir de la disolución final de la etapa de precipitación.

En conclusión, los resultados obtenidos en esta tesis son interesantes y representan un avance significativo en el campo de la extracción de metales de LIBs. Sin embargo, lo que está por venir es aún más prometedor. Los futuros trabajos de investigación propuestos prometen abrir nuevas vías para mejorar aún más la eficiencia y sostenibilidad de estos procesos. Esto no es más que el comienzo, de la que espero, sea una larga carrera académica e investigadora.

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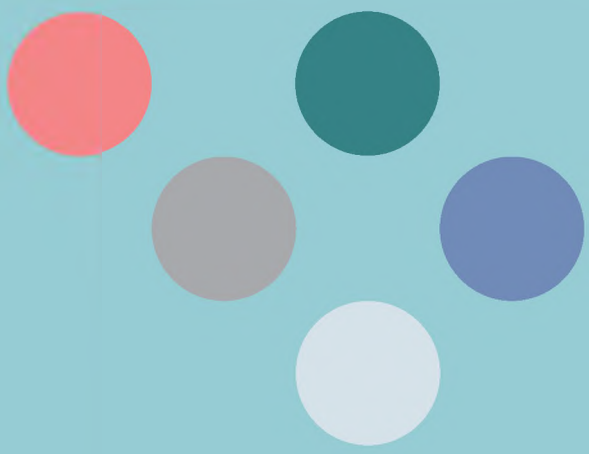

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