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Towards a closed loop recycling process of end-of-life lithium-ion batteries: Recovery of critical metals and electrochemical performance evaluation of a regenerated LiCoO₂

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ABSTRACT

The growing demand for lithium-ion battery technology emphasizes the critical need to establish effective recycling and proper disposal methods for used batteries, ensuring the long-term sustainability and security of the battery supply chain. This study addresses this need by exploring two hydrochemical routes, using sulfuric acid and nitric acid, respectively. The objective is to investigate the influence of the acid used in the leaching process on the properties of the regenerated final product, LiCoO₂. Moreover, a novel and simplified approach for extracting lithium as lithium carbonate is proposed.

In evaluating the recycled batteries, careful examination of their physicochemical properties and electrochemical performances reveals striking similarities to batteries produced from commercial sources. This comparison provides evidence of the successful recycling process. By optimizing the leaching conditions, we were able to extract more than 98% of both cobalt and lithium from the used cathode materials of cell phone batteries.

Significantly, our study demonstrates that nitric acid offers a straightforward method for separating and obtaining a pure product, surpassing the outcomes achieved with sulfuric acid using the same steps. Additionally, we thoroughly investigate and compare the electrochemical performances of the synthesized cathode materials with those synthesized from pure commercial reagents. This systematic analysis confirms the effectiveness and viability of the proposed recycling process.

The key advantage of this approach lies in its ability to achieve a complete recycling of the initial spent cathodic elements, which is crucial for establishing a circular economy. This comprehensive recycling method not only addresses the increasing demand for lithium-ion battery technology but also contributes to the sustainable utilization of resources and the preservation of the battery supply

Keywords: Recycling, Hydro-metallurgical processes, Electrochemical performances, Circular economy, Critical elements

1. Introduction

Lithium-ion batteries (LiBs) are becoming the leading energy storage technology for the future, and they are more and more applied in the automotive industry and for the storage of renewable energies. The global LiB business, considering applications as electric vehicles alone, is estimated to expand at a compound annual growth rate of 25.3%, from USD 27.3 billion in 2021 to USD 67.2 billion in 2025 [1], and According to a report by Statista, the number of smartphone shipments worldwide reached 1.38 billion units in 2020, and it is expected to increase to 1.57 billion units by 2024. As virtually all smartphones rely on it is evident that the use of these batteries in cell phones is extensive [2]. The widespread use of these rechargeable batteries is due to their exceptional performances such as long life, high energy density, and low self-discharge [3]. During their operation, LiBs undergo degradation mechanisms that affect all battery components including the positive and negative electrodes, the current collectors, the electrolyte, and the separator, leading eventually to their end of life [4–7]. Degradation is usually due to the loss of lithium-ion caused by disruptive reactions such as surface film formation (formation of the solid electrolyte interphase) [8,9], and the loss of positive and negative electrode active material through loss of electrical contact caused by resistive surface layers and particle damage. The latter block lithium-ion insertion into the electrodes causing a loss of capacity [10–12].

LiCoO₂ was the first cathode material used in LiB technologies and in particular in the portable electronics field given its high volumetric energy density and stable cyclability [3,11,12]. A direct consequence is the consideration of elements such as Co and Li as critical by number of countries and institutions. Another consequence of the exponent use of these materials is the large amounts of wastes that are generated at all stages of the life-cycle of the products, which potentially results in toxic emissions and hazardous chemicals in landfill [13]. In particular, spent LiBs contain harmful components affecting health and water resources, and can also provoke spontaneous fires. On the other hand, recycling is still in its infancy, whereas this waste represents a real mine of critical elements. Then in a context of natural resource depletion, recycling of LiBs appears as essential solutions that will both i) help reducing the environmental impacts of these wastes ii) provide new supply sources from the technosphere i.e the conversion of resources to actual reserves. The increase interest for LiBs recycling is illustrated by the exponential increase of scientific publications and patents in the past ten years (Fig. S1).

The recycling of used LiBs can be achieved through multiple methods, including Pyrometallurgical, Solvometallurgical, and Hydrometallurgical processes. Pyrometallurgical recycling melts the used battery to separate the metals, while solvometallurgical recycling utilizes solventbased processes to dissolve the metals from the used battery components. Hydrometallurgical

recycling dissolves the active materials of the battery electrode using acidic or alkaline aqueous solutions. This method is particularly appealing for LiBs recycling due to its numerous advantages, including high metal recovery rates, cost-effectiveness, versatility, sustainability, and its environmentally friendly approach, which produces less waste and emissions compared to other methods [14]. In this work, nitric and sulfuric acids were used to dissolve the cathodic material of used batteries. This choice was made due to the high dissolve efficiency of the cathode materials, its relatively safe handling properties, compared to others inorganic acid as hydrofluoric acid and its lower cost compared to organic acids, and widely available.

Many recent works have revealed the use of hydrometallurgical process as one of the most efficient processes for recycling of spent LiBs. Gratz et al. (2014) reported the use of sulfuric acid leaching for the recovery of Ni, Mn and Co from the cathode active materials

($\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}(\text{OH})_2$) [15]. Li et al. (2011) disclosed the use of nitric acid leaching for the recovery of cobalt [16]. All these works have encountered difficulties in recovering lithium in the form of pure lithium carbonate present in the active material of the cathode such as the lithium concentration after Co recovery, which makes direct precipitation difficult to recover lithium as lithium carbonate [17]. Moreover, on an industrial scale, lithium recovery is one of the major challenges, especially for pyrometallurgical processes [18]. In the present work, after the total recovery of cobalt, we propose simple steps that guarantee a high degree of purity of the recovered lithium in form of lithium carbonates.

The cathode part of the battery represents more than 35% of the manufacturing cost because it contains precious metals (Co, Li) [19]. Thus, the aim of this paper was to develop a process for recycling the positive electrode of a cell phone battery to extract valuable metals (Co, Li, Al). Our study has achieved a maximum recovery of metals (Li, Co) while minimizing acid content. In fact, we have developed new conditions that enable the recovery of over 98% of the desired metals. In particular, while the recovery of lithium after the leaching step and precipitation with carbonate is challenging due to its low concentration in solution after cobalt precipitation, we have developed an innovative and a simple method for its recovery. This involves drying the solution and washing it with a small quantity of water, taking advantage of the low solubility of lithium carbonate compared to sodium nitrate and sodium carbonate. It is important to note that this work diverges from most published studies that highlight the challenges of recovering this essential element [22,23]. Additionally, we investigated the impact of the acid used in the leaching step on the extracted product through XRay Diffraction and SEM analysis. It was evidenced that nitric acid yields better extraction results in the leaching step compared to sulfuric acid. We also investigated the separation of sodium nitrate and lithium carbonate compared to sodium sulfate and lithium carbonate and how this affects the electrochemical performance of LiCoO_2 . One goal of the study was to minimize the number of wastes by recovering most of the elements initially present in the cathodes as well as the chemicals used for the process including salts. The recovered cobalt and lithium were then used to prepare a new LiCoO_2 cathode. A comparison was made between using sulfuric acid (H_2SO_4) and nitric acid (HNO_3) as leaching agents of the targeted valuable metals contained in the end-of-life cathode active materials. The recovered elements were used to synthesize a new LiCoO_2 cathode. In parallel, LiCoO_2 have been elaborated from commercial cobalt sulfate and cobalt nitrate using the same synthesis conditions. The structural, morphological, and electrochemical performances of the different synthesized phases either by sulfuric acid or nitric acid, and the oxides synthesized by commercial reagents were compared. In the optic of reducing the amount of waste and increasing the recycling performance of the entire process, sodium sulfate, sodium nitrate and aluminum hydroxide were recovered as by-products.

2. Experimental section

2.1. Recycling process

A spent cell phone battery (type Samsung) with a LiCoO_2 cathode was used for this study. The recycling of the battery consisted in the following successive steps: (1) dismantling and manual separation of the different constituents, (2) leaching of remaining Al in alkaline conditions and its recovery by precipitation with HNO_3 , (3) leaching of Co and Li using either nitric or sulfuric acid, (4) precipitation of Co with NaOH, (5) recovery of Li through precipitation with carbonates, (6) synthesis of the new cathodic material from recovered Co and Li metals. The flowsheet is summarized in Fig. 1. Detailed of each step is further described below:

2.1.1. Battery dismantling

The used cell phone battery was first discharged to prevent any potential explosion. As the battery charges, lithium metal accumulates on the surface of the negative electrode, forming branches and crystallizing. If a charged battery is manually disassembled, the battery casing can be damaged, which allows oxygen to come into contact with these lithium crystals, causing an explosion. That's why it is crucial to discharge the battery before disassembling it. To achieve this, a BioLogic MPG2 battery cycler is utilized to discharge the battery (Torphan.,2021).

The discharged LiB was manually disassembled to separate the cathode part from other components (anode, separator, plastic). The electrolyte was evaporated by drying the electrodes at room temperature.

2.1.2. Recovery of aluminum

The cathode body is composed of two parts: the current collector (aluminum foil) and the cathodic active mass (black mass) which contains the targeted metals (Co, Li) and a binder of polyvinylidene fluoride (PVDF). To separate the two parts, several strategies exist. One of the most described is thermal treatment at 550 °C to remove the PVDF, but this method requires a significant amount of energy and produces toxic emissions [22]. Another approach is the dissolution of PVDF by N-

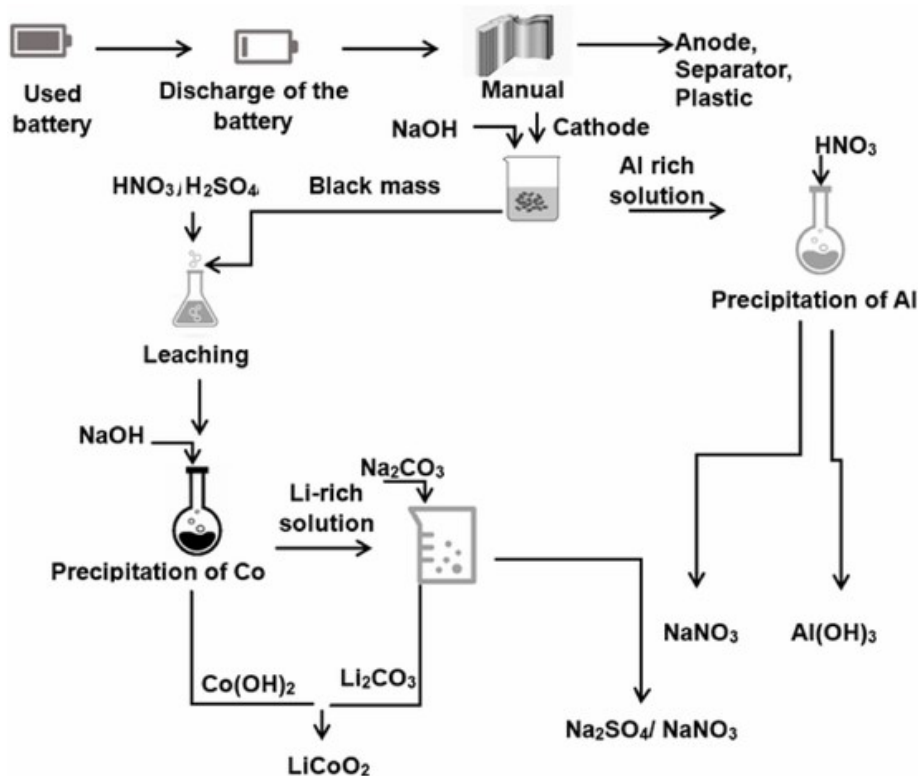


Fig. 1. Flow sheet of the process used for recycling cathode active material of Samsung type cell phone battery.

Méthyl-2-pyrrolidone (NMP), however, this method does not completely dissolve PVDF and has limitations due to the toxicity of NMP.

A third method was chosen, which involves dissolving the aluminum foil in sodium hydroxide, 1 M for 2 h with a solid-liquid ratio of 100 g/L. This method results in the complete dissolution of the aluminum current collector and a total recovery of the cathodic active material (containing binder and carbon black). The aluminum-rich solution is filtered to separate it from the cathodic active material and the aluminum is recovered as hydroxide $\text{Al}(\text{OH})_3$ through precipitation at pH = 6.3 using nitric acid (1 M). After 2 h of reaction, the $\text{Al}(\text{OH})_3$ precipitate is filtered and the Na-rich solution is evaporated to recover sodium nitrate powder.

2.1.3. Recovery of cobalt

The leaching process was performed using a ceramic hotplate from IKA (model C-MAG HP 10) and an Erlenmeyer flask covered with glassware. The temperature was monitored with a stainless-steel IKA thermometer (\varnothing 3 mm, 230 mm, PT 1000.6).

After the leaching step, the pH of the obtained solutions was adjusted to 12 by adding NaOH (1 M) to selectively precipitate $\text{Co}(\text{OH})_2$. The solutions were then stirred for 2 h and left to rest for 12–14h. This step aims to guarantee the complete precipitation of cobalt hydroxide minimizing its loss. The precipitated powders were filtered and washed to recover the cobalt hydroxide and separate it from the Li-rich solution.

2.1.4. Recovery of lithium

Lithium was recovered through evaporative crystallization using sodium carbonate to extract lithium as lithium carbonate to be used as a lithium source for lithium cobalt oxide LiCoO_2 synthesis with molar ratio of $\text{Na}/\text{Li} = 1$. The solution was evaporated in the oven at 100 °C. The obtained powder was washed on a filter (Whatman filter) with deionized water to separate Li_2CO_3 from dissolved salts (Na^+ , $\text{NO}_3^-/\text{SO}_4^{2-}$) using liquid solid ratio of 5 ml/g. The recovery of lithium carbonate was very difficult due to the low mass concentration of lithium in the solution after the cobalt precipitation. The

remaining sodium-rich solution was dried at 100 °C to recover sodium nitrate/sulfate powders.

2.1.5. Synthesis of LiCoO_2

A specific amount of lithium carbonate was added to the dried cobalt hydroxide (molar ratio of $\text{Li}/\text{Co} = 1.1$), ground manually for 10 min and calcined at 900 °C for 12 h in air to synthesize LiCoO_2 . So, two LiCoO_2 products were generated depending on the leaching agent used for the Lithium and cobalt recovery. These products were labelled LCO-N (Nitric acid process) and LCO-S (Sulfuric acid process).

For comparison, LCO was also prepared by using commercial CoSO_4 (VWR Chemicals; ≥ 98 wt%) and $\text{Co}(\text{NO}_3)_2$ (VWR Chemicals;

≥ 98 wt%). Co salts were previously transformed into cobalt hydroxide ($\text{Co}(\text{OH})_2$) in water by precipitation at pH 12 using NaOH (1 M) and used as raw material with commercial Li_2CO_3 (HIMEDIA; ≥ 98.5 wt%) to prepare LCO using the same process used in the case of recycled metals. The two oxides formed from commercial metals are hereafter referred as LCO-CN for cobalt nitrate and LCO-CS for cobalt sulfate.

2.2. Material characterization

The quantification of chemical elements at different stages of the process, Li and Co was performed by inductively coupled plasma optical emission spectrometry (ICP-OES) using PerkinElmer Optima 7000 DV (PerkinElmer, Waltham, USA).

Mineralogical analysis of the synthesized materials was performed by X-ray diffraction on a Rigaku Smart Lab SE X-ray diffractometer (XRD) in the 2θ range of 15–75° and with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) and a power of 2 kW ($V = 50\text{kv}$, $I = 40 \text{ mA}$). The morphology of the studied samples was evidenced by a TESCAN VEGA3 scanning electron microscope instrumented with an EDAX EDS microanalysis system voltage of 10 keV. Energy dispersive spectroscopy was used to confirm the atomic composition of the synthesized materials.

Electrochemical tests have been performed in CR2030 coin cells using commercial electrolyte 1 M LiPF₆ dissolved in 50:50 ethylene carbonate (EC): dimethyl carbonate (DMC). The cathode consists of 80 wt% LCO, 10 wt% conductive carbon black, and 10 wt% polyvinylidene difluoride (PVDF) binder. The anode is a lithium metal foil (LF). Whatman glass fiber membranes were used as the separator. The cells were assembled in an Argon-filled glove box. Electrochemical tests were performed on a BioLogic MPG2 battery cycler at room temperature. Galvanostatic cycling with potential limitation was conducted at different current rate over 2.5–4.5 V potential window. These electrochemical tests were conducted using a current rate of C/10.

3. Results and discussion

3.1. Aluminum recovery

Fig. S4 shows the XRD results of the recovered powder at the step after dissolution in alkaline conditions and precipitation of the Al-rich filtrate at pH 6.3. The XRD results reveal the formation of Al(OH)₃, meaning that the used conditions allow great control of the precipitation step and lead to the formation of a pure aluminum hydroxide phase. However, the presence of additional peaks is associated with Al(OH)₃·3H₂O due to the adsorption of water molecules on the surface of the formed Al(OH)₃. Nevertheless, the successful recovery of the entire aluminum content was achieved by analyzing the solution after Al recovery, which showed an Al concentration of less than 0.01 ppm as determined by ICP-OES.

3.2. Characterization of the Al-free cathode active material

Chemical composition and mineralogy of the recovered black mass was analyzed. According to the obtained XRD pattern, presented in Fig. 2, the diffraction peaks of active material revealed the presence of a layered structure with rhombohedral symmetry (α -NaFeO₂ type-structure; space group R-3m). The peaks represented in this pattern are assigned to (003), (101), (104), and (015) plans, respectively. The elemental analysis using ICP-OES results presented in Table S1 indicates that the cathode active material of the used cell phone battery is composed of 59.55 0.03 wtwt% of cobalt and 5.65 0.02 wtwt% of lithium. These results indicate that the active material is constituted mainly of LiCoO₂.

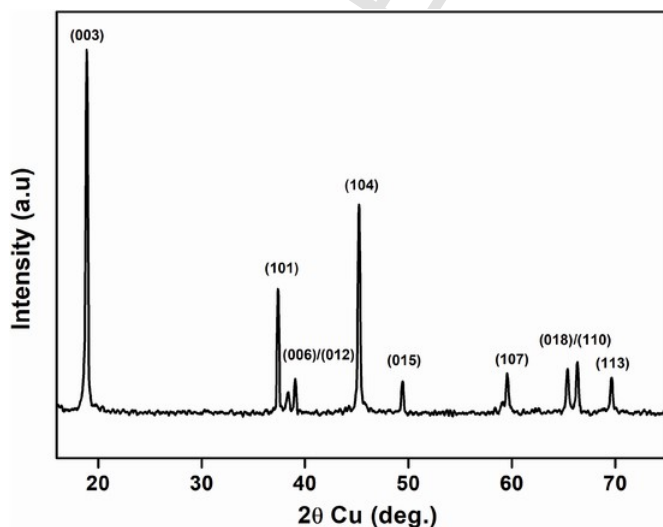


Fig. 2. X-ray diffractogram of the spent cathode active material of the Samsungtype cell phone battery after separation of Al.

3.3. Leaching optimization

3.3.1. Nitric acid

The leaching step was thoroughly investigated by systematically varying multiple parameters. Nitric acid was employed as the leaching agent for extracting LiCoO₂ from used batteries. During this investigation, the temperature was carefully adjusted within the range of 60–100 °C while the other parameters were kept constant (2 M, 2h, 1.5 vol% H₂O₂, 25 g/L) (Fig. S2 (a)). It was clearly demonstrated that a notable trend in the extraction yield of Co and Li in response to temperature changes. As the temperature increased up to 90 °C, the extraction yield of Co and Li exhibited an upward trend. This can be attributed to the favorable influence of higher temperatures on the dissolution process. Elevated temperatures enhance ion mobility and accelerate the chemical reactions involved in the leaching process. Furthermore, the increased temperature promotes the breakdown of solid particles and increases the interaction between the nitric acid and the cathode material. However, an intriguing observation emerged beyond the 90 °C mark. The extraction yield of both Co and Li started to decline. This phenomenon can be linked to the decomposition of nitric acid at higher temperatures. Specifically, the heat leads to the formation of nitrogen dioxide (NO₂) gas, which subsequently escapes from the solution. Consequently, the concentration of nitric acid available for leaching decreases, resulting in a reduction in extraction efficiency.

After setting the temperature at 80 °C to achieve extraction yields of over 95.4 wt% and 95.5 wt% for Co and Li, respectively, and to minimize energy consumption, we evaluated the impact of nitric acid concentration on the extraction process. The parameters were fixed at 80 °C, 2h, 1.5 vol% H₂O₂, and 25 g/L. Through our evaluation (as depicted in Fig. S2 (b)), we observed that as the acid concentration increased from 0.5 to 1.5 M, the extraction yield exhibited a corresponding increase, rising from 41.1 wt% and 43.2 wt% to 95.4 wt% and 95.65 wt% for Co and Li, respectively. This relationship can be attributed to the increase in protons within the acid solution, which enhances the dissolution of the used cathode materials. Considering these findings, we opted for the acid concentration setting at 1.5 M in order to optimize the remaining parameters while minimizing excessive acid usage.

Regarding the optimization of the leaching time, we conducted a comprehensive series of experiments, systematically varying the duration from a minimum value to 90 min (Fig. S2 (c)). Strikingly, we achieved extraction yields exceeding 95 wt% for both lithium (Li) and cobalt (Co) within this significantly reduced timeframe, surpassing the extraction yields obtained in previous 2-h leaching tests. The key reason for this remarkable outcome lies in the optimized contact between the leaching solution and the cathode material, leading to the minimization of the energy consumption.

The use of H₂O₂ for leaching cobalt (Co) and lithium (Li) from used cathode materials is attributed to its role in enhancing the dissolution of cobalt. The addition of H₂O₂ converts Co³⁺ ions to Co²⁺ ions, effectively increasing the leaching efficiency. Through several series of experiments, we observed that increasing the concentration of H₂O₂ promotes the dissolution of metals (Fig. S2 (d)). With 1v% concentration of H₂O₂, we were able to achieve extraction yields exceeding 96.2 wt% and 96.4 wt% for cobalt and lithium, respectively. However, it is important to note that there is a difference in extraction yields compared to previous results. This discrepancy can be attributed to the excessive concentration of H₂O₂, which may lead to side reactions that limit the overall extraction efficiency. It is crucial to strike a balance in H₂O₂ concentration to ensure optimal leaching conditions and maximize the extraction yield while minimizing any detrimental side reactions.

The impact of the solid-liquid ratio on the extraction yield of both cobalt (Co) and lithium (Li) was investigated through a series of experiments (Fig. S2 (d)). It was observed that increasing the solid-liquid ratio resulted in a decrease in the extraction yield of Co and Li. This phenomenon can be attributed to the limitation in surface area contact between the acid solution and the used cathode material, which hinders the dissolution of metals.

The optimal leaching conditions involving nitric acid (1.5 M concentration, 80 °C temperature, 1.5-h duration, 1 vol% H₂O₂, and 20 g/L solid-liquid ratio) resulted in extraction yields exceeding 98.99 wt% for cobalt (Co) and 98.23 wt% for lithium (Li). These findings demonstrate significant improvements compared to previous studies, such as the work conducted by Yuliusman et al. where they achieved a cobalt extraction yield of 98.01 wt% at 90 °C with a 3 M acid concentration [23]. Our study highlights the advantage of achieving higher extraction yields while minimizing acid usage and reducing energy consumption during the leaching process. By optimizing the leaching conditions, we were able to enhance the efficiency of metal extraction from the used cathode materials. This not only contributes to maximizing the recovery of valuable cobalt and lithium but also offers a more sustainable and energy-efficient approach to the leaching process.

3.3.2. Sulfuric acid

In the case of leaching process using sulfuric acid, we conducted experiments to investigate two key parameters: sulfuric acid concentration and solid-liquid ratio. In comparison to the optimized conditions for nitric acid, we found that sulfuric acid resulted in lower extraction yields for both cobalt (Co) and lithium (Li). At a sulfuric acid concentration of 1 M, the extraction yields were measured at 69.8 wt% for Co and 70.5 wt% for Li. However, increasing the sulfuric acid concentration to 4 M significantly improved the extraction yields to 95.4 wt% for Co and 95.6 wt% for Li.

Regarding the parameter related to the variation of solid-liquid ratio, we observed that increasing this ratio from 20 g/L to 60 g/L led to a slight decrease in extraction yields, with only marginal impact on the overall extraction efficiency. Specifically, at a solid-liquid ratio of 60 g/L, the extraction yields were measured at 94.96 wt% for Co and 94.69 wt% for Li.

The optimized conditions for sulfuric acid leaching were determined as follows: 4 M sulfuric acid concentration, 80 °C temperature, 1.5-h leaching duration, 1 vol% H₂O₂ addition, and a solid-liquid ratio of 60 g/L. These conditions allowed for the extraction of over 94 wt% of both Co and Li, surpassing the results obtained in previous studies done by Partinen et al. where the extraction yield for cobalt and lithium was reported at 90 wt% [24].

The main reason for this difference can be attributed to the disparity in the oxidizing potential between these two acids. Nitric acid is a strong oxidizing acid, while sulfuric acid is a strong acid but lacks the same level of oxidizing power. The oxidizing properties of nitric acid enable it to more effectively dissolve cobalt and lithium species compared to sulfuric acid.

3.4. Mineralogical analysis of the precipitated Co, Li and Na products

The structural analysis of both lithium precipitates formed from nitric and sulfuric acid leaching solutions reacted with Na₂CO₃ are presented in Fig. 3. In both cases Li₂CO₃ is formed as expected. As shown in Fig. 3a, the powder elaborated from the leachate obtained with nitric acid provides a pure phase consistent with previous studies [26,27]. For the second one (Fig. 3b), some additional peaks can be observed on the XRD pattern attributed to sodium sulfate despite washing.

Finally, after recovery of Co and Li precipitates, Na present in the washing solutions was precipitated as NaNO₃ or Na₂SO₄ as confirmed by XRD (Fig. 4). The XRD patterns of the final products recovered at the end of the process are shown in Fig. S5. These products were recovered after the twelfth step of the precipitation of Li-carbonate, as well as the step after the precipitation of aluminum hydroxide wherein. The XRD results confirm the formation of sodium nitrate of high crystallinity in comparison with the obtained powders by Wang et al. (NaNO₃) [26].

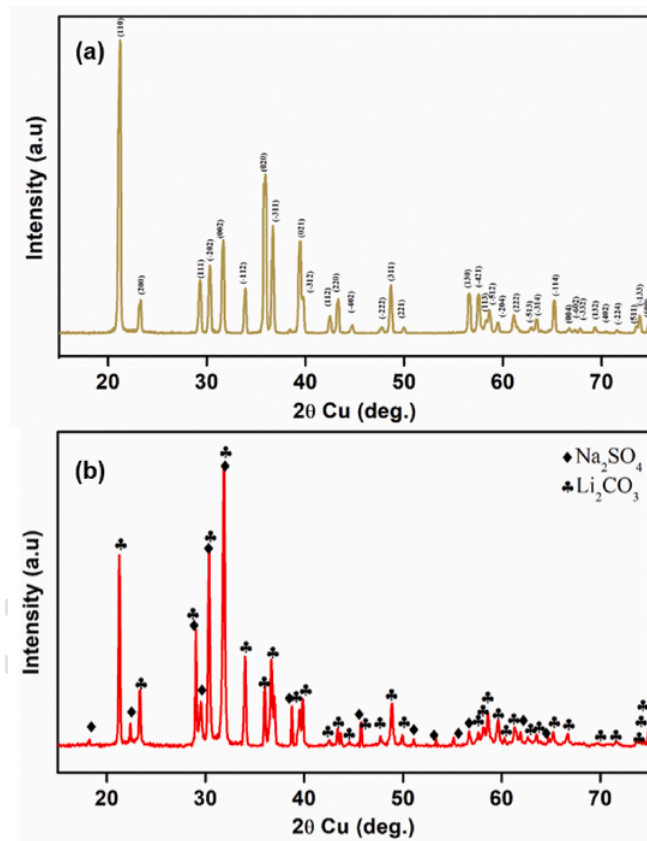


Fig. 3. XRD diffractogram of the recycled lithium carbonate by (a) nitric and (b) sulfuric acid.

Regarding the final product obtained in the sulfuric route, sodium sulfate was formed with additional lithium carbonate impurities. Although the XRD peaks of Na₂SO₄ elaborated by Masood et al. confirm the obtained peaks shown in Fig. S5 b [27].

3.5. Synthesis of new cathodic material

LCO material was synthesized from both commercial and recycled metals. The elaborated phases synthesized from recycled and commercial Li and Co, exhibit identical mineralogy as observed by X-ray diffraction patterns (Fig. 4). The diffraction peaks observed for the obtained products reveal the formation of a rhombohedral α-NaFeO₂ type structure corresponding to the R-3m space group. The peaks shown in the diffractograms are assigned to the (003), (101), (006), (012), (104), (105), (107), (018), (110), and (113) plans that are characteristic of LCO oxide. We can say that, as for the LCO prepared by coprecipitation using commercial precursors, the regenerated active material gives a pure (in term of crystallinity) LCO phase since no additional peaks were observed. Moreover, both samples are highly ordered layered structure, shown by the well-splitting peaks (006)/(102) at 38° and (108)/(110) at 66° [28].

The hexagonal unit cell parameters calculated of the phases developed either by recycled or commercial solutions (Table S3) are equal to a = 2.815 Å and c = 14.05 Å, in agreement with the standard reference of LiCoO₂ (JCPDS:01-077-1370). The value of c/a ratio gives an idea of the flexibility of the LCO structure for Li⁺ intercalation/deintercalation [29]. Based on the values of commercial products (c/a = 4.99), we can say that the recycled products (c/a = 5.00) will probably exhibit the same behavior as the commercial ones in term of Li⁺ insertion/extraction in LiCoO₂. The two peaks (003) and (104) are very important for the crystallization of the structure because the first peak (003) shows the characteristic of the layered structure of LCO and the second shows

the characteristic of the base unit of the Co–O–Co bond [30]. Thus, the higher the value of the intensity ratio $I(003)/I(104)$, the higher the crystallinity of the prepared oxide [29]. It can be concluded that recycled products are as well-crystallized as those synthesized by commercial products.

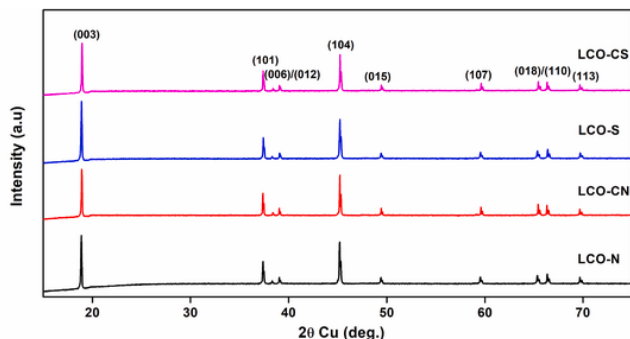


Fig. 4. X-ray diffractogram for synthesis LiCoO_2 .

3.6. Morphological analysis

The SEM micrographs of LCO from recycled CoSO_4 and $\text{Co}(\text{NO}_3)_2$ along with synthesized LCO using commercial CoSO_4 and $\text{Co}(\text{NO}_3)_2$ are shown in Fig. 5.

Fig. S6 indicates the particle size distribution of the four synthesized phases. The histograms of the as-prepared oxides depict a broad and unimodal particle size distribution. The average elliptical long diameter of particles of LCO-S, LCO-CS, LCO-N, and LCO-CN are 580 nm, 10 μm , 1.5 μm , and 14 μm , respectively. The difference in the particles size could be attributed to the presence of impurities in the recycled products potentially affecting growth of the particles leading to smaller particles when formed from recycled Co and Li compared to commercial materials. In addition, particles formed from sulfate salts are smaller than the ones formed from nitrate salts.

It is found from the results of the energy dispersive spectroscopy (Fig. S7) that the elaborated oxides are mainly composed of cobalt and oxygen atoms. It should also be noted the presence of a small peak of aluminum in LCO recycled from both leaching solution, which indicates that the attack of the cells by NaOH does not allow the total solubilization of the aluminum current collector. In addition, a sulfur peak was observed in LCO-S due probably to the presence of NaSO_4 in the lithium carbonates powder extracted by sulfuric acid. Lithium was not detected because its emission line ($K\alpha = 54 \text{ eV}$) was below the energy range of the instrument. 3.7. Electrochemical test

Fig. 6 represents the electrochemical performance of LCO synthesized from the recycled and commercial precursors. The first charge capacities of the LCO-S, LCO-N, LCO-CS, and LCO-CN are 174.5, 198.2, 195.8, and 214.5 mAh.g^{-1} , respectively. While their discharge capacity are 126.8, 165.5, 184.3, and 199.1 mAh.g^{-1} respectively. During the first cycle, LCO-N provides a higher discharge/charge capacity than LCO-S. In addition, the discharge/charge capacity of LCO-N exceeds the practical discharge/charge capacity of LiCoO_2 (140 mAh.g^{-1}) [31].

From Fig. 7, it appears that between the 1st and the 20th cycle, the discharge capacity decreases from 165.4 mAh.g^{-1} to 148.2 mAh.g^{-1} for LCO-N and from 214.5 mAh.g^{-1} to 149.1 mAh.g^{-1} for LCO-CN. Hence, the capacity loss is assumed to be 10.4 wt% for LCO-N and 30.5 wt% for LCO-CN. Thus, the recycled LCO gives better reversibility compared to LCO elaborated with commercial precursor.

Fig. 8 represents the electrochemical performance of LCO-S and LCO-CS. The discharge capacity of these oxides decreases between the 1st and 20th

cycle from 126.8 mAh.g^{-1} to 121.3 mAh.g^{-1} and from 184.3 mAh.g^{-1} to 171.3 mAh.g^{-1} respectively, which represents a loss of discharge capacity of 4.3 wt% for LCO-S and 7 wt% for LCO-CS. The obtained results confirm, similarly to the nitric system, that the regenerated LCO-S allows better reversibility than LCO-CS.

Based on the results obtained after the electrochemical tests, it can be concluded that the recycled LCO phases provide enhanced reversibility than the LCO performed with commercial precursors. This performance of the regenerated LCO could be related to morphological properties (particle size). On the other side, and in terms of the capacity of the recycled cathode, LCO-N has a higher capacity than LCO-S, but in terms of reversibility of the capacity (coulombic efficiency and loss of capacity after 20 cycles), it is obvious that LCO-S is more efficient. This difference in electrochemical performance is due to the difference in particle size [32].

In fact the comparison of the electrochemical performance of two prepared LCO, namely LCO-N and LCO-S, needs more detailed investigations as it depends on many intrinsic features of the electrode materials. One of the main parameter influencing the electrochemical behavior is the morphology of the electrode material. It is obvious that the morphology directly impacts the three components of lithium insertion/extraction: the charge transfer at the interface between the electrolyte and the active material, the transport phenomena evolving in the volume of the active material and the diffusion paths. Changing the morphology thus changes the performance in terms of power density, stored capacity and long-term cycling.

The EDX analysis of the prepared materials indicated the presence of impurities in the recycled product compared to the one prepared from commercial sources. This presence of impurities has been found to affect the particle size growth, as demonstrated by the particle size distribution analysis and SEM analysis. Furthermore, the absence of additional peaks in the XRD results for the recycled product indicates that the impurity content is below 0.4 wt%, as mentioned in the previous study by Shi Chen et al. [33]. The observed particle distribution has a significant impact on the electrochemical performances, specifically in terms of improved reversibility. This finding is consistent with the previous work by Choi et al. [32], who demonstrated that nanoparticles enhance the reversibility of LiCoO_2 while larger micro particles exhibit higher discharge capacity. These results align with our findings, highlighting the influence of particle size on the electrochemical behavior.

4. Conclusion

In this work, we have successfully recycle the cathodic part of the phone portable battery using two different leaching acids. The leaching efficiencies of Li and Co in nitric acid are 98.23 wtwt% and 98.99 wtwt%, respectively. While they attain 94.96 wtwt% and 94.69 wtwt% in the case of sulfuric acid. The comparison between the two recycled LiCoO_2 oxides as well as their comparison with the LiCoO_2 oxides prepared from commercial reagents showed that the recycled LCOs have identical structural characteristics to the commercial LCOs. However, the difference in morphological properties leads to distinguished electrochemical performances of the prepared LCOs. It has been demonstrated that the process followed in this work allows recycling of the cell phone battery and regeneration of LiCoO_2 cathode identical to the commercial one. Moreover, it has been proved that the elaborated LCO electrochemical behavior strongly depends on the leaching acid. Aluminum was also recovered as hydroxide along with the sodium used during the process in the form of Na_2SO_4 and NaNO_3 aiming for the further environmental and economic profit. These findings clearly give a proof-of-concept and the efficiency of the recycling process of end-of-life lithium-ion batteries within a circular economy approach.

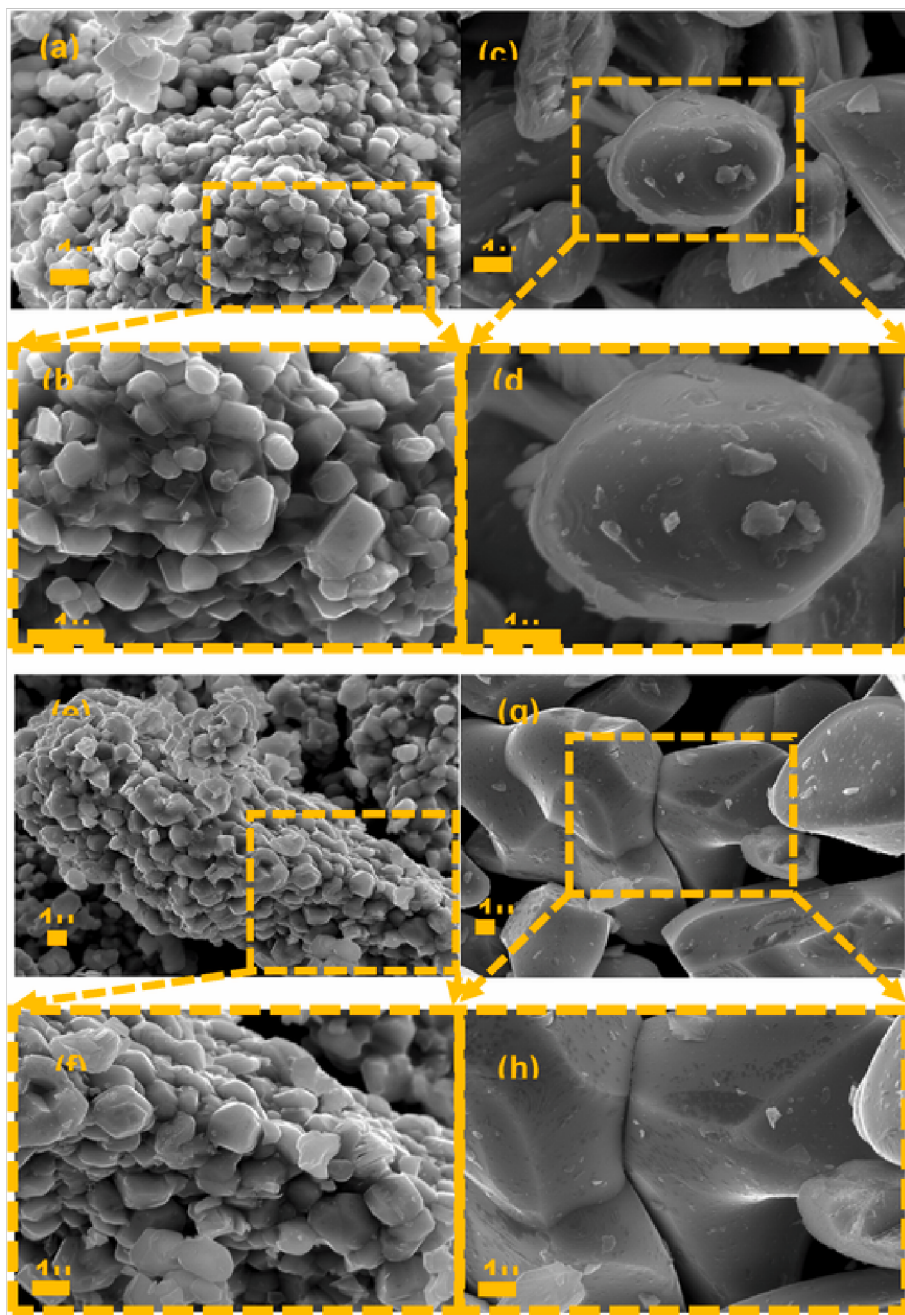


Fig. 5. SEM images of LCO-S (a),(b), LCO-CS (c),(d), LCO-N (e),(f), LCO-CN (g),(h).

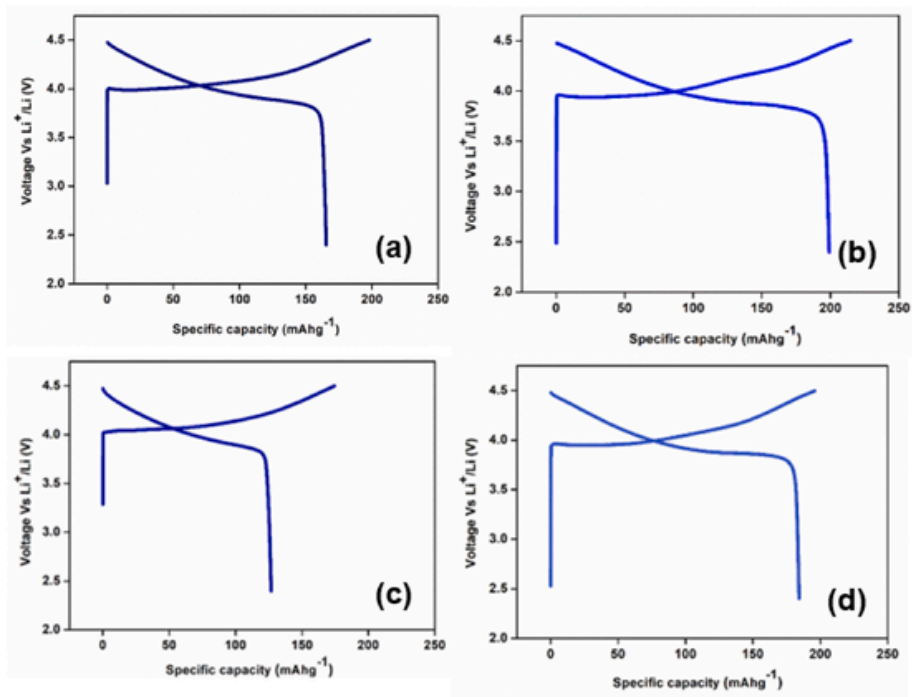


Fig. 6. 1st charge/discharge of (a) LCO-N (b) LCO-CN (c) LCO-S, (d)LCOCS using C/10 rate.

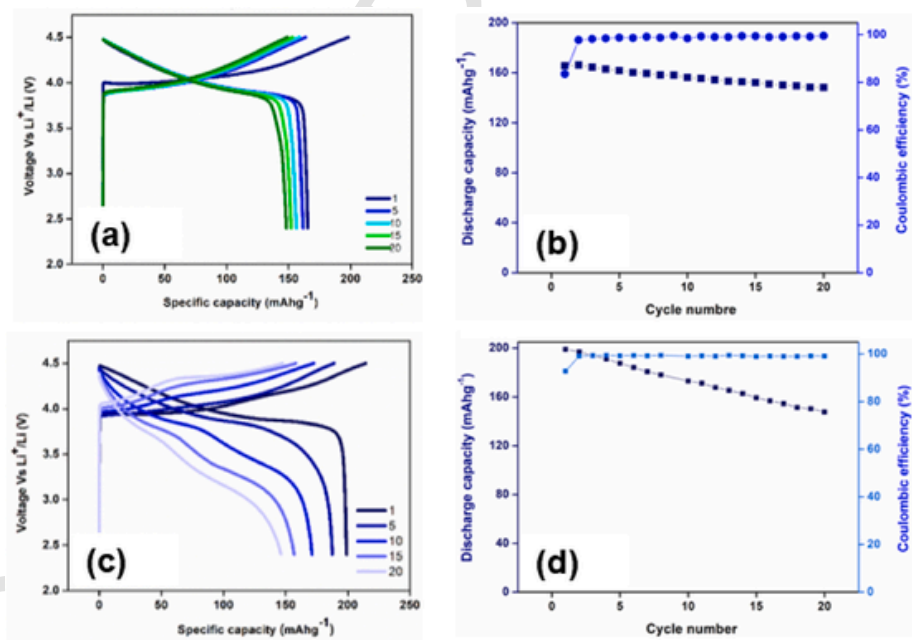


Fig. 7. Coulombic efficiency/specific capacity of charge/discharge cycles for the first twenty cycles LCO-N(a)(b), LCO-CN (c)(d) using C/10 rate.

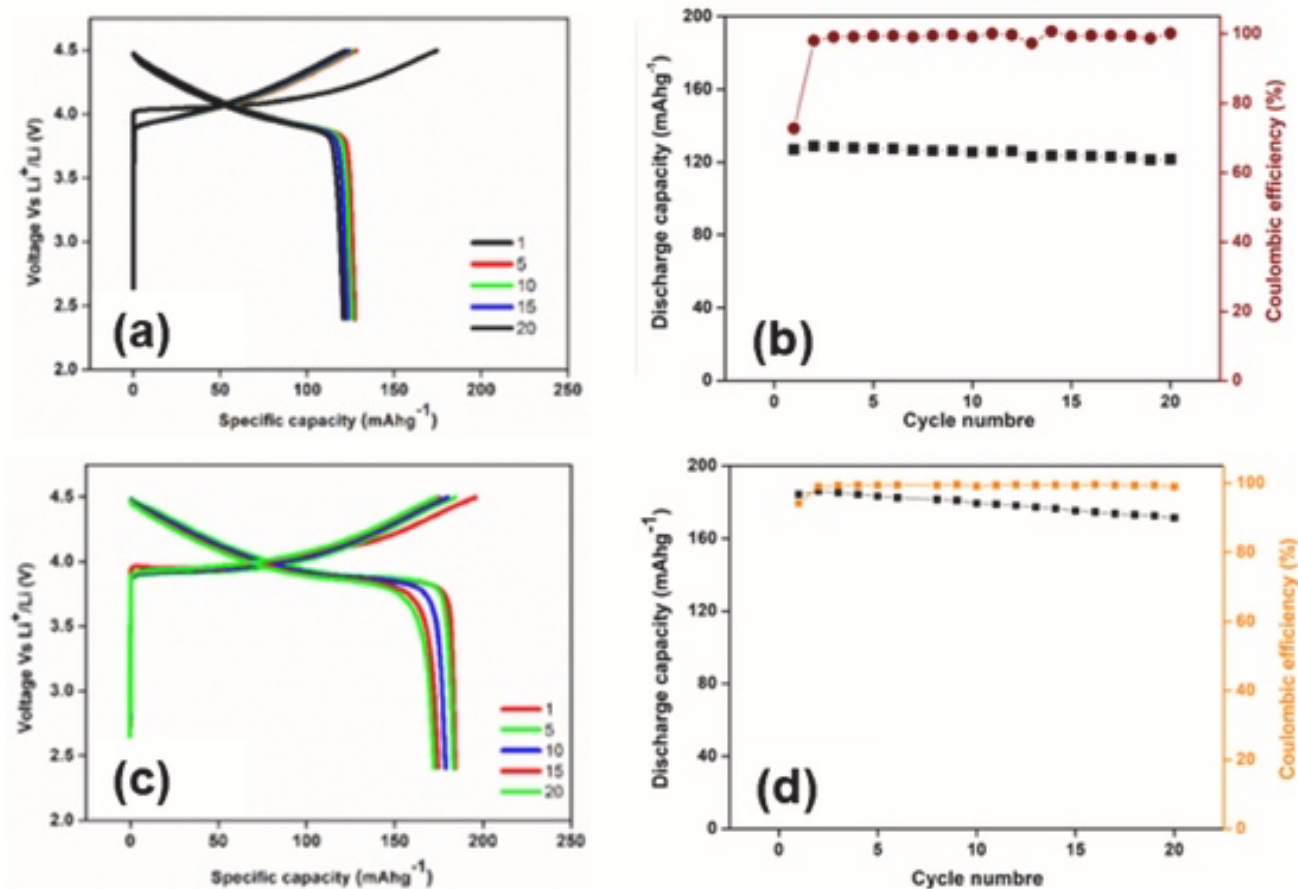


Fig. 8. Coulombic efficiency/specific capacity of charge/discharge cycles for the first twenty cycles LCO-5(a)(b), LCO-CS(c)(d) using C/10 rate.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jpowsour.2023.233341>.

References

- [1] ReportBuyer, Global electric vehicles battery market: focus on battery electric vehicle, plug-in hybrid electric vehicle, lithium-ion battery, and passenger car application - analysis & forecast - <https://www.prnewswire.com/news-releases/global-electric-vehicles-battery-market-focus-on-battery-electric-vehicle-plug-in-hybrid-electric-vehicle-lithium-ion-battery-and-passenger-car-application-analysis-forecast-2017-2026-300648997.html>, 2017-2026 (consulté le 13 septembre 2022).
- [2] Smartphone shipments worldwide 2009-2022 », Statista. <https://www.statista.com/statistics/271491/worldwide-shipments-of-smartphones-since2009/> (consulté le 9 mars 2023).
- [3] Y. Lyu, et al., An overview on the advances of LiCoO₂ cathodes for lithium-ion batteries, *Adv. Energy Mater.* 11 (2) (2021) 2000982, <https://doi.org/10.1002/aenm.202000982>.
- [4] P. Verma, P. Maire, P. Novák, et, A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries, *Electrochim. Acta* 55 (22) (sept. 2010) 6332–6341, <https://doi.org/10.1016/j.electacta.2010.05.072>.
- [5] Understanding the degradation mechanisms of LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cathode material in lithium ion batteries - jung - 2014-advanced energy materials - wiley online library. <https://onlinelibrary.wiley.com/doi/abs/10.1002/aenm.201300787> (consulté le 19 juillet 2022).
- [6] V. Agubra, J. Fergus, et, Lithium ion battery anode aging mechanisms, *Materials* 6 (4) (avr. 2013) <https://doi.org/10.3390/ma6041310>, no 4.
- [7] D. Aurbach, B. Markovsky, I. Weissman, E. Levi, Y. Ein-Eli, et, On the correlation between surface chemistry and performance of graphite negative electrodes for Li ion batteries, *Electrochim. Acta* 45 (1) (sept. 1999) 67–86, [https://doi.org/10.1016/S0013-4686\(99\)00194-2](https://doi.org/10.1016/S0013-4686(99)00194-2).
- [8] J. Vetter, et al., Ageing mechanisms in lithium-ion batteries, *J. Power Sources* 147 (1) (sept. 2005) 269–281, <https://doi.org/10.1016/j.jpowsour.2005.01.006>. [9] M.B. Pinson, M.Z. Bazant, et, Theory of SEI formation in rechargeable batteries: capacity fade, accelerated aging and lifetime prediction, *J. Electrochem. Soc.* 160 (2) (déc. 2012) A243, <https://doi.org/10.1149/2.044302jes>.
- [10] E. Prada, D.D. Domenico, Y. Creff, J. Bernard, V. Sauvart-Moynet, F. Huet, et, A simplified electrochemical and thermal aging model of LiFePO₄-graphite Li-ion batteries: power and capacity fade simulations, *J. Electrochem. Soc.* 160 (4) (févr. 2013) A616, <https://doi.org/10.1149/2.053304jes>.
- [11] R. Deshpande, M. Verbrugge, Y.-T. Cheng, J. Wang, P. Liu, et, Battery cycle life prediction with coupled chemical degradation and fatigue mechanics, *J. Electrochem. Soc.* 159 (10) (août 2012) A1730, <https://doi.org/10.1149/2.049210jes>.
- [12] Y. Bai, W.B. Hawley, C.J. Jafta, N. Muralidharan, B.J. Polzin, I. Belharouak, et, Sustainable recycling of cathode scraps via Cyrene-based separation, *Sustain. Mater. Technol.* 25 (sept. 2020) e00202, <https://doi.org/10.1016/j.susmat.2020.e00202>.
- [13] K. Yamada, Cobalt: its role in health and disease, *Interrelat. Essent. Met. Ions Hum. Dis.* (2013) 295–320.

- [14] E. Asadi Dalini, Gh Karimi, S. Zandevakili, M. Goodarzi, et, A review on environmental, economic and hydrometallurgical processes of recycling spent lithium-ion batteries, *Miner. Process. Extr. Metall. Rev.* 42 (7) (oct. 2021) 451–472, <https://doi.org/10.1080/08827508.2020.1781628>.
- [15] E. Gratz, Q. Sa, D. Apelian, Y. Wang, et, A closed loop process for recycling spent lithium ion batteries, *J. Power Sources* 262 (sept. 2014) 255–262, <https://doi.org/10.1016/j.jpowsour.2014.03.126>.
- [16] L. Li, R. Chen, F. Sun, F. Wu, J. Liu, et, Preparation of LiCoO₂ films from spent lithium-ion batteries by a combined recycling process, *Hydrometallurgy* 108 (3) (juill. 2011) 220–225, <https://doi.org/10.1016/j.hydromet.2011.04.013>.
- [17] A. Porvali, et al., Mechanical and hydrometallurgical processes in HCl media for the recycling of valuable metals from Li-ion battery waste, *Resour. Conserv. Recycl.* 142 (mars 2019) 257–266, <https://doi.org/10.1016/j.resconrec.2018.11.023>.
- [18] H. Dang, et al., Recycled lithium from simulated pyrometallurgical slag by chlorination roasting, *ACS Sustain. Chem. Eng.* 6 (10) (oct. 2018) 13160–13167, <https://doi.org/10.1021/acssuschemeng.8b02713>.
- [19] Z. Li, D. Zhang, F. Yang, et, Developments of lithium-ion batteries and challenges of LiFePO₄ as one promising cathode material, *J. Mater. Sci.* 44 (10) (mai 2009) 2435–2443, <https://doi.org/10.1007/s10853-009-3316-z>.
- [20] G. Battaglia, et al., Recovery of lithium carbonate from dilute Li-rich brine via homogenous and heterogeneous precipitation, *Ind. Eng. Chem. Res.* 61 (36) (sept. 2022) 13589–13602, <https://doi.org/10.1021/acs.iecr.2c01397>.
- [21] Qu'est-ce qui fait exploser une batterie au lithium-ion, Nanjing torphan Co., Ltd. <http://fr.torphanbattery.com/news/what-causes-a-lithium-ion-battery-to-explode47125454.html> (consulté le 18 juillet 2022).
- [22] H. Wang, et al., Separation of the cathode materials from the Al foil in spent lithium-ion batteries by cryogenic grinding, *Waste Manag.* 91 (mai 2019) 89–98, <https://doi.org/10.1016/j.wasman.2019.04.058>.
- [23] Yuliusman, R. Fajaryanto, A. Nurqomariah, et Silvia, Acid leaching and kinetics study of cobalt recovery from spent lithium-ion batteries with nitric acid », *E3S Web Conf* 67 (2018) 3025, <https://doi.org/10.1051/e3sconf/20186703025>.
- [24] J. Partinen, P. Halli, S. Helin, B.P. Wilson, M. Lundström, et, Utilizing Cu⁺ as catalyst in reductive leaching of lithium-ion battery cathode materials in H₂SO₄–NaCl solutions, *Hydrometallurgy* 208 (févr. 2022) 105808, <https://doi.org/10.1016/j.hydromet.2021.105808>.
- [25] B. Han, R. Anwar Ui Haq, M. Louhi-Kultanen, et, Lithium carbonate precipitation by homogeneous and heterogeneous reactive crystallization, *Hydrometallurgy* 195 (août 2020) 105386, <https://doi.org/10.1016/j.hydromet.2020.105386>.
- [26] The promotional effect of sodium chloride on thermophysical properties of nitrate - IOPscience. <https://iopscience.iop.org/article/10.1088/1757-899X/772/>