Recycling of Lithium-Ion Batteries: Overview of Existing Processes, Analysis and Performance

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Lithium-ion batteries (LIBs) have become a widespread technology for electrochemical energy storage in the current era of digitalization and transport electrification, being used as electric stationary storage as well as for powering electric vehicles, e-bikes and portable electronic devices such as smartphones and laptops. However, LIBs contain valuable materials, such as cobalt, nickel, lithium and graphite, whose supply has become critical to meet the increasing demand of batteries. Therefore, proper recycling processes are required in order to recover these materials from spent batteries and re-use them to produce new batteries in a sustainable cycle. This contribution provides an extensive survey of the main recycling routes available today, focusing specifically on pyrometallurgical and hydrometallurgical processes based in Europe, North America and Asia. Attention is also devoted to the recycling behaviour of individuals and companies and to the possible ways to increase their recycling rate. The comparison of different processes allows for the ranking of best practices as well as the drawbacks of different process units, with identification of which materials can be recovered, their recovery rate, and an assessment of the overall recycling efficiency of the process for different battery sizes (small and large, for portable electronics and electric vehicles, respectively). The analysis reveals that pyrometallurgical processes can flexibly treat different LIB chemistries but, since the electrolyte and graphite are burnt in the process, the global recycling efficiency cannot compete with hydrometallurgical processes, especially for small format batteries. Nevertheless, hydrometallurgical processes typically require preliminary mechanical separation treatments to separate the black mass, which contains valuable electrodic materials, as well as complex precipitation steps, which eventually reduce the material recovery rate and the applicability to diverse LIB chemistries. Finally, the study reports an analysis of the electrochemical performance of a battery made with recycled materials, showing that even if recycled cathodic materials had a lower gravimetric capacity and solid-state diffusivity, the performance of a recycled battery could be compensated by simple minor changes to the cell design which would ultimately decrease the specific energy density by a few percent compared to a LIB made with virgin materials.

1. Introduction

The abuse of natural resources and climate change are forcing the society to move towards a sustainable way of life. The decarbonization of the transport sector points in this direction, witnessing a rapid growth of electric vehicle (EV) utilization. Lithium-ion batteries (LIBs) are a central component of this electric revolution, powering different types of EVs, from hybrid and plug-in electric vehicles to EVs powered solely by a battery pack. In addition, LIBs are increasingly used for large stationary energy storage applications, while being still abundant in portable electronics and small power tools. However, considering the expected lifetime of a LIB, which is in the order of 10-15 years, a significant flow of spent batteries is expected in the future, summing cumulatively to 11 Mt in 2030 (Thompson et al., 2020). Such a flow of spent batteries may represent a waste-management challenge on one hand, while it can be turned into a valuable opportunity to recycle critical raw materials such as cobalt, lithium and nickel (Harper et al., 2019).

There exist different routes for LIB recycling. The most established one is pyrometallurgy, which consists of smelting the battery at high temperature to recover an alloy of precious metals among which nickel, copper and cobalt; instead, lithium is lost in the slag while graphite, plastics and electrolyte solvents are burnt (Harper et al., 2019). The hydrometallurgical route replaces the smelting step with the leaching of the battery components after crushing and mechanical separations; the resulting metal ions in solution are selectively precipitated and/or extracted to recover high-quality metal salts or even precursors ready for LIB manufacturing (Harper et al., 2019). Thus, different recycling strategies allow for diverse capabilities of material recovery and quality of recycled outputs, affecting both the potential of closed-loop recycling solutions and the overall sustainability of the lithium-ion battery chain.

This study is meant to provide an updated overview of LIB recycling processes from an engineering perspective in order to give a preliminary quantitative assessment of recycling efficiency of different processes, with concurrent identification of best practices and bottlenecks. Finally, the potential of a closed-loop battery chain is discussed by assessing which design strategies at the cell level can be adopted to compensate for the reduced performance of recycled cathode active materials.

2. Overview and analysis of LIB recycling strategies

The format and size of LIBs are not standardized. From a recycling viewpoint, they can be classified into two broad categories: i) large format LIBs, as those used in EVs, which comprise system peripheries such as cables, external plastics, aluminium or steel casing in addition to the battery cells, and ii) small format LIBs, as those used in power electronics, which basically consist of the battery cell only. In any case, the battery cell is the basic unit of both formats. A battery cell contains several materials within a relatively thin case (typically of aluminium), such as copper and aluminium current collector foils, graphite, organic solvents and $LiPF_6$ as liquid electrolyte, a polypropylene porous separator and particles of cathode active materials, among which the most common ones nowadays are $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC), $LiNi_xCo_yAl_{1-x-y}O_2$ (NCA), $LiFePO_4$ (LFP) and $LiCoO_2$ (LCO) (Schröder et al., 2017).

Figure 1 reports a schematic representation of the principal recycling strategies, where the different steps are marked with a different colour to distinguish mechanical, pyrometallurgical, hydrometallurgical and co-precipitation operations. The pyrometallurgical route (Figure 1a) starts with a manual disassembly of cables, casing and other system peripheries, which sum up to ca. 45 % of the weight of large format batteries (Dai et al., 2019). The disassembled cells are merged with small format ones and sent to a furnace to operate the smelting of the battery. Sand, limestone, coke, other reducing agents and slag formers are added to LIB cells, in a ratio that can vary from 50 to 200 % weight compared to the battery input depending on the cell casing (steel or aluminium, respectively) (Cheret and Santen, 2007). A vertical shaft furnace is typically used: the feed enters a pre-heating zone at 300 °C to evaporate electrolyte solvents, then a temperature increase to 700 °C in the second zone causes plastic pyrolysis, followed by a final zone at 1200-1400 °C at the bottom of the furnace where smelting and reduction take place (Tanong et al., 2014). Two fractions are produced from the furnace: i) a metal alloy containing Cu, Ni, Co and Fe, and ii) a slag fraction which contains Li, Al, Mn and other elements such as Si and Ca in oxidised state (Velàzquez-Martínez et al., 2019). The metal alloy is typically refined via hydrometallurgical steps of leaching and selective precipitations or solvent extractions to recover single metal salts such as CuS, $Ni(OH)_2$, $CoCl_2$ and $Fe(OH)_3$, which can re-enter in the LIB manufacturing chain. The slag can potentially follow a similar hydrometallurgical refining process to recover Li, Al, Mn and Fe salts (Li et al., 2019); however, currently the value of such end products is not sufficient to make slug refining economically attractive, thus the slug is typically downcycled by selling it as an additive for the construction industry.

Figure 1b shows the principal steps used by a hydrometallurgical process (Kwade and Diekmann, 2018). The first section of the process comprises mechanical treatments to obtain the black mass, which is the powder containing the valuable cathodic and anodic materials. Hence, after discharging and disassembly of large battery packs, LIB cells are crushed under inert atmosphere to reduce the risks associated to electric sparks and flammable electrolyte. The liquid electrolyte is then removed by adopting different techniques, among which thermal drying, extraction with organic solvents or with sub/super-critical CO_2 (Nowak and Winter, 2017). A series of mechanical separations, comprising air classification with zig-zag sifters, crushing, sieving, magnetic and optical separations, enable for the recovery of different streams, such as a light plastic fraction, Al foils fraction, Cu foils fraction, steel fraction and the black mass (Kwade and Diekmann, 2018). The black mass, which contains graphite, cathode active material and impurities of metal scraps, is leached typically with H_2SO_4 and H_2O_2 as reducing agent, so that the metals contained in the cathode active material are dissolved in solution while graphite remains unleached and can be separated by filtration (Gratz et al., 2014). The resulting solution containing Ni, Co, Li, Mn ions, with impurities of Fe, Al and Cu ions, can either be processed by classical hydrometallurgical steps of selective precipitations and extractions to recover single metal salts (blue steps at the bottom of Figure 1b) or can undergo a co-precipitation process (green steps in Figure 1b). The latter is an

innovative strategy particularly suited for NMC input streams, where a ternary hydroxide of Ni, Co and Mn can be co-precipitated and then sent to the sintering step, along with Li_2CO_3 (or LiOH) recovered via precipitation at high pH from the leached solution, in order to re-synthetize the cathode active material in oxide form (Kwade and Diekmann, 2018).
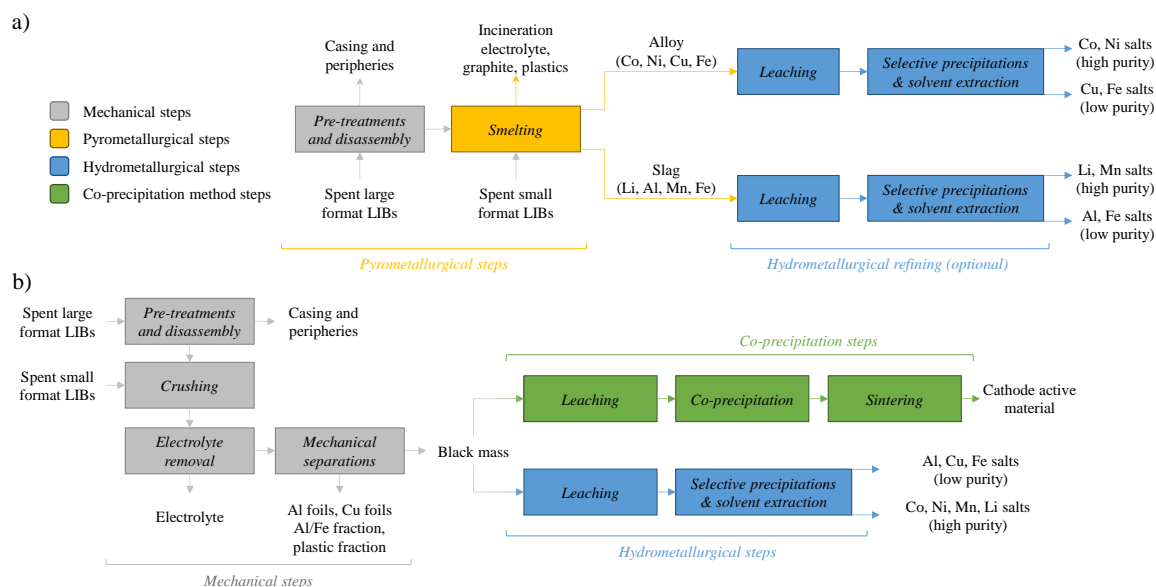

Figure 1: Schematic block diagram of LIB recycling strategies based on: a) pyrometallurgy, with optional hydrometallurgical refining, b) hydrometallurgy, comprising preliminary mechanical separations and two alternative hydrometallurgical/co-precipitation routes of the black mass.

Table 1 summarizes the main companies which operate LIB recycling across three different continents. As the table shows, in Europe there are several companies which carry out only mechanical separations (i.e., the first steps in Figure 1b) up to the black mass; only a few companies follow the hydrometallurgical route, while the most established companies with higher capacities carry out battery smelting as in the pyrometallurgical strategy, often followed by a hydrometallurgical refining of the metal alloy as in Figure 1a. In North America and in Asia the company distribution is different: North America is characterized by LIB recyclers which tend to achieve a closed loop of cathode materials via hydrometallurgical processes, while in Asia there is a significant recycling capacity provided by different companies, which mainly treat production scraps from LIB manufacturing giga-factories via hydrometallurgical processes.

Table 1: List of LIB recycling companies in different continents classified according to the main recycling strategy

Recycling route	Companies in Europe	Companies in North America	Companies in Asia
Pyrometallurgical	Umicore, Accurec, Glencore, SNAM, Valdi	Glencore, Inmetco	Sony Sumitomo, Kobar, Nippon Recycle Centre Corp.
Hydrometallurgical or co-precipitation	Recupyl Valibat, Neometals, Northvolt, Stena	Retrieve, Ascend Elements, American Manganese Inc., Lithion Recycling, Li-Cycle	Hunan BRUNP, Shenzen Green Eco (GEM), SungEel, Huayo
Mechanical separations	Duesenfeld, Akkuser Oy, Batrec, Euro Dieuze, Redux, Fortum Oyj, uRecycle		

In any case, different recycling processes enable for different recycling efficiencies and material recovery rates. In a pyrometallurgical process some materials contained in the LIB cells are burnt, including graphite, plastic separator and the electrolyte. As such, considering the mass composition of a LIB cell (Dai et al., 2019), the recycling efficiency of a pyrometallurgical process is in the order of 55 % for small format LIBs, where the recycling efficiency is calculated as the mass of recovered materials compared to the mass of the input stream;

the recycling efficiency can achieve 70 % and beyond in case of large format LIBs since the casing and other peripheries can be disassembled and easily recovered. Valuable metals, such as Ni, Co and Cu, can be effectively recovered in high-quality streams with material recovery rates in the order of 90-95 %; in particular, ca. 60 kg of critical cathodic elements as Ni and Co can be recovered from a ton of mixed batteries (75 % large format, 25 % small format). However, all the Li ends in the slag phase and cannot be recovered as a high-quality product, thus it cannot re-enter the LIB manufacturing chain. In any case, the pyrometallurgical route stands out as the most mature strategy, being flexible to accommodate different battery chemistries.

Hydrometallurgical and co-precipitation processes enable for higher recycling efficiencies due to the absence of the smelting step. More than 80 % of the LIB mass can be recovered from small format batteries, value which can potentially increase to more than 90 % in case of large format LIBs. Such an increase in recycling efficiency is basically due to the recovery of electrolyte, graphite and the light plastic fraction. However, typically the quality of electrolyte and graphite is not sufficient to be reused in the manufacturing of a new battery, although some companies as OnTo Technologies and Lithion claim that, thanks to additional treatments, these components can be considered as battery-grade. Thus, the main benefit of recycling routes based on leaching of the black mass consists in the recovery of lithium, achieving a material recovery rate of ca. 75 % (i.e., ca. 7 kg of Li recovered from a ton of spent batteries). On the other hand, the main limitations of the hydrometallurgical route lie in the mechanical separation section, where part of the cathode active materials is lost due to the strong adhesion to current collector foils given by the organic binders used in all battery formulations (Harper et al., 2019). Moreover, the co-precipitation steps are susceptible to the presence of phosphates, which cause undesired precipitation of Ni, Co and Mn phosphates, thus limiting the applicability of such a recycling strategy to spent batteries which should not contain LFP as a cathode material (Kwade and Diekmann, 2018).

3. Guidelines to compensate performance limitations of recycled materials

The overview of recycling strategies reported in the previous section highlights that there is a concrete potential for achieving a closed loop of materials in the LIB recycling chain, thus enabling for the manufacturing of a second generation of batteries with materials coming from recycled streams rather than from virgin sources, at least for the cathode materials. While secondary raw materials resulting from pyrometallurgical and hydrometallurgical recycling processes may arguably entail the same properties of virgin ones, recycled cathode active materials obtained via co-precipitation may have decreased electrochemical properties due to the presence of impurities (Beaudet et al., 2020). Therefore, modifications to the electrode design must be conceived to compensate the performance loss introduced by recycled cathode active materials.

Figure 2 summarizes the main design strategies suggested for compensating a reduction in the gravimetric accessible capacity of recycled cathode materials (namely, NMC111 in this specific case), which is in the order of max 10 % of capacity loss (Zhao et al., 2020). Such a gravimetric capacity loss can be due to either a decrease in maximum concentration of lithium intercalated in the cathode material (Figure 2a, yellow box) or by a decrease in solid-phase diffusivity of lithium ions in the cathode material (Figure 2a, green box), estimated in the order of -10 % and -50 %, respectively (Lagnoni et al., 2022). In both cases, the reduced accessible capacity can be compensated by an increase in cathode thickness; alternatively, the reduced solid-phase diffusivity can be compensated by a decrease in the particle size of cathode particles. These compensation measures do not have, in general, any effect on the design of the anode, except for the case where a reduction in solid-phase diffusion at the cathode is compensated by an increase in cathode thickness, where the anode thickness must be increased too in order to keep a balanced anode-to-cathode nominal capacity ratio.

Figure 2b reports the results of the compensation measures by using a physics-based thermo-electrochemical battery model (Lagnoni et al., 2021) tuned to replicate the electrochemical response of the graphite-NMC111 Samsung SDI 94 h battery used in the BMW i3 electric vehicle (Lagnoni et al., 2022). Figure 2b shows that, compared to the electrode thicknesses of the reference battery made with virgin materials (namely, 90.5 μm for the cathode, 98 μm for the anode), different compensation measures lead to different designs of LIBs produced with recycled materials. If a recycled cathode active material features a 10 % loss in nominal capacity (yellow box in Figure 2a), a corresponding increase by 10 % in cathode thickness has to be foreseen (Figure 2b) to guarantee the same accessible capacity during operation. On the other hand, a decrease in solid-phase diffusivity (green box in Figure 2a) can be compensated by either a minor increase in cathode and anode thicknesses (less than 2 % increase cumulatively, Figure 2b) or by a reduction in the diameter of cathode particles from 8 μm to 6 μm. The latter strategy may arguably reduce the battery life because of the increased specific surface area of cathode particles, which may trigger parasitic reactions. On the other hand, the strategies based on increasing the electrode thicknesses appear to be totally feasible since the volume increase of the jelly roll is minimal and can be accommodated within the cell casing, resulting only in a marginal reduction in energy density at the pack level (from 142 Wh/kg to 137 Wh/kg as a minimum), which is still suitable for electric vehicle applications.
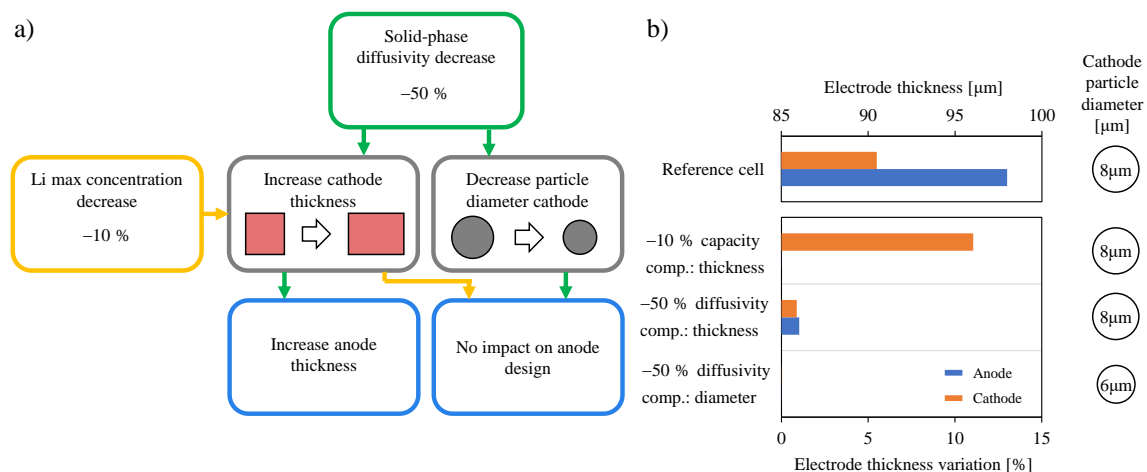
Figure 2: a) Strategies to cope with reduced properties of recycled cathode active materials via increase of electrode thickness or reduction of particle size; b) effect of compensation measures on electrode thickness and size of cathode particles to ensure the same battery capacity.

Hence, the numerical analysis reported in Figure 2 indicates that recycled cathode active materials, even with reduced electrochemical properties, can be accommodated in the manufacturing of secondary lithium-ion batteries by adopting marginal changes to the electrode design, enabling for a closed loop of materials in the battery chain.

4. Conclusions

This paper gave an overview on the status of recycling processes for lithium-ion batteries from an engineering perspective, assessing the current limitations and the feasibility of reusing recycled cathode materials in the manufacturing of new cells.

The survey of LIB recycling companies in different continents indicates that in Europe a large fraction of recyclers performs only mechanical separation treatments to obtain the black mass; however, the black mass cannot be considered as an end product from a recycling viewpoint. The alternative strategy adopted mostly in Europe is pyrometallurgy, which has the clear benefit of being only marginally affected by the chemical composition of spent batteries in the input stream. However, since graphite, electrolyte and plastics are burnt, the recycling efficiency of pyrometallurgy lies in the order of 55-70 % for small format and large format batteries, respectively; moreover, Li is downcycled in the slag and currently its recovery via hydrometallurgical refining processes is not economically feasible. In North America and Asia recyclers adopt mostly the hydrometallurgical and co-precipitation recycling routes. While the leaching phase is not problematic in terms of material recovery rate, the preliminary mechanical separation steps limit the recovery of valuable cathodic metals. Nevertheless, the overall recycling efficiency can potentially be up to 90 %, along with the possibility to recover ca. 75 % of lithium in battery-grade products such as Li_2CO_3 and LiOH. Therefore, the hydrometallurgical and co-precipitation strategies should be promoted at industrial level, especially in Europe, to cope with the expected lack of lithium from natural sources, by investigating better mechanical separations, refining operations for electrolyte and graphite to make them battery-grande, and the use of water-soluble binders.

The use of recycled materials in the manufacturing of new batteries was also investigated in this study. In particular, compensatory measures in electrode design were suggested in case of reduced electrochemical properties of cathode active materials. The numerical results showed that a 10 % decrease in nominal volumetric capacity of the cathode active material can be compensated by a 10 % increase in cathode thickness, resulting only in a 3.5 % reduction in gravimetric energy density at the pack level, which is still suitable for electric vehicle applications. A similar strategy is suggested in case of reduced solid-phase diffusivity of the cathode active material, which produces an even smaller loss in energy density (< 1 %). On the other hand, decreasing the size of recycled cathode active particles does not seem to be a viable alternative because the battery life might be negatively affected.

In summary, the survey of existing LIB recycling processes and the compensatory measures suggested in the study indicate that a close loop of materials in the lithium-ion battery chain is technically feasible, at least for Ni, Co, Cu, Al and Mn, while the recycling of Li, graphite and electrolyte still needs further technological advancements before being adopted at industrial scale.

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