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Review

Direct Recycling Technology for Spent Lithium-Ion Batteries: Limitations of Current Implementation

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Abstract: The significant deployment of lithium-ion batteries (LIBs) within a wide application field covering small consumer electronics, light and heavy means of transport, such as e-bikes, e-scooters, and electric vehicles (EVs), or energy storage stationary systems will inevitably lead to generating notable amounts of spent batteries in the coming years. Considering the environmental perspective, material resource sustainability, and terms of the circular economy, recycling represents a highly prospective strategy for LIB end-of-life (EOL) management. In contrast with traditional, large-scale, implemented recycling methods, such as pyrometallurgy or hydrometallurgy, direct recycling technology constitutes a promising solution for LIB EOL treatment with outstanding environmental benefits, including reduction of energy consumption and emission footprint, and weighty economic viability. This work comprehensively assesses the limitations and challenges of state-of-the-art, implemented direct recycling methods for spent LIB cathode and anode material treatment. The introduced approaches include solid-state sintering, electrochemical relithiation in organic and aqueous electrolytes, and ionothermal, solution, and eutectic relithiation methods. Since most direct recycling techniques are still being developed and implemented primarily on a laboratory scale, this review identifies and discusses potential areas for optimization to facilitate forthcoming large-scale industrial implementation.

Keywords: lithium-ion batteries; direct recycling; end-of-life

1. Introduction

Lithium-ion batteries (LIBs) stand out as a pivotal technology with numerous advantages compared to other electrochemical storage technologies these days. These include higher cell voltage, increased energy density, extended lifespan, minimal memory effect, simplicity to charge and maintain, low self-discharge, potential for miniaturization, and different packaging shapes. Thus, the LIBs set a turning point in the field of power sources, where they are utilized in a variety of applications encompassing small consumer electronic systems, including watches, smartphones, or laptops; portable power tools, such as drills or saws; home or industrial systems for energy storage (BESS); and light or heavy means of transport, including electric bikes, scooters, and electric vehicles (EVs) [1–4].

The typical composition of LIBs predominantly comprises a cathode, anode, separator, and electrolyte. Ordinarily, batteries also have an electronic control unit, a protective metal casing, and plastic coverings according to shape, composition, and structure, as illustrated in Figure 1 [5]. Cathodes are predominantly composed of a mixture involving a polyvinylidene fluoride (PVDF) binder, carbon powder, and lithium (Li) transition metal oxides such as lithium cobalt oxide (LCO or $LiCoO_2$), lithium manganese oxide (LMO or $LiMn_2O_4$), lithium iron phosphate (LFP or $LiFePO_4$), lithium nickel cobalt aluminum oxide (NCA or $LiNi_xCo_yAl_zO_2$), and lithium nickel manganese cobalt oxide (NMC or $LiNi_xCo_yMn_zO_2$). These materials are coated onto a current collector, typically an aluminum (Al) foil. Similarly, anodes commonly utilize graphite, providing a structure capable of holding Li within

its layers. The active carbon material is attached to a copper (Cu) conductor plate using a PVDF binder. Electrolytes consist of a solution containing a lithium-containing salt, such as lithium perchlorate ($LiClO_4$), lithium tetrafluoroborate ($LiBF_4$), or lithium hexafluorophosphate ($LiPF_6$), dissolved in an organic solvent like dimethyl carbonate (DMC) or ethylene carbonate (EC). As a medium, the electrolyte facilitates the transport of ions between battery electrodes. A separator, crafted from polymeric materials such as polypropylene (PP) or polyethylene (PE), acts as a non-conductor or barrier; thus, it is inserted between the anode and cathode to eliminate the risk of short-circuiting caused by direct contact between the electrodes [1,6,7]. The composition of LIBs slightly differs between manufacturers and commonly consists of 5–20% Co, 5–20% Mn, 5–30% Ni, 5–10% Li, 5–40% of other metals, 10–15% organic chemicals, and 3–10% plastics [8–10].
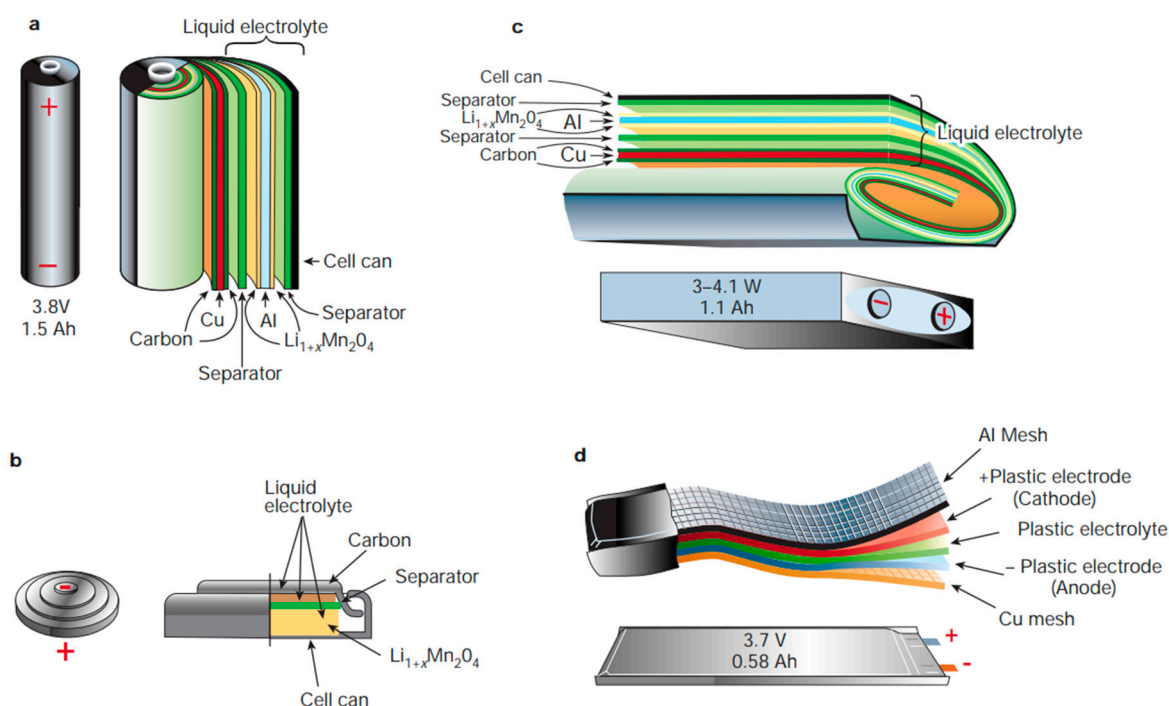

Figure 1. Schematic drawing showing the shape and components of various Li-ion battery configurations: (**a**) cylindrical; (**b**) coin; (**c**) prismatic; and (**d**) thin and flat. Reprinted from [5], with permission from Springer Nature, Copyright (2001).

The lifespan of LIBs varies according to their application field; in a small electronic device, it can last between 2 and 5 years, whereas in EVs or BESSs, it may range from 8 to 15 years [1,11]. Considering the significant difference between the utilization of LIB within small portable electronic devices and longer-life applications, currently standing at an 80:20 ratio, the annual increase in end-of-life (EOL) batteries is evident [12]. Projections of trends have become a focal point in numerous predictions; according to them, the estimation of spent LIBs will increase to 464,000 tonnes by 2025 [13]. In response to the challenges of the battery raw material supply chain and environmental footprint reduction, a series of global or European initiatives have been implemented. The simplified hierarchy for EOL battery management is outlined as follows [1,14]:

- **Prevention:** designing LIBs with less-critical materials and creating electronic devices with smaller/lighter LIBs to prevent and minimize waste generation.
- **Re-use:** entailing secondary usage of LIBs to prolong their service life, especially for EV batteries.
- **Recycling:** involving the recovery of valuable materials from spent LIBs and their return to the value chain.

- **Recovery:** considering using certain materials from spent LIBs as fuel in processes like pyrometallurgy to extract energy from waste.
- **Disposal:** discarding spent LIBs without recovered value, directing them to specialized landfills or municipal waste combustion facilities for incineration.

Given the LIBs' toxic content, which can cause severe environmental pollution risks and pose a threat to human health, and the significant quantities of valuable and other essential metals, such as Li, Co, Ni, Mn, Cu, Al, and Fe, recycling emerges as an up-and-coming technology for managing waste LIBs. This approach, covering suitable flue gas treatment, mitigates the pollution from hazardous materials and offers alternative sources of essential metals, particularly Li and Co, while reducing emissions associated with mining and post-processing activities [2,15].

Commonly implemented methods to recycle appealing components of spent LIBs are either based on pyrometallurgical or hydrometallurgical methods. The pyrometallurgical procedure, rooted in metal smelting, is a well-established practice based on separation and high-temperature treatment [16]. While the process is energy-intensive and emission-productive, it proves relatively efficient as it yields the most valuable metal resources (e.g., Co or Ni) via metal alloys. However, portions of Li end up in slags, which are not typically recovered [17]. Conversely, hydrometallurgical techniques allow the recovery of all metal elements in their salt states with a higher purity [17,18]. This approach serves at the expense of consuming significant chemical reagents, resulting in elevated costs and environmental concerns related to waste pollution [1,2,19].

These methods represent quick and sufficient solutions for current recycling pressure, but they cannot realize a closed-loop economy in future years without the necessary optimization steps. Therefore, there is a high demand for alternative recycling technologies that can directly reuse degraded energy storage materials for battery manufacturing from an economically and environmentally sustainable perspective. The most promising of them is direct recycling technology [7,20,21].

Lately, direct recycling processes have surfaced as a sustainable recycling technology renowned for healing compositional and structural defects [7]. By preserving the original crystal structure and avoiding the breakdown of electroactive materials into their elemental states, it contrasts conventional recycling methods (pyrometallurgy, hydrometallurgy) [2]. A comparison of the general pros, cons, and challenges of the mentioned recycling processes is shown in Table 1.

Although hydrometallurgy is known for its high process efficiency, which can reach up to 76–98.2%, and the purity of obtained materials between 96.5–99.7%, low energy consumption is typically only observed during the recovery phase [2]. However, when considering additional processes such as wastewater treatment, energy consumption can equal or surpass that of pyrometallurgy [22]. Due to the inherent nature of hydrometallurgical processing, this method requires more water than other techniques. Thus, optimized approaches that minimize water usage can yield significant additional benefits for this recycling method [20].

Despite the advantages of pyrometallurgy, which include process simplicity and speed compared to multi-step chemical leaching processes that span several hours, the energy consumption during the recovery phase is notably high due to the requirement of operating at high temperatures [20]. Moreover, the process leads to significant emission production. Thanks to high-thermal processing, recovering certain materials like Li, Al, and organic compounds is impossible. Although pyrometallurgical processing does not restrict input size, it cannot be used to treat some LIB types, such as LFP. Therefore, the method is often combined with hydrometallurgical recycling steps to enhance efficiency and product quality [2].

Consequently, direct recovery holds considerable promise in delivering recycled electroactive materials to battery manufacturers with heightened sustainability, characterized by decreased energy consumption and limited dependence on chemical agents [20,21].

Nevertheless, it is currently necessary to optimize established techniques to reduce costs and further optimize product performance.

Table 1. Comparisons of advantages and disadvantages and challenges for different methods. Reprinted from [23] under the terms and conditions of the CC BY 4.0 license, Copyright (2020).

Process	Advantages	Disadvantages	Challenge
Hydrometallurgical process	High recovery rate High-purity product Low energy consumption Less waste gas High selectivity	More wastewater Long process	Wastewater treatment Optimize the process
Pyrometallurgical process	Simple operation and short flow No requirement for categories or size of inputs High efficiency	Li and Mn are not recovered High energy consumption Low recovery efficiency More waste gas and the cost of waste gas treatment	Reduce energy consumption and pollution emissions Reduce environ. hazards Combine hydrometallurgy well
Direct recycling process	Short recovery route Low energy consumption Environmentally friendly High recovery rate	High operation and equipment requirements Incomplete recovery	Reduce recovery costs Lower the requirements for categories Further optimize product performance

This work examines the current direct recycling procedures for spent LIB materials, including common cathode (NMC, LFP, LCO, and LMO) and graphite anode treatment. The review introduces the technical challenges, limitations, and barriers of five different direct recycling methods (solid-state sintering, electrochemical, ionothermal, solution, and eutectic relithiation), as illustrated in Figure 2. Although these methods provide high efficiency in restoring the properties of regenerated materials to a level comparable to pristine, the critical challenge in direct recycling revolves around the processing of black mass and the necessity of recycling pre-treatment within the EOL process scenario. Thus, this work discusses potential optimization options that could lead to the industrially scaled implementation of direct recycling.
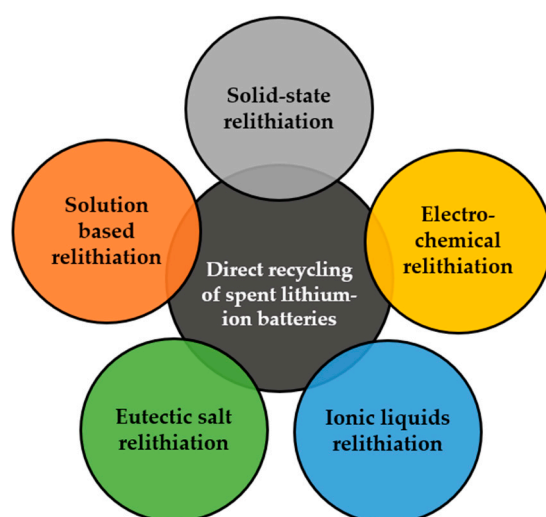

Figure 2. Overview of the current direct recycling approach, covering the relithiation techniques.

2. Direct Recycling Technology

In the realm of recycling spent LIBs, the technological processes are divided into two separate routes: recycling pre-treatment and the subsequent material recovery, i.e., the recycling procedure [2]. The battery pre-treatment precedes further recycling treatment and can improve the efficiency of valuable material recovery, process safety, or lower

energy consumption. These processes primarily separate the active electrode materials from the current buses, separators, electrolytes, and covers or connections. Presently, the pre-treatment process lacks a well-defined design, leading to the adoption of various approaches in recent years. Typically, the process can be outlined through the following seven-step procedure; the short-cuts of the individual steps' details are given in Table 2, and the review work by Kim et al. [19] provides a comprehensive description.

- Discharging;
- Dismantling;
- Comminution;
- Classification;
- Separation;
- Dissolution;
- Thermal treatment.

The main aim of the recycling pre-treatment phase is to eliminate impurities and achieve the highest possible quality in the output product, the so-called "black mass". This finely ground fraction predominantly comprises cathode materials (cathode black mass, also known as CBM) and serves as the input material for the subsequent stages of recycling processing [2,22].

Table 2. Summary of recycling pre-treatment process steps [2,19].

Recycling Pre-Treatment Step	Step Characterization
Discharging	Discharge systems with electric (active or passive) loads, deep discharging < 1 V.
Dismantling	Manual disassembly from battery (pack) to the module or cell level.
Comminution	Crushing active electrode materials into fine fractions, implemented by dry or wet procedures.
Classification	Categorization according to the fraction product size, typically applies by sieving.
Separation	Specialized separation methods, including magnetic, eddy current, or electrostatic techniques.
Dissolution	Chemical separation of active cathode materials from Al foils.
Thermal treatment	Complete removal of the organic parts, such as binders, additives, plastics, or carbon black. Final product: black mass.

Following pre-treatment, the black mass, primarily comprising the gathered spent cathode materials, undergoes regeneration through either pyrometallurgical, hydrometal-lurgical, or direct recycling methods. A complex overview of the implemented pyrometal-lurgy or hydrometallurgy techniques, including a detailed examination of their advantages and disadvantages, along with considerations of economic and environmental perspectives, can be found in works by Pražanová et al. [20], or Lander et al. [24].

Regarding direct recovery pathways, the CBM is set for regeneration, encompassing the restoration of the crystal structure while concurrently mitigating the loss of Li electroac-tivity at its original location—a process commonly referred to as "in situ" electroactivity offsetting. This healing methodology is introduced in response to the common issues of inactive Li supply and the degradation of battery performance resulting from irreversible structural transitions, such as the formation of the solid electrolyte interphase (SEI) layer on the anode surface; changes in volume and crystal phase; structural stress; mechanical strains; and micro-cracks between/in the particles. A detailed description of the struc-

tural changes within the LIB cells, which lead to a performance decrease and Li losses, is presented in work by Wu's [22] and Xu's [7] research groups.

Thus, direct recycling emerges as a promising technique within currently implemented recycling methodologies. It possesses considerable potential for reinstating the electrochemical performance of cathode materials and their rejuvenation to reach quality levels similar to those of fresh materials. This regeneration involves restoring entire structures, not the recovery of individual valuable metals, as illustrated in Figure 3. A notable advantage of this method is that it reduces environmental impacts and lowers economic costs [22].
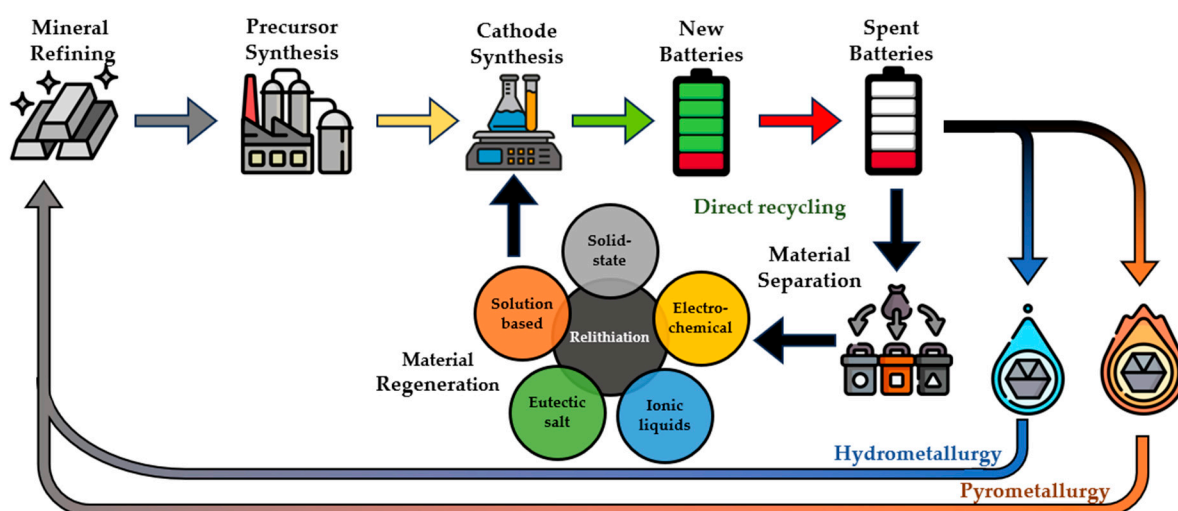

Figure 3. Example of the main direct recycling steps; comparison with pyro-/hydrometallurgy [22].

The example of the cost, energy consumption, and environmental impacts comparison of producing 1 kg of NMC111 cathode (nickel manganese cobalt oxide in a 1:1:1 mass ratio for Ni:Mn:Co) and recycling them with different technologies (namely, pyro-/hydrometallurgy and direct recovery) is shown in Figure 4 [22].
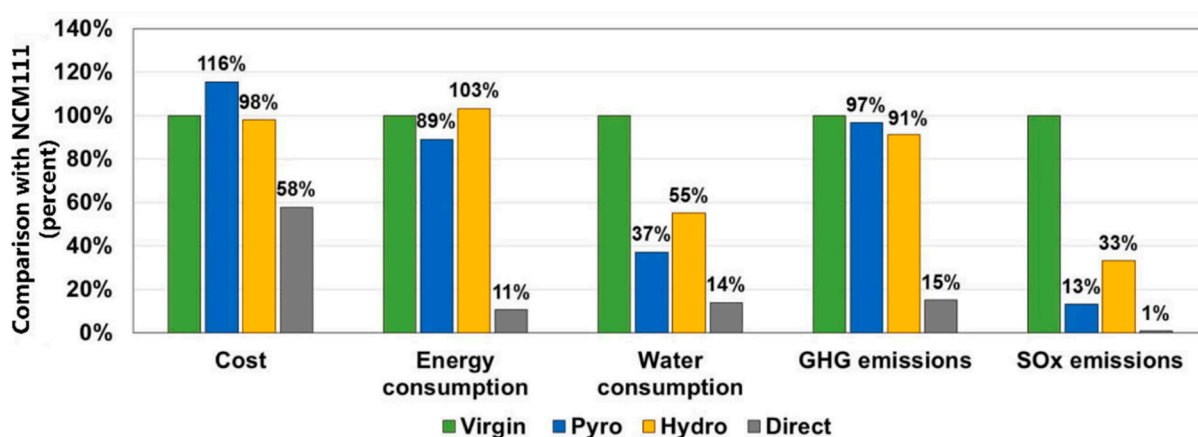

Figure 4. The comparison of the cost, energy consumption, and environmental impacts of producing 1 kg of NMC111 cathode and recycling it with different technologies (namely, pyro-/hydrometallurgy and direct recovery). Reprinted from [22], with permission from Elsevier, Copyright (2023).

However, for quality and highly representative results, evaluating each established process individually with all its technological aspects or additional steps is necessary. While the work by Wu et al. [22] lacks specific compared-process details, the research-based trends can be observed through selected categories [20,25–28]. Generally, hydrometallurgy exhibits the highest energy consumption due to its intricate and energetically demanding steps, particularly in the purification of waste products, notably water. Consequently,

water consumption is the most significant via hydrometallurgical processes. Conversely, pyrometallurgy, characterized by high-temperature processing, contributes significantly to greenhouse gas (GHG) emissions, although sulfur oxide (SO_x) emissions predominantly stem from chemical (hydrometallurgical) processing. Economic evaluations commonly depend on the accuracy of process characterizations. However, given the high technology costs associated with high-temperature processing, pyrometallurgical processes are presumed to incur substantial expenses in terms of investment and operation. Moreover, this comparison underscores the primary objectives of direct recycling, which entail low operating costs and minimal environmental impact.

The direct recycling process can be generally called "relithiation" [29]. These approaches mainly include solid-state sintering, electrochemical relithiation in organic and aqueous electrolytes, ionothermal relithiation, solution relithiation, and eutectic relithiation, whose advantages and challenges are summarized in Table 3 [7].

Table 3. The advantages and challenges of different direct recycling technologies. Reprinted from [7], with permission from Wiley-VCH GmbH, Copyright (2023).

Direct Recycling Method	Advantages	Challenges
Solid-state relithiation	One-step regeneration; Simple operation	Pre-determination of Li deficiencies; Phase impurity
Electrochemical relithiation	Low energy consumption; Low cost	Pre-determination of Li deficiencies; Removal of current collector, binders, . . . Phase impurity; Scalability issue
Ionic liquids relithiation	Self-saturation relithiation	High cost of ionic liquid; Scalability issue
Eutectic salt relithiation	Self-saturation relithiation; Low energy consumption	Removal of solidified salts; mixture after regeneration; Scalability issue
Solution based relithiation	Self-saturation relithiation; Wide applicability; Low cost	Safety concern related to elevated temperature and pressure

Within solid-state sintering regeneration, spent cathode materials are firstly mixed with Li salts, and subsequently, they are treated through different temperature levels in ranges of 600–900 °C. The stoichiometric ratio of Li is reinstalled by adding a supplementary Li source, and the particle bonding is indurated with high-temperature treatment [30,31].

Electrochemical relithiation is typically mediated in a three-electrode station; a spent cathode electrode stands as the working electrode, a platinum plate as the anode electrode, and one Ag/AgCl as the reference electrode with a Li-based solution. Optimal regeneration efficacy can be attained by tuning the concentration of the Li solution and changing the cathodic current. Nevertheless, this method cannot completely restore the cathode crystal structure, and additional temperature treatment is needed [7,32].

Ionothermal relithiation is a form of synthesis where ionic liquid solutions are simultaneously used as both the solvent and potential template or structure-directing agent in forming solids. This approach from the solution-based relithiation field evolves defect-targeted healing and homogeneous Li distribution inside cathode particles [33].

Eutectic molten salts establish a homogeneous environment during re-crystallization and particle growth stages of direct recovery at a eutectic temperature at ambient pressure. Initially, spent cathode materials are blended with Li-based eutectic molten salts; then, the resulting mixture is heated to the eutectic melting point, where re-lithiation and crystal rearrangement occur. Contrary to the previous methods, this approach reduces both the

holding time and annealing temperature without compromising the restored material's crystallinity [7,34].

The selection of the optimal relithiation process depends on several crucial factors. These include not only the chemical composition of the active material but also the intensity and nature of defects present in the cathode structures, desired recovery efficiency, along with evaluations of investment and operating costs.

3. Limitation of Implemented Direct Recycling Procedures

Recycling of LIBs stands as a high-perspective strategy of their waste management, which addresses environmental concerns, marking a crucial step toward the sustainable development of energy storage technologies and the circular economy. In comparison to conventional hydrometallurgical and pyrometallurgical recycling methods, direct recycling serves several benefits in terms of process simplicity, low energy consumption, reduced secondary environmental pollution, and potential higher cost return [1,20,24].

While direct recycling has shown initial success within laboratory-scale settings, recovering a diverse array of cathode and anode materials, its transition to the industrial sector remains impeded. The practical application of this technology encounters significant challenges, signaling the need for further advancements in the research area [20].

The dominant limitation of currently implemented technologies resides in the processing of high-quality CBM or anode materials (black mass form) derived from the LIBs recycling pre-treatment, as shown in Table 4. The demand for ensuring high quality and uniformity in the resulting product increases the complexity of the entire technology and costs, thereby substantially diminishing the number of industrial implementations [1].

Table 4. Overview of the main limitations of currently implemented direct recycling techniques [1].

Limitation	Description
Limited applicability to whole spent LIB systems	The current approaches predominantly target the cathode and anode materials, neglecting other components of spent LIBs; thus, the potential for achieving a closed-loop circular economy for LIBs is not fully harnessed.
Black mass processing	The standard black mass, comprising a mixture of several materials, introduces technical barriers to the direct implementation of direct recycling techniques.
Energy-intensive recycling pre-treatment	Before direct recycling, LIBs undergo recycling pre-treatment processes involving high-temperature treatments and chemical interventions, which result in high energy consumption, emissions, and intricacies in the process of wastewater treatment.

Considering the commonly implemented LIBs recycling pre-treatment processes, whose output products consist of a mixed material output based on cathode and anode materials, conductive agents, PVDF binder, and other residual impurities from a current collector, or battery casings (Al, Cu, Fe, etc.) from a single type or different battery chemistry mixture [6], they pose significant technical obstacles, especially from the perspective of material separation or process efficiency, hindering the immediate progression of the direct recycling method [22]. A comparison of currently treated materials within direct recycling and the future strategy of this method is presented in Figure 5 from a comprehensive review work by Xu et al. [7].

The direct recycling methods are generally individually customized for various material treatments. They are accompanied by a range of limitations influenced by process complexity, readiness, and research status [7,22]. Thus, the direct recovery strategies, limitations, advantages, and disadvantages for crystal structure rearrangements for different types of cathode and anode graphite materials are discussed in the following sections.
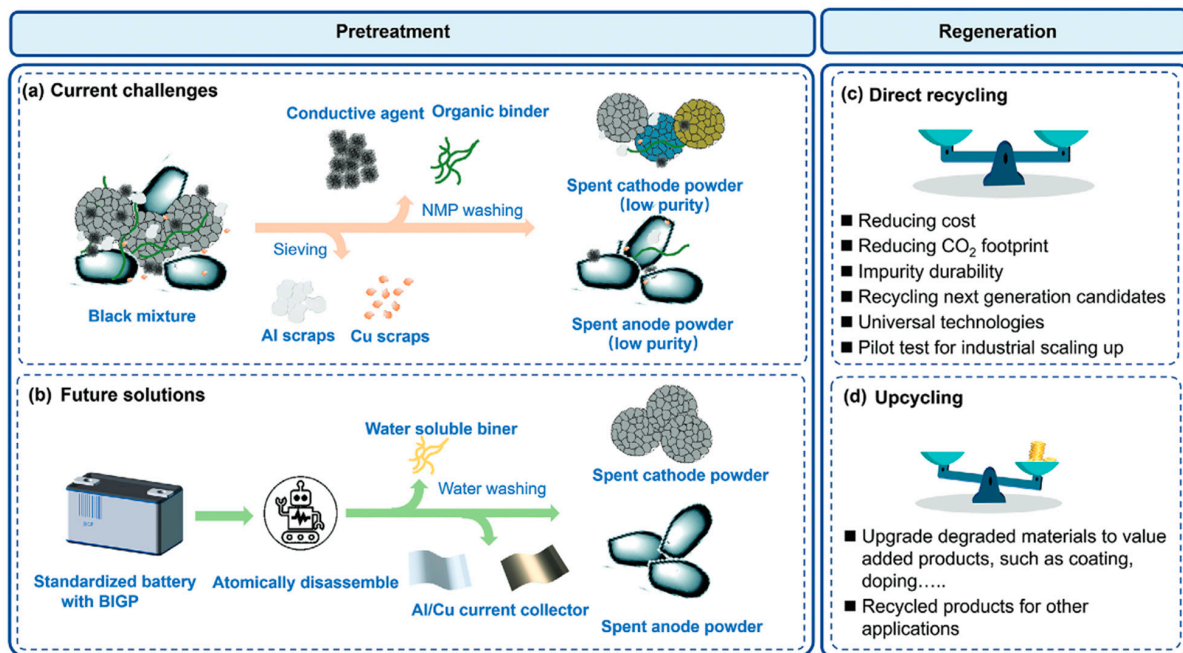
Figure 5. Current challenges (**a**) and future solutions (**b**) toward spent battery pre-treatment, as well as future development directions of electrode material regeneration (**c**) and upcycling (**d**) technologies. Reprinted from [7], with permission from Wiley-VCH GmbH, Copyright (2023).

3.1. Direct Recycling Treatment of Spent Cathode Materials

As a critical component of the battery, cathode materials play a crucial role in determining the overall performance, energy density, and efficiency of LIBs, where their differences within specific energy (capacity), specific power, safety, performance, lifespan, and cost are illustrated in Figure 6 [35].
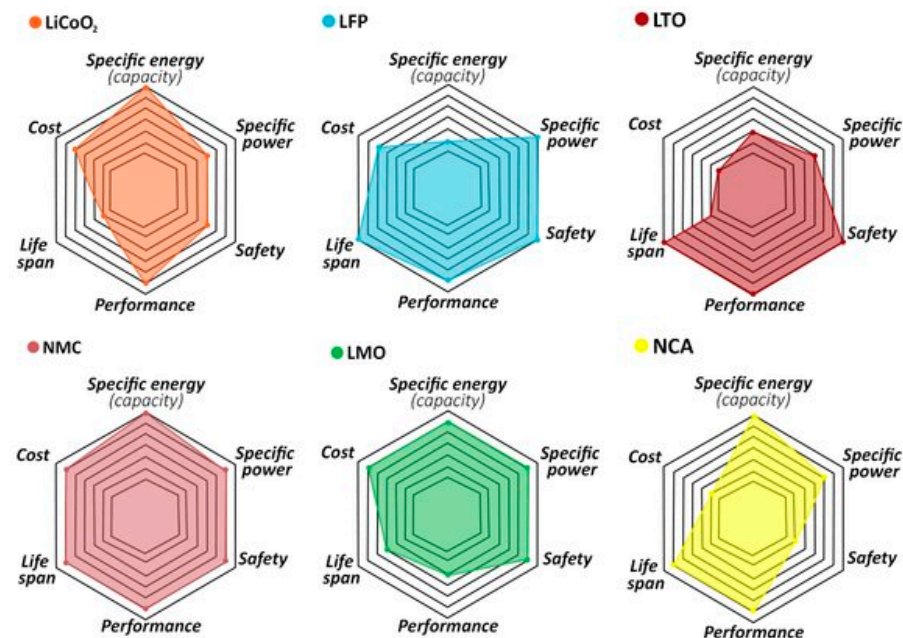

Figure 6. Comparison between different types of cathodes. Reprinted from [35] under the terms and conditions of the CC BY 4.0 license, Copyright (2021).

The demand for efficient energy storage systems has propelled research into enhancing the performance of LIBs and their suitable usage within selected application fields [36,37].

Considering the current implementation stage and ratios between spent LIBs designed for EOL treatment, the spent NMC, LFP, LCO, and LMO cathode material treatments were described. More details about spent NCA materials' direct regeneration are provided, for example, in the study by Elmaataouy et al. [38].

3.1.1. Nickel-Manganese-Cobalt Oxide (NMC)

In the realm of electric vehicle (EV) applications, there is a distinct preference for battery technologies that offer higher energy density at reduced costs. Consequently, alternative ternary transition metal oxides incorporating Ni and Mn within LIBs, such as $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (NCM111), $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM523), $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622), and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811), have garnered widespread adoption and usage via different battery formats [6,39].

Spent battery cells of the NMC type commonly undergo severe phase transformations that result in the loss of Li-ions. The degraded cathode materials exhibit transformations involving spinel and rock salt phases on the surface of the particles. Thus, considering the relithiation techniques, short annealing is required within the treating processes to transfer spinel and rock phases back to a layered structure [7].

In the context of solid-state regeneration of NMC structures, layered cathode materials can be efficiently treated through standard sintering methods. Meng et al. [30] discovered that, before annealing NMC111 materials, milling plays a crucial role in enhancing the efficiency of electrochemical performance recovery by promoting uniform Li diffusion. The sintering properties vary based on the materials' constituents and crystallinity. As demonstrated by Shi et al. [40], polycrystalline NMC523 requires a sintering temperature within the range of 850 °C to 920 °C, while Gao et al. [41] recommend maintaining a temperature around 950 °C for single-crystal NCM523. For materials with a high Ni content, such as NMC622, Jin et al. [42] emphasize the necessity of a pre-oxidation treatment step before sintering. Additionally, higher Ni ratios demand increased oxygen pressure levels for effective treatment.

Within solution/hydrothermal-based relithiation, Shi's group [40] conducted comprehensive research on NMC523 recovery, achieving a recovered cathode material quality comparable to pristine conditions. The process involved a high-temperature short annealing (HT-SA) technique designed to suppress Li/Ni mixing and executed under specific oxygen atmosphere levels, as described in detail in the work by Gao et al. [41]. The re-installed materials are subjected to minimal temperature and pressure loads, capped at 220 °C and 25 bar. Ongoing optimization efforts, such as those by Yu et al. [43], involve the introduction of redox mediation in the hydrothermal Li-bearing solution, resulting in a temperature decrease to 100 °C. In the context of NMC622 material regeneration, Sloop et al. [44] favored treatment with LiOH solutions. However, the efficiency encountered a setback due to the formation of a Li^+ and Ni^{2+} mixture.

The eutectic-mixture-based regeneration method for NMC materials has shown promising results. Shi et al. [34] utilized a eutectic solution consisting of lithium hydroxide (LiOH) and lithium nitrate ($LiNO_3$) to relithiate spent NCM523, successfully reverting the surface salt phase to its original layered structure, comparable to its pristine state. Fan et al. [45] also demonstrated effective regeneration of spent NCM523 using the LiOH and lithium carbonate (Li_2CO_3) system, which forms a molten salt. However, it has been observed that for highly degraded materials, this relithiation may not be optimal and might not fully recover destructed materials. New approaches are being explored, such as the solution proposed by Ma et al. [46], which involves adding cobalt(III) oxide (Co_2O_3) and manganese dioxide (MnO_2) to the eutectic solution to compensate for transition metal loss in cathode materials.

The research on ionic liquids for recovery faces significant limitations, primarily due to high implementation costs. However, as demonstrated by the results of Parnham et al. [47], the method can be effective and lead to full recovery, as shown in the case of NMC111,

where an ionic liquid was served as the flux solvent, accompanied by LiBr as the Li source and ionothermal treatment.

The direct recycling technique for spent NMC materials can be considered an effective method for pristine-like cathode material recovery, with the possibility of using standard sintering methods and a lower environmental impact. However, it serves some notable limitations according to the applied relithiation technique, summarized in Table 5.

Table 5. Limitations and challenges of implemented direct recycling techniques focus on recycling spent cathode (NMC, LFP, LCO, and LMO) and anode graphite materials. "Pre-development phase" refers to an area that has not yet been thoroughly characterized by research. "Development phase" denotes a pilot research area with insufficient readiness for practical industrial application.

Spent Material	Solid-State Relithiation	Electrochemical Relithiation	Ionic Liquids Relithiation	Eutectic Salt Relithiation	Solution Based Relithiation
NMC	Necessity of milling before sintering; Long sintering time at high temperature; Pre-oxidation treatment procedures; Process complexity	Pre-development phase	High implementation costs	Destructed materials may not be fully recovered; Development phase	Formation of a Li^+ and Ni^{2+} mixture; HT-SA technique; Needs for oxygen atmosphere levels
LFP	High temperature treatment; Requisite of carbon and PVDF binders' removal from LFP particles; Structural stability; Sensitivity to sintering atmosphere	Development phase; Integration of pre-lithiated graphite; Poor industrial scalability	Pre-development phase	Development phase	Process complexity
LCO	Necessity of optimal Li/Co ratio; High energy process consumption	Process complexity; Requirement for high-quality delamination and purification steps	Pre-development phase	Development phase	Undescribed: thermodynamics and kinetics of implemented processes
LMO	High environmental demand; Best results: balanced molar ratio of LiOH and LMO, dependent on SOH	Pre-development phase	Pre-development phase	Pre-development phase	Necessity of optimal LiOH solution concentration; Not dependent on SOH
Graphite	High temperature treatment; Combined process (annealing, chemical leaching)	Pre-development phase	Pre-development phase	Pre-development phase	Necessity of impurities removal; Sensitivity to process atmosphere; High demand for wastewater treatment

3.1.2. Lithium Iron Phosphate (LFP)

Due to its good thermal stability, cost-effectiveness, and long cycle life, LFP technology plays a pivotal role in the LIB market, particularly in applications like portable electronics, grid energy storage systems, and EVs [48]. The absence of valuable metals, such as Co and Ni, in LFP cells reduces the economic motivation of their EOL treatment via conventional recycling methods [1]. Thus, implementing direct recycling methods with reduced energy-consumptive processes has the potential for wide-range extension in waste management [7].

The primary cause of capacity decay in LFP cells is the loss of Li inventory within the crystal structure while maintaining material stoichiometry. The regeneration process involves supplementing Li ions into the crystal structure. Familiar Li sources include inorganic Li, such as Li_2CO_3 or LiOH, lithium halides like lithium iodide (LiI) or lithium bromide (LiBr), and organic lithium salts, such as polycyclic aryl-lithium compounds [7].

The solid-state regeneration of LFP involves reloading the lost Li^+ ions in the cathode during cycling by annealing a mixture of Li-containing salt and spent cathodes at high temperatures between 350 and 700 °C [49]. However, the complete removal of conductive carbon and PVDF binder from LFP particles while preserving structural stability poses a challenge, affecting the quality of defect restoration and material purity. Research conducted by Li et al. [50] and Sun et al. [51] has demonstrated that the regenerated product is highly sensitive to the sintering atmosphere, where the inert or reductive atmosphere is preferred to prevent LFP oxidation, which can impact the final product quality.

Current research on electrochemical regeneration indicates that the electrochemical properties of the regenerated LFP are comparable to those of commercial materials. For

instance, the study by Peng et al. [52] demonstrated that the recovered structure exhibited a discharge capacity of 135.2 mAh g^{-1} at 1 C, with a capacity retention of 95.3% after 500 cycles. However, the processes involve integration with a pre-lithiated graphite anode or separator, which may impose limitations on the industrial scalability of the process.

The solution-based recovery method for LFP materials holds promise for restoring both Li losses and the formation of Fe-Li defects, particularly in cases of severe degradation and substantial capacity decay [53]. The revival of these defects is crucial for achieving complete material recovery and optimal performance. However, the complexity of this method is a limitation, as demonstrated in the work by Panpan et al. [54], where a procedure involving strong electrostatic repulsion with various reduction agents was employed in a LiOH solution.

The main benefit of eutectic solution regeneration is that it covers relatively low-temperature treatment primarily via a reductive atmosphere, which increases the possibility of an LFP structure oxidation decrease [7]. Nevertheless, the crucial results of this method are under investigation in ongoing research.

The LFP direct regeneration covers several benefits, such as the recovery of high-quality materials with comparable electrochemical properties to commercial materials; nevertheless, the procedure covers some of its limitations, which are shown in Table 5.

3.1.3. Lithium Cobalt Oxide (LCO)

Batteries based on LCO structures find extensive applications, especially within the portable electronic field, due to their high energy density and compact size [6]. A notable reduction in Li content within the bulk crystal structures occurs throughout the degradation process, accompanied by significant damage to the surface of spinel phases. Consequently, recovery efforts focus on replenishing Li deficiencies and restoring degraded spinel phases to their original layered form. The relithiation process typically initiates in a solid or aqueous medium and progresses through annealing treatments [7].

Solid-state regeneration of LCO involves directly mixing degraded cathode materials with solid lithium sources, such as Li_2CO_3 or LiOH, followed by thermal treatment within the range of 800–950 °C. According to findings by Gao et al. [55] and Chen et al. [56], successful repair of material composition and structural defects occurs when the Li/Co ratio falls within the range of 1.0–1.2. A lower ratio results in incomplete structural repair, while a higher ratio introduces Li_2O impurities, negatively impacting the final performance.

The electrochemical relithiation approach for LCO materials encompasses several highly efficient procedures, with the primary drawbacks residing in process complexity and higher cost. Yang et al. [57] outlined a regeneration technique for cycled LCO in their work. The spent cathode material (working electrode) was paired with a new LCO electrode, the electron donor, and the Ag/AgCl reference electrode. During discharge, ions from the Li_2SO_4 electrolyte infiltrate damaged structures, reinstating Li deficiencies. A notable advantage was the absence of observed Al corrosion on the working electrode. After a brief annealing process, the cathode structure fully recovered, exhibiting capacity and cycle performance on par with the pristine commercial batch. However, a key limitation of this method is the necessity for high-quality delamination and purification steps in regenerating materials.

The solution-based regeneration of spent LCO requires further exploration, particularly regarding microstructure revitalization and the Li$^+$ replenishment process in an aqueous solution. Current results, as presented in the work by Kim et al. [58], describe a regeneration conducted at 200 °C for 20 h in a LiOH solution. The resulting structure of LCO demonstrated a capacity of 144 mAh g^{-1} with 92.2% retention after 40 cycles. Additionally, Shi et al. [59] conducted experiments involving highly effective hydrothermal relithiation, followed by post-sintering; however, the thermodynamics and kinetics of these steps remain uncharacterized.

The eutectic solvent regeneration offers several advantages, including non-toxicity, low cost, and recyclability. However, these procedures are primarily in the development

phase. As an illustration, Wang et al. [60] present a well-designed procedure using the lithium chloride (LiCl) and urea (CH_4N_2O) eutectic system, which features a reduced eutectic point to below 120 °C, for the direct regeneration of degraded LCO.

Compared to other recovery techniques, direct recycling of spent LCO materials serves several advantages, such as low environmental impact and the absence of Al corrosion. However, they are connected to the limitations summarized in Table 5.

3.1.4. Lithium Manganese Oxide (LMO)

The prominence of LIBs with Mn-rich cathodes is increasing in EVs and large-scale energy storage due to their stable performance and cost-effectiveness [7]. This trend is particularly notable in scenarios where high energy density is not the primary consideration. Likewise, for LFP recycling, the economic viability of traditional pyrometallurgical and hydrometallurgical recycling methods for recovering Mn compounds from spent LMO cathode materials is constrained by their relatively low market value [24]. Consequently, the economic motivation for the recycling of LMO is circumscribed. In this context, direct recycling emerges as a pertinent and economically viable strategy for effectively managing spent LMO cathode materials [5].

The deterioration of LMO materials is due to Mn^{2+} dissolution [61], resulting from the disproportionation of Mn^{3+} [62]. In the initial charge, Mn^{3+} undergoes a reaction, forming spinel-type $Li_4Mn_5O_{12}$ and soluble trimanganese tetraoxide (Mn_3O_4). During discharge, $Li_2Mn_2O_4$ spinels are generated with Jahn–Teller distortion. As a benefit, cycled LMO retains the spent spinel LMO phase without impurities [7].

Regarding the recovery of spent LMO materials, solid-state and electrochemical (aqueous) relithiation regeneration are the preferred methods. Typically, LiOH solutions in various concentrations are utilized to treat structural defects. However, as demonstrated in review work by Panpan et al. [7], highly concentrated solutions exceeding 0.4 M induce the formation of Li-rich phase lithium manganite (Li_2MnO_3) impurities during the recovery process. Wang et al. [63] have shown that hydrothermal methods yield superior recovery results compared to solid-state sintering in terms of phase purity and electrochemical capacity of the treated LMO. Solid-state techniques restore the lost capacity by maintaining a well-balanced molar ratio of LiOH and aged LMO, dependent on the degraded materials' state of health (SOH). In contrast, hydrothermally recycled products recover lost capacity irrespective of the SOH of the spent LMO. The primary difference among these approaches is reflected in their energy and environmental implications, with hydrothermal processes demonstrating markedly reduced energy consumption compared to solid-state sintering, as provided in the LCA study by Xio et al. [64].

Although the direct recycling of spent LCO cathodes offers low energy consumption, it also has some limitations, as detailed in Table 5.

3.2. Direct Recycling Treatment of Spent Anode Materials

Graphite stands out as a frequently used anode material in LIBs [65], attributed to its excellent electrical conductivity, high thermal and mechanical stability, prolonged cycle life, good capacity, and low working voltage. Nevertheless, the recycling of spent graphite anodes received comparatively less focus due to the absence of transition metals. Thus, spent anodes are either incinerated or disposed of in landfills. Considering the potential demand for graphite minerals, which is projected to be approximately 13 times higher than the demand for Li minerals, especially in the context of the 2025 EV market, there is a critical need to streamline and enhance the recycling processes for these materials [66].

Several research groups have devoted their work to graphite direct regeneration [67,68]. Yang et al. [69] introduced a comprehensive direct recycling perspective for all anode material recovery, including graphite, Cu foil, aluminium hydroxide ($Al(OH)_3$), and Li_2CO_3. This approach combines heating and leaching treatment steps and leads to the recovery of 99.9% pure graphite with significantly improved specific capacity and excellent cycling performance. The anode materials may contain impurities such as transition metals, which,

as demonstrated by Ma et al. [70], can be effectively treated and removed through sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) leaching. However, this approach increases the complexity of wastewater treatment, posing a limitation to full-scale industrial applications. In response, Wu's [71] and Wang's [72] research groups focused on cleaner methods, leveraging the highly reactive properties of LiC_x in spent anode materials with water, enabling the removal of residual Li from graphite particles. The oxidation degradation of LiC_x is mitigated by an inert atmosphere, albeit resulting in higher costs.

Acid or water treatments prove effective in eliminating impurities from spent graphite anodes. However, subsequent high-temperature annealing steps become imperative to attain the complete recovery of graphite anodes. A review by Panpan et al. [7] reveals atom rearrangement and structural recovery after a 6 h treatment at 3000 °C in an N_2 environment. Nevertheless, the primary limitation lies in their high energy consumption.

The EOL processing of spent anode graphite-based materials is currently in the developmental stage and requires further optimization, as current approaches indicate. However, the limitations of the implemented direct recycling methods for treating spent graphite anode materials are outlined in Table 5.

4. Discussion

Recycling spent LIBs represents an effective waste-management strategy that mitigates the environmental impacts by preserving raw resources, especially valuable metals, reducing the emission footprint of mining and post-processing, and fostering the principles of a circular economy. Given the prevalent global practices in recycling, such as pyrometallurgy or hydrometallurgy, which often entail high energy consumption, emissions, or the extensive use of chemicals, a pressing need arises for alternative recycling technologies. These alternatives should enable the direct reutilization of deteriorated energy storage materials in battery manufacturing, aligning with economic and environmental sustainability objectives.

The currently employed direct recycling methods focus on treating high-quality cathode or anode materials obtained through the recycling pre-treatment of the same type or different types of LIBs. Consequently, these direct regeneration approaches do not encompass the treatment of entire spent LIB systems; instead, they specifically target the most economically valuable products in the EOL treatment chain, commonly referred to as the black mass. During the recycling pre-treatment phase, materials are subjected to high-temperature treatments, incurring substantial operating costs and emissions. Moreover, these materials may undergo treatment with various chemicals, introducing complexities to wastewater treatment or necessitating specialized equipment to ensure compliance with safety regulations and produce high-quality end products. The combined approach of pre-recycling and the selective recycling of specific materials, as illustrated in Figure 7, significantly influences the operation's environmental and economic aspects, impacting the overall motivation for the industrial implementation of direct recycling techniques.

Direct recycling methods are typically customized for specific material treatments. Presently, "relithiation" techniques, encompassing solid-state sintering, electrochemical relithiation in organic and aqueous electrolytes, ionothermal relithiation, solution relithiation, and eutectic relithiation, are predominantly utilized for the regeneration of cathode materials. This review provides an overview of the direct recycling of LIB cathode types, including NMC, LFP, LCO, and LMO, and graphite anodes generally in laboratory scaled-up treatments. Nevertheless, significant challenges persist in applying these techniques on a larger industrial scale.

While individual methods exhibit high efficiency in restoring the properties of regenerated materials, bringing them to a comparable level with pristine ones, the primary challenge in direct recycling lies in processing black mass obtained from different LIB types. The product typically consists of shredded cathode and anode materials, conductive agents, PVDF binder, and various residual impurities (Al, Cu, Fe, etc.). Material diversity sets several technical burdens for subsequent processing, such as product separation or

implementation complexity. These additional treatments represent a vital process stage in the current research state. They aim to achieve highly efficient direct recycling results while increasing economic demands and environmental burdens.

Figure 7. Current direct recycling process, including recycling pre-treatment and recycling steps, covering application of different relithiation techniques.

Furthermore, it is essential to consider the potential application field of regenerated materials. When considering currently common optimizations, covering alterations in material ratios or substitutions of utilized compounds, it is crucial to assess the potential of complex regeneration processes compared to the regeneration of chemical compounds individually. The introduction of direct recycling processes should be up-to-date and fully respect the demand of the battery market. If the current development trend continues to be maintained, regenerating outdated battery structures would not be an advantage and, on the contrary, could bring significant economic losses.

Before full-scale industrial implementation, careful consideration of the mentioned factors is imperative. Presently, direct recycling remains in its beginning stages. Research predominantly revolves around simplified models, focusing on single-type materials or black mass sourced from specific battery types. Most processing occurs at a laboratory scale, with pilot operations representing the extent of practical application thus far. Only through more thorough evaluations can it be determined whether direct recycling will emerge as a distinct, standalone recycling approach for managing waste LIBs or whether it will function as an adjunct process alongside established techniques.

An overview of the limitations of selected direct recycling techniques identified within this work, depending on the processed material, is shown in Table 5. Besides these summarized limitations for common cathode and anode materials, state-of-the-art direct regeneration technologies need more exploration and optimization within the following areas, which are discussed point-to-point subsequently.

- Direct recycling pre-treatment;
- Complex material composition;
- Black mass processing;
- Environmental and economic impact;
- Perspective of industrial scale.

4.1. Direct Recycling Pre-Treatment

Current direct recycling methods mainly focus on high-quality cathode or anode materials (black mass) derived from recycling pre-treatment steps, which ensure the removal of unsolicited materials. Thus, integrating recycling pre-treatment into the EOL process is essential; however, it leads to the non-recovery of selected material groups and significant process losses. Furthermore, the procedures become increasingly technologically complex when considering the simultaneous processing of various chemical types of batteries, a scenario that is quite common across other recycling techniques. The pre-treatment commonly consists of complex chemical treatment followed by energy- and emission-demanding steps, which decrease the environmental and economic benefits of direct recycling procedures. Therefore, future optimization should involve comprehensive treatments suitable for the entire battery system, ensuring a closed-loop circular economy for LIBs, and maximizing material recovery and process efficiency.

4.2. Complex Material Composition

Current methods commonly deal with the processing of single-type materials or the processing of cathodes and anodes of one type of battery. However, conventional recycling often involves processing various battery types, producing multi-material black mass. If it is not technologically possible to process this type of product via direct recycling, it would be necessary to extend the recycling pre-preparation by, e.g., a sorting step, where the batteries would be classified according to their chemistry type. In this context, leveraging the Battery Passport system would be feasible and logistically appropriate. Otherwise, processing and sorting the black mass would be necessary by implementing proper separation techniques. Moreover, it is imperative to consider the advantages of recovering entire cathode structures, while also accounting for technological advancements and preferences within changes in material ratios. This includes exploring optimal methods for industrial-scale recycling, considering the aging of technology and new possibilities for their utilization.

4.3. Black Mass Processing

Although high-quality black mass can be obtained as a typical product of recycling pre-treatment, there is a high possibility that it will contain impurities in the form of residual current collectors, organic materials, system casings, or anode/cathode materials in the scenario of direct processing of spent cathodes/anodes. Thus, before the direct recycling procedure itself, it is necessary to add a series of additional treatment steps, such as high-temperature annealing, chemical leaching, or precipitation post-treating, to remove impurities and achieve the desired high efficiency of the process. Nevertheless, this sequence of procedures is characterized by high energy consumption, significant emissions, and the generation of additional waste products, all of which contribute to elevated process costs and a larger overall environmental footprint. Thus, future optimization efforts should still be focused on developing effective methods to separate and treat black mass, ensuring the recovery of valuable materials, minimizing impurities, and achieving as high a purity level in regenerated materials as possible. Nevertheless, the processing and purification of black mass present a drawback inherent in currently implemented procedures, mainly for the pre-recycling lines, with the output product constituting black mass, whose quality directly influences its market value. Mitigating energy consumption and minimizing the environmental impact of these procedures would benefit all waste LIB recycling processes.

4.4. Environmental and Economic Impact

Direct recycling methods should be optimized to minimize energy consumption, economic demands, and environmental impact. Current direct recycling processes involve high-temperature treatments, such as annealing, smelting, or roasting, and chemical interventions, leading to elevated energy consumption, emissions, and complications in wastewater treatment, mainly as part of recycling pre-treatment or additional separation

procedures as part of black mass post-processing. Future optimization efforts should prioritize environmentally sustainable practices and ensure an eco-friendlier approach. The incorporation of environmentally friendly processes has the potential not only to contribute to sustainability but also to impact operational costs positively over subsequent years. By adopting eco-friendly practices, companies can anticipate reducing the required investment, for example, through specialized equipment prices. This dual benefit—environmental sustainability and cost effectiveness—creates a favorable environment for the advancement and widespread adoption of these processes.

4.5. Perspective of Industrial Scale

At present, direct recycling is primarily encountered at the laboratory level. The introduction of effective procedures on this smaller-scale level represents an initial step that can ensure fewer demanding processes from environmental and economic perspectives when fully implemented on the industrial level. To ensure effective EOL management, especially of LIBs, it will be necessary to evaluate the possibilities offered by direct recycling and to focus on pilot projects and recycling plants, where processing at the industrial scale level is presented. Based on that, decisions can be made regarding whether direct recycling will be replaced or implemented as a supplemental procedure to the currently established methods.

Considering current results and the wide range of optimization possibilities, there is a high potential for global and large-scale implementation of direct recycling as the major or supplementary EOL treatment technique for spent LIBs. Moreover, it can be perceived as a sustainable and eco-friendly alternative to conventional recycling processes because it complies with crucial environmental, economic, and technological factors. By minimizing the use of harsh chemicals and reducing energy consumption and emissions of high-temperature treatments, these methods contribute to a smaller carbon footprint and align with global efforts toward environmental sustainability. Regarding the increase in environmental legislative restrictions, LIB's waste management requests, and market trends that prioritize sustainability, the demand for eco-friendly battery recycling methods grows. Thus, direct recycling can be positioned as a key player in addressing these evolving dynamics and fostering a more sustainable future. Nevertheless, the significant shortcomings of current direct recycling processes must be considered and addressed before full-scale implementation.

5. Conclusions

This review outlines the limitations of current direct recycling methods for common cathode materials (NMC, LFP, LCO, and LMO) and anode graphite in spent LIBs, mainly from a laboratory-scale perspective. The work points out the main limitations of state-of-the-art direct recycling technologies, including solid-state sintering, electrochemical relithiation, ionothermal relithiation, solution relithiation, and the eutectic relithiation method, which are typically used for highly effective regeneration of spent materials, including the restoration of their electrochemical and structural properties. Additionally, this work summarizes the main challenges of selected direct recycling methods, which are essential for potential optimization steps leading to larger-scale (fully industrial) applications. The current techniques of direct recycling typically treat the output of recycling pre-treatment, the black mass. The necessity of energy-demanding pre-treatment steps impairs the perspective of subsequent, direct regeneration techniques and is the dominant limitation of current industrial implementation. Thus, this review emphasizes the critical constraints and the need for further optimization within direct recycling, representing a promising EOL treatment for spent LIBs in future years.

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