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Review

A Minireview on the Regeneration of NCM Cathode Material Directly from Spent Lithium-Ion Batteries with Different Cathode Chemistries

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Abstract: Research on the regeneration of cathode materials of spent lithium-ion batteries for resource reclamation and environmental protection is attracting more and more attention today. However, the majority of studies on recycling lithium-ion batteries (LIBs) placed the emphasis only on recovering target metals, such as Co, Ni, and Li, from the cathode materials, or how to recycle spent LIBs by conventional means. Effective reclamation strategies (e.g., pyrometallurgical technologies, hydrometallurgy techniques, and biological strategies) have been used in research on recycling used LIBs. Nevertheless, none of the existing reviews of regenerating cathode materials from waste LIBs elucidated the strategies to regenerate lithium nickel manganese cobalt oxide (NCM or $LiNi_xCo_yMn_zO_2$) cathode materials directly from spent LIBs containing other than NCM cathodes but, at the same time, frequently used commercial cathode materials such as $LiCoO_2$ (LCO), $LiFePO_4$ (LFP), $LiMn_2O_4$ (LMO), etc. or from spent mixed cathode materials. This review showcases the strategies and techniques for regenerating $LiNi_xCo_yMn_zO_2$ cathode active materials directly from some commonly used and different types of mixed-cathode materials. The article summarizes the various technologies and processes of regenerating $LiNi_xCo_yMn_zO_2$ cathode active materials directly from some individual cathode materials and the mixed-cathode scraps of spent LIBs without their preliminary separation. In the meantime, the economic benefits and diverse synthetic routes of regenerating $LiNi_xCo_yMn_zO_2$ cathode materials reported in the literature are analyzed systematically. This minireview can lay guidance and a theoretical basis for restoring $LiNi_xCo_yMn_zO_2$ cathode materials.

Keywords: NCM cathode materials; spent lithium-ion batteries; regeneration; spent LCO batteries; renovated cathode material

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1. Introduction

Lithium-ion batteries (LIBs) have become the dominant technology for portable electronic and energy-storage devices like laptops, smartphones, communication, and consumer electronics, electric vehicles, and electric hybrid vehicles. However, after several thousand charge–discharge cycles, LIBs come to the end of their service life, being powerless for the proper operation of portable devices, and then are discarded [1]. The ever-growing demand for LIBs implies that more batteries will be spent in the near future. Currently, most waste LIBs are landfilled in different countries, which poses a tremendous threat to human and environmental health [2]. In addition, waste LIBs contain expensive, scarce, and high-valuable metals such as Ni, Mn, Co, and Li and may serve as a cost-effective source for these metal elements [3,4]. For these reasons, significant efforts have been paid to recycle and regenerate spent LIBs.

The existing research on recycling lithium-ion batteries is mainly focused on the recovery of high-valuable metals like cobalt, nickel, manganese, and lithium in the cathode materials [5–11]. Although extensive investigations have been carried out on the typical recycling routes of the waste LIBs [5,12–15], only few studies are devoted to discussing the strategies for regenerating cathode active materials from the mixed systems of used LIBs [16].

It can be a significant challenge to collect and recover used batteries that may contain various types of cathodes (e.g., $LiNi_xCo_yMn_zO_2$, $LiFePO_4$, $LiMn_2O_4$, and $LiCoO_2$) in real-life recycling practice. The difficulty of separating one cathode material from another is due to the great similarity of the chemical and physical properties of their constituent metals, such as Ni, Co, and Mn. To overcome the challenge of recovering the mixed spent batteries with different cathode chemistries, some researchers adopted regenerating high-performance $LiNi_xCo_yMn_zO_2$ materials from the initial LIBs mixture without sorting them [17].

In recent years, a new strategy has been developed to regenerate cathode active materials directly from spent LIBs. Separating many metal ions with the same chemical properties is often difficult, and often leads to the concentration of one particular metal ion and the depletion of others. This strategy has been shown to better avoid this problem and is not only more efficient but also more environmentally friendly [17,18].

Frequently-used cathode materials, such as $LiCoO_2$, $LiNi_xCo_yMn_zO_2$, and $LiFePO_4$, can all be directly resynthesized from the discarded LIBs and then reused to produce new batteries [19–22]. Thus, a cycle is formed from the waste cathode active materials to new ones. Accordingly, the direct conversion of used LIBs into new cathode active materials has considerable economic advantages. Furthermore, it is more environmental-friendly than traditional recycling technologies [23–25].

The traditional industrial technologies for regenerating cathode materials from the spent LIBs consist of three major steps [26]:

1. Separating the active cathode materials and aluminum current collectors using solvent dissolution method, thermal treatment method, alkaline solution dissolution method, mechanical method, or ultrasonic-assisted separation;
2. Separating and recovering individual valuable metals (e.g., Co, Ni, Mn, Cu, Fe, and Li) from cathode material fabricated through pretreatment methods [27];
3. Synthesis of new cathode materials.

However, the prevailing industrial technologies for recycling cathodic active materials from waste LIBs have some remarkable shortcomings [26,28,29]:

- They have many complicated separation steps and overall, recycling routes are often complex;
- Secondary pollution occurs due to the elimination of impurities and precipitation of metal ions using different solvents, acids, and alkalis in the conventional recycling process;
- Some valuable materials lost in the recycling process;
- High intake of chemicals, the low recovery efficiency of valuable metallic elements from spent cathode materials, costly solvents, and intricate recycling routes in the techniques of chemical precipitation, solvent extraction, or ion-exchange method are hindering the large-scale application of the hydrometallurgical technique in the industry;
- Traditional approaches to recycling cathode materials (pyrometallurgical or hydrometallurgical processes) cannot handle the complex system of LIBs (i.e., the mixture of cathodes such as LCO, LMO, NMC, and LFP);
- The pyrometallurgical treatment process (i.e., smelting) recovers only cobalt, iron, copper, and nickel as alloys or molten metals and does not recover the essential components like lithium that is lost as slag with other gases and refractory oxides. Moreover, the recovered alloys require further refinement by hydrometallurgical steps. It is worth mentioning that most of the constituent materials (60–70%) of waste lithium-ion batteries are volatilized or added to the remaining slag, indicating another crucial disadvantage of the pyrometallurgical process. In addition, pyrometallurgical treatment is accompanied by direct carbon and hazardous gas emissions from the recycling process. To meet strict environmental regulations, poisonous emissions must be eliminated with flue-cleaning systems;
- At the end of the hydrometallurgical recycling process, there is wastewater discharge that must be disposed of;

- Lengthy and expensive purification steps are often required to produce battery-grade materials.

Unlike the traditional recycling technologies, the direct cathode regeneration process has more benefits of fewer recycling steps, no material loss, environmental friendliness, less energy-intensive, and desirable economic profits [30]. By eliminating complicated separation processes, direct regeneration techniques become more profitable due to their lower costs and higher recovery efficiency [31]. For instance, Wang and co-workers [32] developed one of the first direct regeneration technologies, which made it possible to directly synthesize new cathode materials from any spent LIBs regardless of their shape, size, or cathode chemistry. Additionally, steel, graphite, copper, aluminum, and plastics are also recovered. Moreover, the direct regeneration strategy allows for the removal of impurities in the regenerated products so that cathode powders can be recovered as new cathode active materials, which account for more than 70% of the LIB value [17,32,33]. Therefore, the direct regeneration process has considerable economic benefits over traditional recycling technologies, where only the metal value is recovered.

During the regeneration process of cathode powders from the discarded LIBs, the recovered cathodes obtained by pretreatment can be directly employed to regenerate new cathode active materials via co-precipitation method, solid-state synthesis, hydrothermal treatment, and the sol–gel technique [18,34].

Recently, layered $LiNi_xCo_yMn_zO_2$ cathode material is considered to be one of the most prospective cathodes, showing high discharge capacity (>150 mAh/g), high energy density (200–300 Wh/kg), and relatively high voltage window (3.6–4.5 V) [35–41]. Ni, Co, and Li are high-valuable metals; therefore, reusing and recycling $LiNi_xCo_yMn_zO_2$ leads to significant economic benefits. This review presents the approaches and strategies for regenerating $LiNi_xCo_yMn_zO_2$ cathode materials directly from both some commonly used cathode materials and different types of mixed-cathode materials.

2. $LiNi_xCo_yMn_zO_2$ Regeneration Strategy and Its Economic Benefits

Currently, the primary methods for $LiNi_xCo_yMnzO_2$ regeneration include the sol–gel method, hydrothermal treatment, spray drying, carbon-thermal reduction, co-precipitation, and solid-state reaction.

Table 1 summarizes the advantages and disadvantages of the NCM regeneration strategies from various literature data.

Table 1. Comparison of NCM regeneration strategies.

Regeneration Strategy	Advantages	Disadvantages
Co-precipitation synthesis	• High cathode purity • High metal recovery rate • The regenerated NCM showed better discharge capacity due to the more uniform distribution of elements in the cathode powders [42,43]	• Difficult procedure • High cost
Hydrothermal method	• Lower energy consumption • The regenerated NCM particles retain their original structure and morphology • Shorter reaction time • $LiNi_xCo_yMn_zO_2$ regenerated by the hydrothermal method usually has a better rate capability than NCM particles regenerated via solid-state reaction [44]	• Strict requirements for regeneration equipment

Table 1. *Cont.*

Regeneration Strategy	Advantages	Disadvantages
Solid-state reaction method	• Less-step regeneration [45] • Simple regeneration process	• High energy consumption • Uneven mixing of raw materials causes the inferior electrochemical properties of the regenerated NCM [46,47] • Difficult to remove impurities in recovered $LiNi_xCo_yMn_zO_2$ [48,49]
Sol–gel method	• Make full use of metal ions [5] • The regenerative NCM cathode material has the same morphology and electrochemical performances as the freshly synthesized one [12] • High cathode purity • The regenerated NCM materials exhibit smaller particle sizes (100–300 nm) than that of NCM regenerated via the co-precipitation method [5]	• The operation process is more complicated compared with solid-state and hydrothermal methods • High production cost • The long preparation time of the regenerated $LiNi_xCo_yMn_zO_2$ impedes its large-scale application in industry • High energy consumption
Thermal method	• The simplest direct recycling method	• Determining the amount of lithium that needs to be supplemented is challenging [25]

The results obtained by different researchers confirmed that the regeneration method of $LiNi_xCo_yMn_zO_2$ from the mixed cathode materials cannot be only economically justifiable but also save energy.

For instance, Zou et al. [33] proposed a low-temperature methodology for recovering NCM111 from the mixed cathode scraps consisting of $LiMn_2O_4$, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$, $LiCoO_2$, and $LiFePO_4$ by precipitating $Ni_{0.33}Mn_{0.33}Co_{0.33}(OH)_2$ and reacting the obtained precipitate with Li_2CO_3, which is synthesized by reacting the remaining LiOH with Na_2CO_3. The electrochemical performance and rate-capability test results, as well as specific capacity and Coulombic efficiency as a function of the cycle plot, as illustrated in Figure 1, demonstrated that the recycled NCM111 displayed excellent electrochemical properties. The discharge capacity and Coulombic efficiency of the recovered $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ in the first two cycles were 173.96 mAh/g and 172.92 mAh/g; 81.07% and 94.86%, respectively. The findings obtained in the research [33] were in line with and similar to previously published results.

Later, Gratz et al. [32] adopted a closed-loop strategy to regenerate NCM111 from the mixed system of spent LIBs, which are primarily composed of $LiCoO_2$ cathode chemistry. In their second experiment, NCM111 was recovered from different types of waste Li-ion batteries with $LiMn_2O_4$, NCM111, and $LiFePO_4$ cathode powders added to the shredded waste batteries. They determined the economic profits and recovery efficiency of the regeneration process developed by them. The findings demonstrated that the recovery efficiencies of valuable cathode metals such as Mn, Ni, and Co were greater than 90%. Moreover, they conducted a cost-beneficial analysis to estimate the benefit of their regeneration strategy. The cost of chemicals to recycle 1 ton of used LIBs was estimated at \$1419, while the profit of the recovered products (above 90% from the newly regenerated cathodes) was estimated at \$6432 per ton. Hence, based on material balance 1 ton of spent LIBs has the potential to generate \$6432 − \$1419 = \$5013 profit margin.

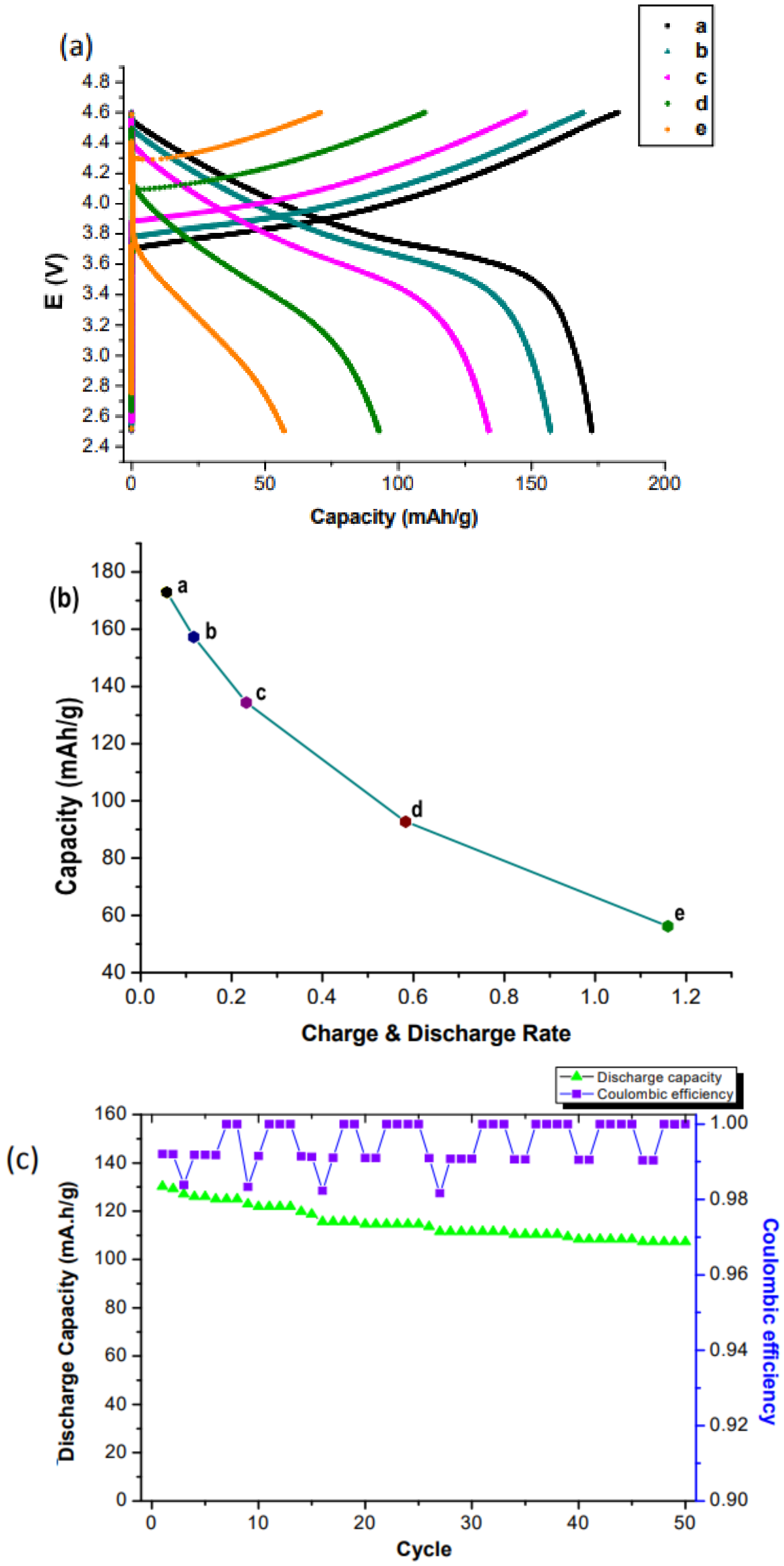

Figure 1. Electrochemical performance of synthesized NCM111, (**a**) charge and discharge curves for different rates (a 11.67, b 23.33, c 46.67, d 116.67, e 233.34 mA/g), (**b**) discharge capacity as a function of rate, (**c**) cycle test at a current density of 46.6 mA/g and voltage of 2.5–4.6 V. Used with permission of Royal Society of Chemistry, from Ref. [33]; permission conveyed through Copyright Clearance Center, Inc.

Zou et al. [33] also determined the economic profits of their regeneration process. The results indicated that the cost of synthesizing NCM111 with virgin materials was estimated at \$16,635 per ton, while the cost of synthesizing NCM111 with recycled materials was only \$6195 per ton. The cost differential was \$16,635 − \$6195 = \$10,440 per ton, which corresponded to the benefit of \$10,440 per ton that could be gained during their regeneration process.

Chen et al. [50] developed a closed-loop recycling process consisting of a sulfuric acid leaching process, co-precipitation technique, and sintering to regenerate ultra-high quality cathode materials. As they claimed, this regeneration strategy is simple, highly economical, and eco-friendly and shows great potential for wide-scale industrial application. Their findings demonstrated that the scale of the regeneration approach had been successfully scaled up from 1 kg to 30 kg of spent batteries per experiment.

Recently, Fang et al. [51] developed a green, closed-loop hydrometallurgical strategy, shown in Figure 2, for regenerating spherical NCM523 cathode material based on the electrolysis of Na_2SO_4 solution. This strategy consists of the following steps:

1. Electrolysis of Na_2SO_4 solution;
2. Recycling of aluminum;
3. Leaching of cathode material (H_2SO_4 and NaOH generated by electrolysis of Na_2SO_4 solution are employed as leachate);
4. Precipitation of the recycled $Ni_{0.5}Co_{0.2}Mn_{0.3}CO_3$ precursors and recycled Li_2CO_3 regeneration of spherical NCM523;
5. Recycling of Na_2SO_4.

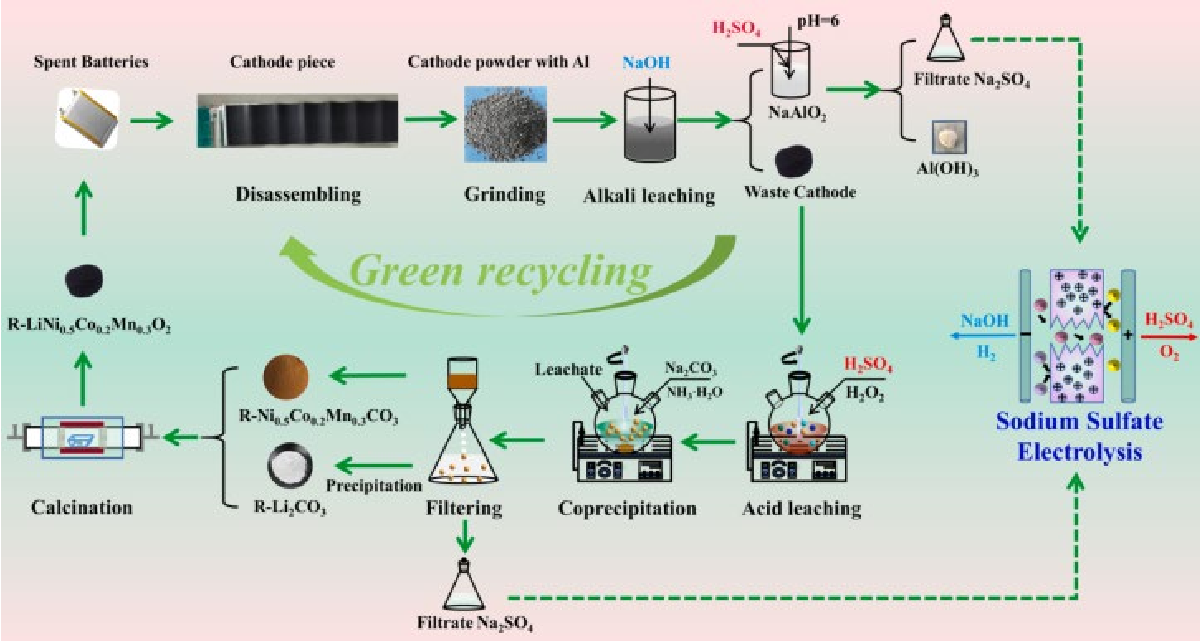

Figure 2. Schematic representation of the green recycling strategy of waste LIBs proposed by Fang and co-workers. Used with permission of Elsevier Science & Technology Journals, from Ref. [51]; permission conveyed through Copyright Clearance Center, Inc.

The regenerated NCM523 has an excellent initial discharge capacity of 167.04 mAh/g at the 0.05 C charge–discharge rate, with a good capacity retention of 87% after 100 cycles. Moreover, this novel strategy assessed the economic benefit of recycling spent LIBs. It was calculated that recycling one ton of spent ternary lithium-ion batteries can produce a profit of up to \$6992.

2.1. $LiNi_xCo_yMn_zO_2$ Regeneration via the Thermal Method

To regenerate new $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode powder from the spent LIBs, Zhang, et al. [52] presented an innovative process for leaching cathode scraps with mild oxalic acid followed by heat treatment. During this simple and effective oxalic-acid-based hydrometallurgical regeneration process, the transition metals contained in the cathode scraps are transformed into oxalate precipitates $MC_2O_4{\cdot}2H_2O$ (M = Ni/Co/Mn). Subsequently, the resulting precipitates serve as raw materials for resynthesis new NCM cathode active materials. An illustration of this regeneration approach is presented in Figure 3.

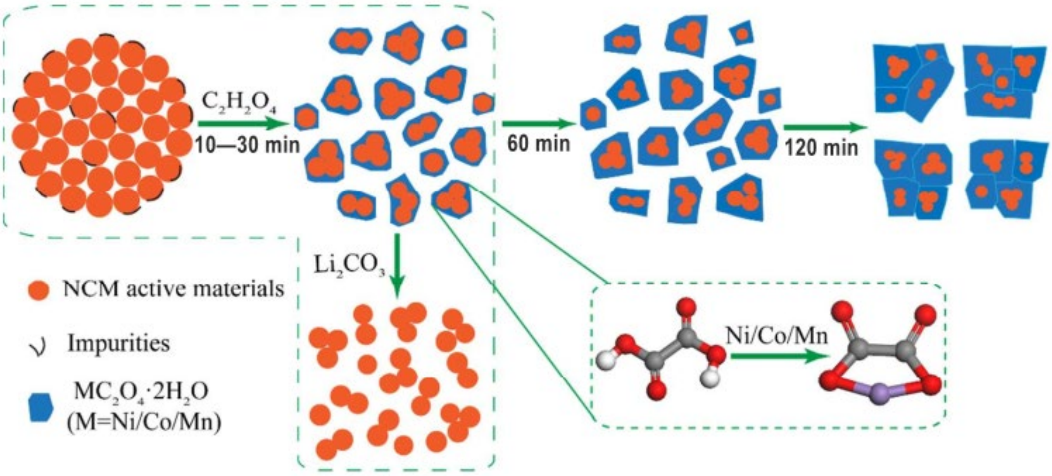

Figure 3. Schematic of the proposed regeneration process of waste NCM cathode materials using environment-friendly oxalic acid. Reprinted with permission from Ref. [52], Copyright 2018, American Chemical Society.

Owing to this strategy, more than 98.5% of valuable transition metals (i.e., Ni, Co, and Mn) stay in the precipitates and are recovered directly. In their investigation, the extent of the acid leaching reaction, which presumably affects the electrochemical performances of the regenerative NCM111, could be regulated by controlling the leaching time. The results implied that the regenerated NCM cathode active material with the leaching time of 10 min exhibited the highest initial discharge capacity of 168 mAh/g when cycling at a rate of 0.2 C, and discharge capacity maintained at 153.7 mAh/g after 150 cycles with the best capacity retention of 91.5%. The overall regeneration strategy of NCM cathode materials from retired LIBs proposed by Zhang and co-workers [52] is shown in Figure 4.

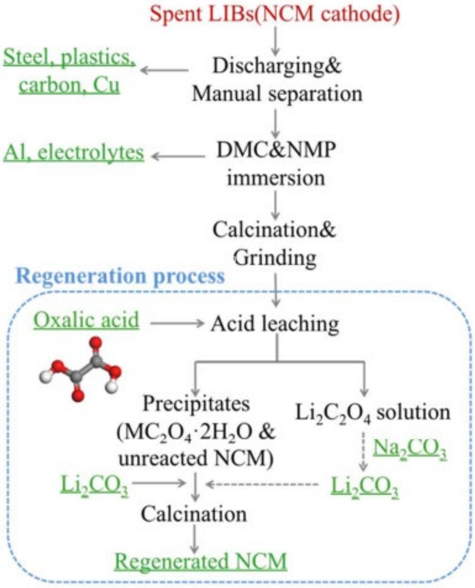

Figure 4. Schematic illustration of the whole regeneration processes of NCM cathode materials from waste LIBs. Reprinted with permission from Ref. [52], Copyright 2018, American Chemical Society.

In their previous work, Zhang et al. also employed a direct calcination process to regenerate $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode active materials [53]. Then, they used heat treatment to regenerate the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ electrode scraps. In their research, the effect of heat treatment temperature (ranging in temperature from 300–700 °C, in increments of 100 °C) on the cycling performances of recovered NCM111 cathode active materials was systematically investigated. They found that the NCM111 cathode material regenerated through a direct calcination method at 600 °C shows not only optimal electrochemical performances (its best discharge capacity was 145.4 mAh/g at the 0.2 C rate) but also has better spherical morphology.

Li et al. [45] proposed an acidless process route for regenerating NCM523 cathode materials by calcining the mixture of spent NCM523 cathodes and $LiOH{\cdot}H_2O$. During this regeneration route, various Li contents (12, 14, and 16%) in NCM523 were extensively investigated. At a Li content of 14%, the regenerative NCM523 cathode material exhibited improved rate performance and enhanced cycling stability as well as the optimal discharge capacity (161.25 $mAhg^{-1}$ at the 0.1 C rate).

Likewise, Zhang et al. [54,55] employed the solid-state reaction technique to directly recycle and regenerate new NCM111 cathode powder from waste LIBs. They added a certain amount of Li_2CO_3, $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, and $Mn(NO_3)_2{\cdot}4H_2O$ to the recovery powder, and then the obtained mixture was calcinated for regeneration. The batteries assembled with the regenerated NCM111 exhibited good electrochemical performances. Its initial specific discharge capacity was 155.4 $mAhg^{-1}$ at the 0.1 C rate in the voltage window of 2.8–4.5 V, which is competitive with some commercialized NCM111 materials.

To acquire the regenerated NCM523 cathode active material, Zhou et al. [49] blended the recovered materials from used LIBs with CH_3COOLi at a certain proportion and subsequently calcinated the obtained mixture at a high temperature. In their study, the regenerated mechanisms were investigated in a systematic manner, and the electrochemical properties of recycled material (denoted as S-NCM), commercial NCM523 (denoted as C-NCM), and regenerated material (denoted as R-NCM) were extensively studied. Their findings showed that the electrochemical properties of regenerated NCM523 cathode powders had been noticeably improved, which could be related to the increase in the cathode lattice parameters and the reduction in insulating films. The initial discharging capacities of the R-NCM, S-NCM, and C-NCM at the 1 C rate were 147, 82, and 152 $mAhg^{-1}$, respectively. However, as can be seen, a minor difference remained between the electrochemical performances of the regenerated and commercial NCM523 batteries, which are due to the presence of insulting impurities in the regenerated cathodes that, unfortunately, could not be fully eliminated. The capacity retention rates of regenerated, recycled, and commercial NCM523 material after 100 cycles of the 1 C rate were 89.12%, 69.51%, and 88.82%, respectively. The findings obtained in research [49] demonstrated that the electrochemical performance of regenerated NCM523 cathodes was close to that of the commercial $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode materials.

Bai and co-workers [56] regenerated NCM622 by treatment $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ cathode scraps with Cyrene solvent, filtration, and then calcination at 600 °C for 2 h. The received NCM622 cathode materials showed a discharge capacity of 158.0 $mAhg^{-1}$ after 40 cycles at the C/3 charge–discharge rate, between 3.0 and 4.3 V, with an increased capacity retention of 100.9% after 40 cycles.

2.2. $LiNi_xCo_yMn_zO_2$ Regeneration via the Sol–Gel Method

$LiNi_xCo_yMn_zO_2$ cathode material with perfect electrochemical properties can be successfully regenerated through the sol–gel synthesis method [57–61], in which organic acid can simultaneously serve as a chelating and leaching agent.

In their investigation, Li et al. [57] utilized a sol–gel method to regenerate NCM111 with good electrochemical properties from the spent LIBs. They used lactic acid as a chelating and leaching agent. According to their proposed lactic acid leaching mechanism, as illustrated in Figure 5, this process can be explained in two simple steps. The first stage relates to the transition of high-valence Ni, Co, and Mn to the corresponding metal ions in the presence of hydrogen peroxide and subsequent dissolution of waste NCM111 in the acid leaching solution; the second stage is the chelation of obtained Ni^{2+}, Co^{2+}, Mn^{2+}, and Li^{+} ions with lactic acid.

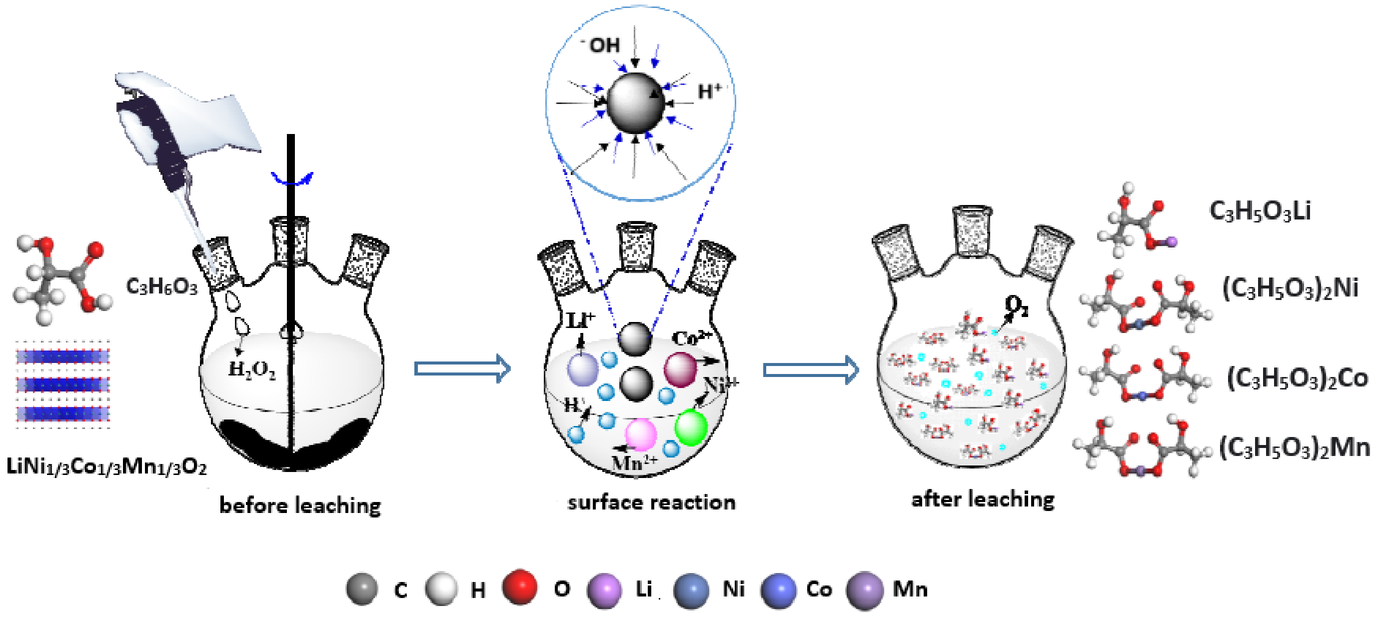

Figure 5. Schematic representation of the possible mechanism and products in the lactic acid leaching process of NCM cathode materials regenerating from discarded LIBs. Reprinted with permission from Ref. [57], Copyright 2017, American Chemical Society.

The findings [57] demonstrated that the efficiencies of Li, Mn, Ni, and Co leaching reached 97.7%, 98.4%, 98.2%, and 98.9%, respectively. In addition, the results indicated that the regenerated NCM111 delivers a high discharge capacity of 138.2 mAh/g at the 0.5 C rate after 100 cycles.

In their next work, Li et al. [58] regenerated NCM111 cathode active material from citric acid and hydrogen peroxide leachate using the sol–gel strategy and found that the electrochemical properties of NCM111 regenerated from the leaching solution of waste mixed-cathode materials ($LiCoO_2$, NCM111, and $LiMn_2O_4$) containing aluminum was better than that of NCM111 synthesized by pure chemicals. This is due to the trace amount of aluminum retained in the leaching solution, which is known to stabilize the cathode structure during Li intercalation and deintercalation. In addition, the findings demonstrated that the leaching efficiencies of target metals (Li, Ni, Co, and Mn) exceeded 95% in a mixed solution of a citric acid concentration of 0.5 M and a hydrogen peroxide concentration of 1.5 vol %. Moreover, the regenerated NCM111 material displayed a perfect initial discharge capacity of 152.8 $mAhg^{-1}$ at the 0.1 C rate.

Yao et al. [59] proposed a similar approach in which citric acid was chosen as both a chelating and leaching agent to re-synthesize NCM111 cathode material. Re-synthesized NCM111 displayed excellent electrochemical properties and a good initial discharge capacity of 147 mAh/g. In addition, the results suggested that the leaching efficiency of nickel, manganese, lithium, and cobalt ions reached more than 98% under optimum leaching conditions.

In their next study, Yao et al. [60] employed another organic acid to regenerate NCM111 through the sol–gel process. D, L-malic acid acts as both a chelating agent and leaching reagent. The schematic illustration of the D, L-malic acid leaching and the complexing process is presented in Figure 6. The NCM111 cathodes produced from D, L-malic acid leachate were calcined in the temperature range from 650 to 950 °C in increments of 100 °C for 2–8 h to acquire good cycling performance. With regards to electrochemical performance, the regenerated NCM111 cathode active material displayed the initial discharge capacity of 147.2 mAh/g at the 0.2 C rate in the voltage range of 2.75–4.25 V.

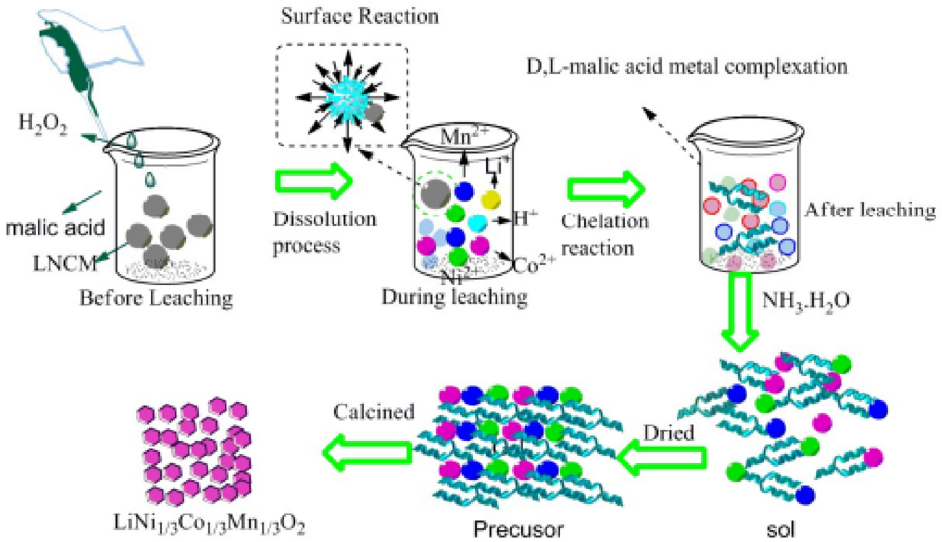

Figure 6. The illustration of the D, L-malic acid leaching process of the waste NCM and the coordination of the main metal ions with D, L-malic acid. Used with permission of Royal Society of Chemistry, from Ref. [60]; permission conveyed through Copyright Clearance Center, Inc.

Recently, Sita et al. [62] reported a simple strategy to regenerate NCM111 by sol–gel technique. To resynthesize NCM111, they employed the cathode material extracted from a batch of waste $LiCO_2$ batteries. Sita et al. [62] found that the best parameters to synthesize a crystalline and well-ordered NCM111 by the sol–gel method were a pre-calcination at 450 °C for 6 h followed by calcination at 850 °C for 16 h, all in air, under a heating-ramp rate of 10 °C per min. Figure 7 displays a specific charge capacity equal to 107 ± 3 $mAhg^{-1}$, which was achieved for the NCM111 cathodes, whether for the cathode material resynthesized using Li and Co extracted from the discarded LCO batteries or produced from fresh materials (commercial acetates). In other words, the specific charge capacity of resynthesized NCM111 cathode materials was equal to the average of the various published values.

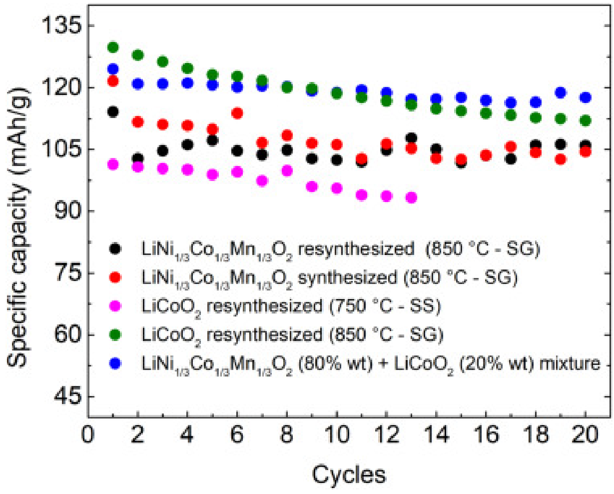

Figure 7. Cycling performance for electrodes of LCO, NCM111, and their mixture. The compounds were obtained from resynthesis and synthesis by sol–gel (SG) and solid-state reaction (SS). Used with permission of Elsevier Science & Technology Journals, from Ref. [62]; permission conveyed through Copyright Clearance Center, Inc.

2.3. $LiNi_xCo_yMn_zO_2$ Regeneration via the Co-Precipitation Method

Co-precipitation (hydroxide or carbonate) is another widely used method to regenerate $LiNi_xCo_yMn_zO_2$ cathodes, which has the following advantages:

- This method allows directly recover of the mixed discarded LIBs without their preliminary separation;
- Different kinds of $LiNi_xCo_yMn_zO_2$ cathode materials can be produced;
- The method is economically beneficial and has high recovery efficiency.

2.3.1. $LiNi_xCo_yMn_zO_2$ Regeneration via the Hydroxide Co-Precipitation Method

In their work, Yang et al. [63] regenerated NCM111 cathodes from the mixture of discarded alkaline Zn-Mn batteries and spent $LiCo_2O_4$ batteries using the hydroxide co-precipitation technique. The regenerated NCM111 cathode materials displayed a high initial discharge capacity of 160.2 $mAhg^{-1}$ and excellent Coulombic efficiency of 99.8%.

Likewise, Zheng et al. used the hydroxide co-precipitation technique followed by solid-state synthesis to regenerate NCM111 from the mixed cathodes, including LCO, LMO, $LiNi_xCo_yMn_zO_2$, and LFP [43]. The regenerated NCM111 powder showed such electrochemical performance, comparable to the pristine cathode material. The pristine and regenerated NCM111 cathode materials delivered the initial discharge capacities of 150.3 and 148.8 $mAhg^{-1}$ between 2.7 and 4.3 V at the 0.2 C rate, with a capacity retention of 97.1% and 97.0% after the 100th cycle, respectively. Cycling performance and the initial charge–discharge profiles of the fresh-synthesized and the regenerated NCM111 are presented in Figure 8.

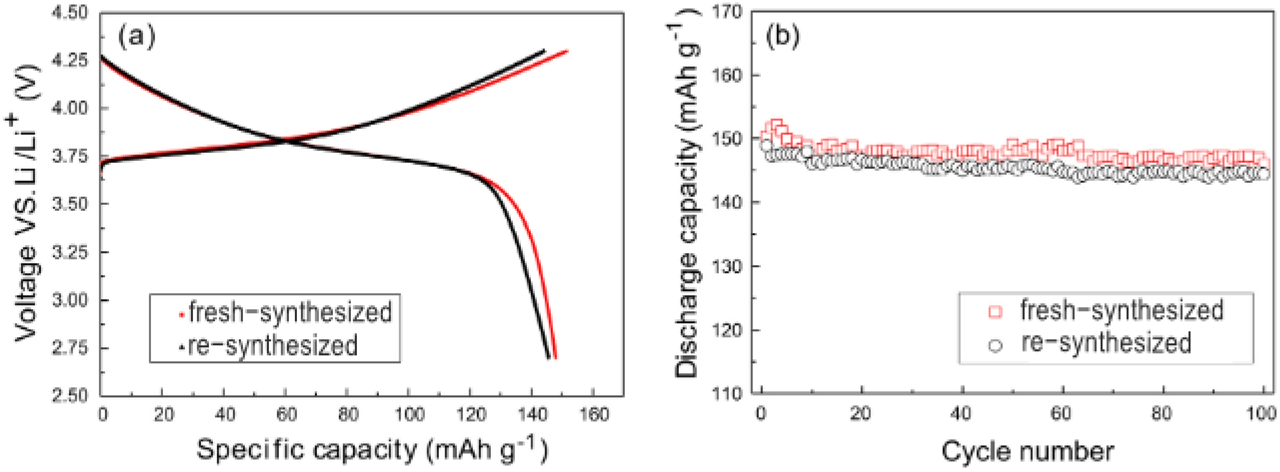

Figure 8. The initial charge–discharge curves (**a**) and cycling performance (**b**) of the fresh-synthesized and the regenerated NCM111 between 2.7 and 4.3 V at the 0.2 C rate [43]. Ref. [43] is an open access article published by Elsevier under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

As seen in Figure 3, no obvious difference was found between regenerated and freshly synthesized NCM111 samples in the cycle and charging–discharging performance.

It is worth mentioning that the hydroxide co-precipitation method allows to fabrication of diverse $LiNi_xCo_yMn_zO_2$ cathode materials such as NCM111, MCM523, NCM622, or NCM811 by adjusting the concentration of elements in the leaching solution of a complex waste LIB recovery stream consisting of LIBs with different cathode chemistries [17,64,65]. In their works, Sa et al. [17,64] regenerated different kinds of $LiNi_xCo_yMn_zO_2$ cathodes such as NCM622, NCM111, and NCM532 by changing the molar ratio of metal ions in the leaching solution through co-precipitation method and a solid-state sintering step. The findings demonstrated that all the regenerated $LiNi_xCo_yMn_zO_2$ cathodes exhibited perfect initial discharge capacities higher than 155 mAh/g at the 0.1 C rate with capacity retentions of above 80% after 100 cycles at the 0.5 C rate.

Yang et al. [65] followed the same approach to regenerate a series of $LiNi_xCo_yMn_zO_2$ cathodes with different compositions via the hydroxide co-precipitation method. The first discharge capacity (between 2.7 and 4.3 V at the 0.1 C rate) of the regenerative $LiNi_xCo_yMn_{1\text{-}x\text{-}y}O_2$ were 197.7 $mAhg^{-1}$, 174.3 $mAhg^{-1}$ and 168.3 $mAhg^{-1}$ for x = 0.8, 0.5 and 0.33, respectively.

Zheng et al. [66] employed the hydroxide co-precipitation method followed by calcination to regenerate NCM111 from four different complex recycling streams of waste LIBs with various blended cathode chemistries. These four recycling streams, as well as the proposed NCM111 regeneration process, is shown in Figure 9. Remarkably, the regenerated NCM111 showed little differences in morphology, tap density, and particle size distribution. More intriguingly, results revealed that the regenerated NCM111 cathode materials from all four various recycling streams have superior rate capability than commercial NMC111 cathode material synthesized from virgin chemicals.

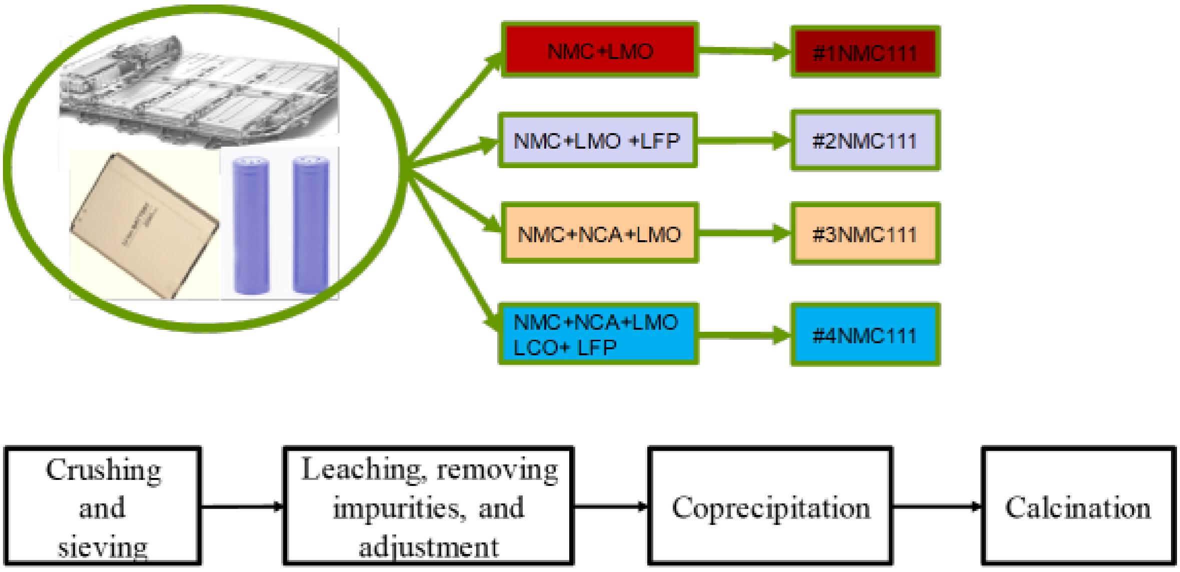

Figure 9. Schematic illustration of four various recycling streams, and the entire NCM111 regeneration process from spent LIBs. Reprinted with permission from Ref. [66], Copyright 2018, American Chemical Society.

A combined method [67] consisting of reduction roasting, two-step leaching, hydroxide co-precipitation, and solid-state sintering was employed to recover valuable metals from spent LIBs, and direct regenerate NCM523 cathode materials. This regeneration strategy is found to be facile, efficient, and feasible for regenerating the retired cathode material of Li-ion batteries, which can facilitate environmental protection and resource recycling.

2.3.2. $LiNi_xCo_yMn_zO_2$ Regeneration via the Carbonate Co-Precipitation Method

$LiNi_xCo_yMn_zO_2$ cathode material can also be regenerated using carbonate co-precipitation [68,69]. It is commonly considered that carbonate salts are non-toxic and more easily acquired; therefore, they can also be utilized as coprecipitate agents to produce carbonate intermediates for regenerating the retired cathode materials.

Weng et al. [68] used the carbonate co-precipitation method to regenerate NCM111 directly from the leachate of the mixed spent LIBs without complex separation and impurity elimination steps. The acquired NCM111 cathode active materials showed a high initial discharge capacity of 152.7 $mAhg^{-1}$ at the 0.2 C rate, retaining a voltage of 2.7–4.3 V, with capacity retentions of 94% after 50 cycles at the 1 C rate, between 2.7 and 4.3 V.

He et al. [69] also used the same approach to recover valuable metallic resources from the spent lithium-ion batteries and regenerate the NCM111 cathode active material with excellent electrochemical performance and well-ordered layer structure. The spherical

NCM111 cathode particles were resynthesized from spent LIBs by chemical precipitation with aqueous Na_2CO_3 (1.8 M) in the presence of $NH_3 \cdot H_2O$ in a continuous stirred-tank reactor. During this carbonate co-precipitation process, the pH of the reaction solution was maintained at 7.5 at 60 °C for 12 h stirring at 700 rpm. In the overall closed-loop recovery strategy, the recovery efficiencies of Mn, Co, and Ni were 97.45, 96.83%, and 96.13%, respectively. With regards to electrochemical performance, the regenerated NCM111 material exhibited a discharge capacity of 163.5 mA h/g at the 0.1 C rate, between 2.7 and 4.3 V, and maximum capacity retention (94.1%) was reached after 50 cycles. At the same time, freshly synthesized NCM111 showed very similar battery performance as the regenerated NCM111. The findings demonstrated that their electrochemical properties and structures were comparable.

Chen et al. [70] regenerated NCM523 cathode powder from discarded LIBs by co-carbonate precipitation technique. The regenerated NCM523 cathode material was obtained at 830 °C sintering temperature and gained the electrochemical performance as well as the commercial NCM523 electrode. The as-prepared NCM523 powders deliver a high discharge capacity of 149.2 $mAhg^{-1}$ at the 0.2 C rate after 100 cycles, with capacity retentions of 92.4% of its initial capacity after 100 cycles.

2.3.3. $LiNi_xCo_yMn_zO_2$ Regeneration via Organic Acid Co-Precipitation Method

It is worth noting that the typical co-precipitation technique driven by inorganic alkaline agents generally requires an inert environment to avoid the production of uneven precipitates with various crystal structures and compositions [17,71]. Considering this drawback of inorganic hydroxide coprecipitate agents, Refly et al. [72] developed a simple, rapid, and environmental-friendly regeneration technique using oxalic acid as coprecipitate agent to regenerate spent NCM111 cathode materials. Instead of $M(OH)_2$ (where M = Ni, Mn, and Co) intermediates, the metal-oxalate (MC_2O_4) precipitates were produced in this organic acid solution. The regenerated NCM111 exhibited an optimal initial discharge capacity of 164.9 $mAhg^{-1}$ at the 0.2 C charge–discharge rate, with a good capacity retention of 91.3% after 100 cycles, confirming the remarkable ability of organic acid coprecipitate agents in regenerating degraded cathodes.

Benefitting from the preferable organic acid coprecipitate agents, diverse other types of cathodes have also been successfully regenerated. Oxalic acid as coprecipitate agent was also used to regenerate $Li_{1.02}(Ni_{0.8}Co_{0.1}Mn_{0.1})_{0.98}O_2$ cathode material in another work [73]. A proposed route for the individual separation of Li_2CO_3 and the transition metals in NCM-811 cathode material and the formation of recycled NCM-811, is illustrated in Figure 10.

The recovered NCM-811 achieved an initial discharge capacity of 166 mAh/g at the 0.1 C charge–discharge rate, between 2.7 and 4.2 V, which corresponds to 84% of the discharge capacity of the pristine NCM-811 cathode material [73].

Likewise, Li et al. [74,75] applied a combined method consisting of oxalic acid co-precipitation, hydrothermal, and calcination processes to resynthesize Li-rich layered oxide $Li_{1.2}Co_{0.13}Ni_{0.13}Mn_{0.54}O_2$ cathodes from the ascorbic acid leaching solution of spent lithium-ion batteries. The regenerated cathode material exhibited the initial discharge capacity of 258.8 $mAhg^{-1}$ at the 0.1 C rate, with a capacity retention of 87.0% after 50 cycles.

Liu and co-workers [76] also presented a combined method including co-extraction, oxalic acid co-precipitation, and high-temperature calcination steps to regenerate high-purity NCM111 cathode material from hydrochloric acid leaching solution of spent LIBs. The regenerated NCM111 cathode material showed perfect electrochemical performance with 151.0 mA/h discharge capacity at the 0.5 C charge–discharge rate.

To additional corroborate the operability of the as-proposed co-precipitation technique and the reliability of regenerated cathode materials performance in industrial applications, Wang and co-workers [77] produced the regenerated NCM111 cathode materials. Subsequently, they evaluated the electrochemical characteristics of regenerated NCM111 materials by diverse industry-level tests. Surprisingly, the findings showed that 1 Ah cells containing regenerated NCM111 cathodes enabled superior performance, displaying 4200 and 11,600 cycles with 80% and 70% capacity retention, respectively. The electrochemical characteristics were ≈ 33 and 53% better than those of the present commercial NCM111 electrodes in identical conditions. These results give convincing evidence for the practical realizability of such regenerated cathodes for wide industrial applications.

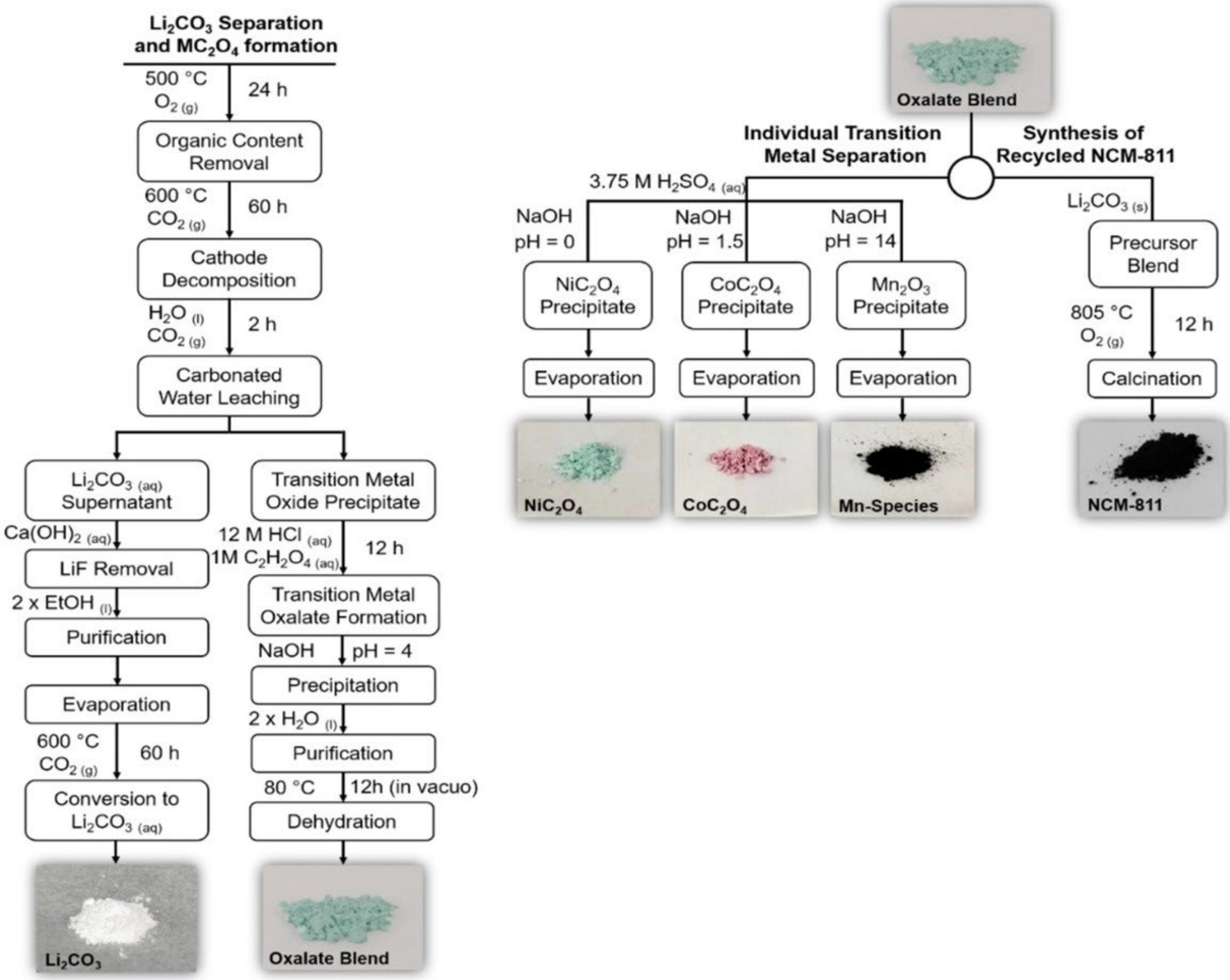

Figure 10. Schematic illustration of the employed recycling technique for NCM-811. During this process, the active material can be regenerated using the Li_2CO_3, and the oxalate blend or each component of the active material can be individually separated [73]. Ref. [73] is an open access article published by Wiley-VCH GmbH under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

2.4. $LiNi_xCo_yMn_zO_2$ Regeneration via Spray Drying

The vanadium-embedded cathode materials, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$-$V_2O_5$, with great electrochemical properties, were synthesized from two conventional heavy-metal-containing waste streams: spent lithium-ion batteries and vanadium-bearing slag [78]. In their work, Meng et al. [78] adopted a route to regenerate high-performance NCM111 cathode containing a thin layer of vanadium oxide (V_2O_5) by spray drying. Unlike the traditional solid-state sintering approach, the proposed strategy has a distinct benefit in energy consumption owing to the shorter sintering time. A specific capacity of the vanadium-embedded NCM111 cathode material was 156.3 $mAhg^{-1}$ after 100 cycles at the 0.1 C rate; even the additive amount of V_2O_5 was only 5%.

2.5. $LiNi_xCo_yMn_zO_2$ Regeneration via Hydrothermal Method

Shi et al. [44] developed a method of direct regeneration of high-performance $LiNi_xCo_yMn_zO_2$ ($0 < x, y, z < 1$; $x + y + z = 1$) cathodes that combine hydrothermal treatment and a short thermal annealing step. In addition, they investigated the effect of various lithium contents on the evolution of particle microphase and stoichiometry of the regenerated NCM. NCM111 and NCM523 were selected as the target materials. In comparison, the NCM cathode was also regenerated by the solid-state sintering approach. After the degraded NCM523 and NCM111 cathodes were regenerated, their cycling stabilities and lithium storage capacities were restored to the original levels of the corresponding pristine cathode materials. However, it is worth noting that in direct solid-state sintering treatment in air, the cycling stability of NCM111 was recovered but not that of NCM523 due to the higher Ni content in the latter type of NCM523 cathode.

Guo et al. [79] adopted a direct regeneration technology to recover the waste NCM523 cathode materials through the hydrothermal technique combined with a solid-state annealing stage in different atmospheres. They found that the formed surface LiOH shell during the hydrothermal process promotes the transformation of the undesirable rock-salt-type structure of the NCM in the following high-temperature annealing step. The regenerated NCM523 cathodes with a LiOH shell had a restored layered crystalline structure in the whole phase region and exhibited high capacity retention above 90% after 500 cycles.

To study the regeneration mechanism of cathodes by a hydrothermal method, Xu and co-workers [80] investigated the influence of experimental parameters on the electrochemical characteristics, microstructure, and composition of the regenerated cathode materials in a systematic manner. It is found that the re-lithiation time is a more key factor for fabricating high-performance regenerated cathodes than the hydrothermal temperature aspect. In a hydrothermal process, an optimal time can be reached, after which the additional hydrothermal time would not be advantageous anymore, as was definitely corroborated by the Rietveld refinement data of neutron diffraction patterns. Furthermore, findings [80] reveal that the electrochemical characteristics of the cathode powders regenerated in both 4 M LiOH and a mixture of 0.1 M LiOH + 3.9 M KOH hydrothermal solutions are almost similar, which additionally indicates the flexibility of such regeneration strategy in a wide variety of lithium concentrations.

2.6. $LiNi_xCo_yMn_zO_2$ Regeneration via the Eutectic Method

In the field of cathode regeneration, Li-based eutectic molten systems have attracted more and more attention today. This system is a homogeneous mixture of compounds that can be melted or solidified at a single temperature (eutectic temperature) lower than the original melting point of any involved component species at atmospheric pressure. Particularly, Li-based eutectic molten systems are served as both the “solvent” and lithium sources to fabricate high-performance LIB cathodes; therefore, researchers are increasingly engaged in the regeneration of the retired cathode materials based on a eutectic strategy.

In their work, Shi and co-workers [81] successfully demonstrated the ambient-pressure re-lithiation of waste NCM523 cathodes via a eutectic Li^+ molten-salt system for the first time. The LiOH and $LiNO_3$ mixture was selected to prepare a binary eutectic system owing to its wide eutectic region. The Li-deficient spent LIBs cathodes could be easily relithiated due to the advantageous Li^+ resources condition in LiOH and $LiNO_3$ eutectic systems. Impressively, after the NCM523 regeneration process via the eutectic molten salt approach, the rock salt phase, which is often formed near the surface region of the waste NCM523 cathodes, was successfully transformed into desired layered phase. Moreover, the regenerated NCM523 cathode materials exhibited the same electrochemical performances as freshly synthesized ones [81].

Jiang et al. [82] proposed the direct renovation of NCM523 cathodes from discarded LIBs using, for the first time, the LiOH-Li_2CO_3-based eutectic molten salts system. The findings demonstrated that the LIBs with regenerated NCM523 cathode active materials via eutectic molten salts exhibited a surprisingly recovered cyclability compared to that of degraded ones.

Figure 11 is illustrated the regeneration process of NCM523 cathode material based on the eutectic strategy proposed by Jiang et al. [82]. First of all, the obtained through pre-treatment NCM523 powder is added to the LiOH−LiNO3 eutectic molten salts (it is a mixture of LiOH and Li_2CO_3 at a molar ratio of 0.86:0.14). Secondly, LiOH−$LiNO_3$ eutectic molten salts formed on the surface of NCM523 cathode particles, and the lithium molten salts passed through the cracks. Thirdly, the surface and bulk of Li-deficient NCM523 cathode particles regenerated by lithium ions diffused and reacted with these molten salts at 440 °C due to the concentration of lithium ions being higher relative to that of the NCM523 cathode particles. At last, the Li vacancies are supplemented by Li, and the NCM523 cathodes are realized by the full regeneration process.

Figure 11. Schematic of the proposed re-lithiation process for lithium composition recovery by eutectic molten salts technique. Reprinted with permission from Ref. [82], Copyright 2020, American Chemical Society.

Compared with a binary molten salt system, a ternary molten salt has a lower density, larger volume, and lower eutectic point, thus promoting the further development of a direct cathode regeneration process via a eutectic strategy. Qin et al. [83] demonstrated a ternary $LiOH{\cdot}H_2O$ + $LiNO_3$ + $CH_3COOLi{\cdot}2H_2O$ hybrid molten salt system to completely eliminate lithium loss and degraded phases problems in waste NCM523 cathodes. The findings revealed that the regenerated NCM523 cathodes exhibited a reversible capacity of 160 mAh/g at the 0.5 C charge–discharge rate with retention of 93.7% after 100 cycles, which is compared favorably to the freshly-synthesized ones, confirming the effectiveness of this ternary eutectic molten salt system to directly regenerate retired NCM cathodes.

Impressively, Deng et al. [84] reported that in a deliberately chosen molten salt medium, waste ternary cathode materials containing acetylene black impurities can be directly recovered. Moreover, the electrochemical performance of cathodes regenerated through their unique approach is even superior to that of commercial materials.

3. Analysis of the Electrochemical Performances of $LiNi_xCo_yMn_zO_2$ Regenerated by Various Methods

The discharge capacities of different $LiNi_xCo_yMn_zO_2$ cathode materials (e.g., NCM111, NCM523, etc.) regenerated by various methods are listed in Table 2. It can be clearly seen from the data in the table that $LiNi_xCo_yMn_zO_2$ regenerated by the co-precipitation method displayed better discharge performances compared with the others. It is due to the uniform distribution of elements in the cathode powders regenerated by the co-precipitation strategy.

One of the reasons why $LiNi_xCo_yMn_zO_2$ regenerated by co-precipitation showed better discharge capacity is because there were more uniformly distributed elements in these materials. However, the discharge performances of NCM cathodes resynthesized by the heat treatment method were better than those resynthesized by the sol–gel process. This might be because some impurities are doped into the NCM lattice in a heat treatment process, affecting its performance after regeneration. In addition, the regenerated NCM cathodes exhibited equal or even better electrochemical performances than commercial cathodes with the same stoichiometry or NCM materials produced by original chemicals.

Table 2. Discharge capacities of regenerated $LiNi_xCo_yMn_zO_2$ cathodes fabricated by diverse methods.

Regeneration Technique	**Regenerated Cathode Material**	**The Initial Discharge Capacity, mAh/g**		**Capacity Retention**		**Source for LIB Regeneration**	**Ref**
		Regenerated LIB	**Fresh LIB**	**Regenerated LIB**	**Fresh LIB**		
Thermal method	NCM523	161.3 (0.1 C, 2.5–4.3 V)	-	95.29% (50 cycles, 0.5 C)	-	Spent NCM523 batteries	[45]
	NCM523	147.0 (1 C, 2.5–4.3 V)	152.0 (1 C)	89.12% (100 cycles, 1 C)	88.82% (100 cycles, 1 C)	Spent NCM523 batteries	[49]
	NCM111	168 (0.2 C, 2.8–4.3 V)	-	91.5% (150 cycles, 0.2 C)	-	Different types of spent NCM batteries	[52]
	NCM111	150.2 (0.2 C, 2.8–4.3 V)	-	95.1% (100 cycles, 0.2 C)	-	NCM111 cathode scraps	[53]
	NCM111	155.4 (0.1 C, 2.8–4.5 V)	-	83.01% (30 cycles, 0.1 C)	-	Cathode scraps	[55]
	NCM622	194.0 * (0.1 C, 3.0–4.3 V)	205.6 (0.1 C)	100.9% (40 cycles, C/3)	-	NCM622 cathode scraps	[56]
Sol–gel method	NCM111	138.2 ** (0.5 C, 2.8–4.3 V)	125.4 ** (0.5 C)	96% (100 cycles, 0.5 C)	-	Spent LIBs	[57]
	NCM111	152.8 (0.2 C, 2.8–4.3 V)	149.8 (0.2 C)	93.9% (160 cycles, 0.2 C)	79.3% (160 cycles, 0.2 C)	Waste mixed-cathode materials (LCO, NCM, LMO)	[58]
	NCM111	154.2 (0.2 C, 2.75–4.25 V)	150 (1 C)	93% (50 cycles, 1 C)	93% (50 cycles, 1 C)	Spent LIBs	[59]
	NCM111	147.2 (0.2 C, 2.75–4.25 V)	-	95.06% (100 cycles, 0.5 C)	-	Spent LIBs with NCM111 cathode	[60]
	NCM111	151.6 (0.2 C, 2.8–4.3 V)	-	83.97% (150 cycles, 0.2 C)	-	Spent LIBs	[61]
	NCM111	107 ± 3 ** (0.2 C, 3.0–4.2 V)	-	Unspecified	-	The discarded LCO battery batch	[62]
Co-precipitation synthesis	NCM111	158.0 (0.1 C, 2.7–4.3 V)	-	More than 80% (100 cycles, 0.5 C)	-	Complex LIB recovery stream (NCM + LCO)	[17]
	NCM111	Unspecified	-	Unspecified	-	Mixed system of spent LIBs, which are primarily composed of LiCoO2 cathode chemistry	[32]
	NCM111	130.2 (46.6 mA/g, 2.5–4.6 V)	-	82.40% (50 cycles, 46.6 mA/g)	-	Mixed cathode materials including $LiCoO_2$, $LiMn_2O_4$, NCM111, and $LiFePO_4$	[33]
	NCM111	150.0 (0.5 C, 2.7–4.3 V)	-	94% (100 cycles, 0.5 C)	-	Spent LIBs contained NCM111 cathodes	[42]

Table 2. *Cont.*

Regeneration Technique	Regenerated Cathode Material	The Initial Discharge Capacity, mAh/g		Capacity Retention		Source for LIB Regeneration	Ref
		Regenerated LIB	Fresh LIB	Regenerated LIB	Fresh LIB		
Co-precipitation synthesis	NCM111	148.8 (0.2 C, 2.7–4.3 V)	150.3 (0.2 C)	97.0% (100 cycles, 0.2 C)	97.1% (100 cycles, 0.2 C)	Mixed spent LIBs composed of$LiCoO_2$, $LiNiO_2$, $LiMnO_2$, $LiNi_xCo_yMn_{(1-x-y)}O_2$ and $LiFePO_4$ cathodes	[43]
	NCM111	158 (0.1 C, Voltage range unspecified)	-	~100% (100 cycles, 0.5 C)	-	LIBs of multiple chemistries	[50]
	NCM523	167.04 (0.05 C, 2.7–4.3 V)	168.6 (0.05 C)	87% (100 cycles, 1C)	80% (100 cycles, 1 C)	Spent LIBs	[51]
	NCM111	160.2 (0.1 C, 2.8–4.6 V)	-	88.6% (30 cycles, 0.2 C)	-	The spent alkaline Zn-Mn batteries and spent LIBs ($LiCo_2O_4$)	[63]
	NCM111	>155.0 (0.1 C, 2.7–4.3 V)	-	More than 80% (100 cycles, 0.5 C)	-	Spent LIB cathodes were a random mixture of $LiCoO_2$, $LiNi_xMn_yCo_zO_2$, $LiFePO_4$, Li_2MnO_4, etc.	[64]
	NCM811	197.7 (0.1 C, 2.7–4.3 V)	-	86.3% (50 cycles, 1 C)	-	Spent LIBs, nickel, and cobalt scraps	[65]
	NCM523	174.3 (0.1 C, 2.7–4.3 V)		95% (50 cycles, 1 C)			
	NCM111	168.3 (0.1 C, 2.7–4.3 V)		96% (50 cycles, 1 C)			
	NCM111	152.3 (0.2 C, 2.7–4.3 V)	144.5 (0.2 C)	Unspecified	Unspecified	4 complex recycling streams: (1) NCM + LMO; (2) NCM + LMO + LFP; (3) NCM + NCA + LMO; (4) NCM + NCA + LMO + LCO + LFP.	[66]
	NCM523	172.9 (0.2 C, 2.5–4.3 V)	179.6 (0.2 C)	93.08% (50 cycles, 0.2 C)	91.35% (50 cycles, 0.2 C)	Spent NCM cathodes	[67]
	NCM111	152.7 (0.2 C, 2.7–4.3 V)	-	94% (50 cycles, 1 C)	-	Spent LIBs	[68]
	NCM111	163.5 (0.1 C, 2.7–4.3 V)	167.5 (0.1 C)	94.1% (50 cycles, 1 C)	94.5% (50 cycles, 1 C)	Spent LIBs	[69]
	NCM111	164.9 (0.2 C, 2.5–4.3 V)	157.4 (0.2 C)	91.3% (100 cycles, 0.2 C)	-	End-of-life LIBs	[72]
	NCM811	166 (0.1 C, 2.7–4.2 V)	197.6 (0.1 C)	More than 98% (100 cycles, 0.1 C, 0.25 C, 0.5 C, 1 C, 2 C)	-	Spent LIBs with NCM811 cathode materials	[73]
	$Li_{1.2}Co_{0.13}Ni_{0.13}Mn_{0.54}O_2$	258.8 (0.1 C, 2.0–4.8 V)	264.2 (0.1 C)	87.0% (50 cycles, 0.1 C)	86.3% (50 cycles, 0.1 C)	Spent LIBs	[75]
	NCM111	151.0 (0.5 C, 2.7–4.3 V)	-	87.06% (20 cycles, 1 C) 95.03% (20 cycles, 2 C)	-	Cathode material from spent LIBs	[76]
	NCM111	Unspecified	-	70% (11600 cycles, 2C)	17% (11600 cycles, 2C)	Spent LIBs with NCM111 cathode materials	[77]
	$0.2Li_2MnO_3$ $0.8LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (Mn-rich NMC)	248.3 (0.1 C, 2–4.6 V)	-	88% (50 cycles, 0.1 C)	-	Mixed-type spent cathode materials from different LIBs	[85]
	NCM111	157.1 (0.2 C, 2.6–4.3 V)	125.5 (0.2 C)	More than 95% (100 cycles, 0.2 C)	-	Spent NCM batteries	[86]

Table 2. *Cont.*

Regeneration Technique	Regenerated Cathode Material	The Initial Discharge Capacity, mAh/g		Capacity Retention		Source for LIB Regeneration	Ref
		Regenerated LIB	Fresh LIB	Regenerated LIB	Fresh LIB		
Spray drying	$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$-$V_2$O5	172.4 (0.1 C, 2.8–4.6 V)	-	90.6% (100 cycles, 0.1 C)	-	Spent NCM cathode materials	[78]
Hydrothermal	NCM111 (HT-SA) ***	158.4 (1 C, 3–4.3 V)	145.1 (1 C)	77.4% (100 cycles, 1 C)	85.32% (100 cycles, 1 C)	Spent LCO, NCM111, and NCM523 LIBs	[44]
	NCM523 (HT-SA) ***	128.3 * (1 C, 3–4.3 V)	146.6 (1 C)	-	88.9% (100 cycles, 1 C)		
	NCM523	166.1 (0.1 C, 2.8–4.35 V)	-	90.8% (500 cycles, 1 C)	-	The commercial NCM111/NCM523 pouch batteries with NCM111/NCM523 as cathode materials	[79]
	NCM111 ****	150.4 (C/3)	150.5 (C/3)	93.1% (50 cycles, C/3)	93.2% (50 cycles, C/3)	Degraded NCM111 cathode materials	[80]
Solid-State	NCM111	169.7 (0.1 C, 2.8–4.3 V)	-	86.9% (200 cycles, 0.5 C)	-	Different types of spent NCM batteries	[87]
Eutectic method	NCM523	149.3 (1 C, 3–4.3 V)	146.6 (1 C)	90.2% (100 cycles, 1 C)	88.9% (100 cycles, 1 C)	Degraded NCM523 cathode materials	[81]
	NCM523	146.3 (1 C, 2.8–4.3 V)	-	89.06% (200 cycles, 1 C)	-	Spent LIBs with NCM523 cathode materials	[82]
	NCM523	160 (0.5 C, 3–4.3 V)	165 (0.5 C)	93.7% (100 cycles, 0.5 C)	89.1% (100 cycles, 0.5 C)	Spent NCM523 cathodes	[83]
	NCM523	166.1 (0.2 C, 2.8–4.3 V)	159.6 (0.2 C)	95.5% (100 cycles, 0.2 C)	-	Spent NCM523-type cathodes	[84]

* The initial specific charge capacity by which the electrochemical performance of regenerated NCM was evaluated. ** The discharge capacity after 100 cycles. *** HT-SA is a method of $LiNi_xCo_yMn_zO_2$ regeneration by hydrothermal treatment at 220 °C for 4 h, followed by annealing at 850 °C for 4 h. **** The electrochemical characteristics for the process of $LiNi_xCo_yMn_zO_2$ regeneration by hydrothermal reaction at 220 °C for 2 h, followed by annealing at 850 °C for 4 h.

4. Conclusions, Challenges, and Outlooks on Future $LiNi_xCo_yMn_zO_2$ Regeneration Routes

At present, the market share of LIBs continues to increase. The ever-growing demand for portable electronic and energy-storage devices undoubtedly causes a spike in waste LIBs. Consequently, the regeneration of cathode materials from the spent LIBs has become an urgent task.

The $LiNi_xCo_yMn_zO_2$ regeneration strategies stated above are commonly classified as direct or indirect based on whether the bulk cathode material structure is ruined during the complete recovery route. Indirect regeneration strategies include the sol–gel and co-precipitation methods. On the one hand, these two methods would renovate the waste NCM cathodes from leachates, which solves the existing challenge of element separation in hydrometallurgical technology, optimizing the traditional industrial route for closed-loop recycling of degraded LIBs. On the other hand, due to the inevitable acid leaching process, the sol–gel and co-precipitation methods usually result in significant secondary pollution. In addition, these two regeneration methods are costly and have enormous energy consumption due to the need for long-term thermal treatment at high temperatures.

Relative to the aforementioned indirect regeneration approaches, the direct regeneration strategies, such as eutectic, hydrothermal, and solid-state methods, have great advantages in lower pollution emission, energy consumption, and cost, demonstrating the promising potential to handle the waste LIBs crisis addressing address the inevitable problems caused by the forthcoming waste tide of Li-ion batteries. Moreover, these nondestructive direct $LiNi_xCo_yMn_zO_2$ regeneration techniques are more eco-friendly due to the lack of an acidic leaching process.

In particular, such an energy-consumed technique as solid-state commonly involves two simple steps, including the elemental compensation and following thermal treatment, which provides an excellent regeneration efficiency. Though the strategy is facile, some challenges remain. For instance, the main challenge for the elemental compensation stage of the solid-state strategy is caused by the inconsistent cycling fate of different waste cathodes.

The eutectic method for direct regeneration of $LiNi_xCo_yMn_zO_2$ cathode materials has similar regeneration routes as the hydrothermal technique. This method can be successfully performed at normal pressure, indicating its versatility for regenerating diverse cathode powders more conveniently. Impressively, except for its high regeneration capability, the eutectic salt system is capable of simultaneously dispelling the impurities (e.g., carbon, PVDF, aluminum) in spent cathode materials. This feature of the eutectic method essentially boosts the regeneration efficiency of cathode materials from spent LIBs and simplifies the regeneration process.

The regeneration of $LiNi_xCo_yMn_zO_2$, one of the most prospective cathode materials today, from the mixed system of spent LIBs is a challenging research field, whose methods, approaches, and theories should be expanded, developed, and adapted to handle mixed-type cathode materials. Most of the scientific issues existing in this area should be researched further.

This paper is intended to provide a general overview of $LiNi_xCo_yMn_zO_2$ regenerating from the waste LIBs containing various types of cathodes. As reviewed in this article, the diverse $LiNi_xCo_yMn_zO_2$ regeneration strategies such as hydrothermal, co-precipitation, eutectic, sol–gel, thermal, and solid-state methods are summarized and discussed.

Despite the focused efforts in studying various recycling techniques of LIBs, the development of regeneration of degraded MCM cathodes from waste LIBs remains in its initial stage. A significant challenge remains caused by the necessity to develop more efficient regeneration strategies to recover the physical properties and electrochemical performances of retired NCM cathodes to its original level.

The following conclusions can be drawn from the current review:

- Li-ternary cathode oxides ($LiNi_xCo_yMn_zO_2$) can be directly regenerated from waste lithium-ion batteries through a route of pretreatment steps and various synthetic processes;
- Regenerated $LiNi_xCo_yMn_zO_2$ cathodes have similar or better electrochemical performances as compared with those manufactured by primary resources or commercial cathode materials with equivalent stoichiometry;
- Significant economic benefits can be gained by recycling waste lithium-ion batteries through $LiNi_xCo_yMn_zO_2$ regeneration strategies;
- To regenerate new $LiNi_xCo_yMn_zO_2$ cathode materials, various types of mixed-type waste LIBs (i.e., $LiFePO_4$, $LiNi_xCo_yMn_zO_2$, $LiMn_2O_4$, and $LiCoO_2$) can be directly employed without their preliminary separation;
- Layered oxide $LiNi_xCo_yMn_zO_2$ can also be regenerated from discarded lithium-ion batteries containing only LCO cathode materials.

Finally, several future perspectives concerning the $LiNi_xCo_yMn_zO_2$ regeneration process can be proposed:

- At present, there is no theoretical comprehension of the $LiNi_xCo_yMn_zO_2$ regeneration mechanism of faded cathodes at the molecule-scale level. To this end, it is necessary to conduct comprehensive experimental and theoretical investigations based on state-of-art technologies in order to provide unprecedented and in-depth insights into the mechanic of diverse regeneration strategies;
- Almost all the existing $LiNi_xCo_yMn_zO_2$ regeneration methods have only been conducted on a laboratory scale. Therefore, a few of these strategies can be extended for industrial applications. To facilitate the quick transformation of laboratory meth-

ods to large-scale industrial regeneration lines, great efforts should be devoted to technological majorization and investigation;

- In real-life recycling practice, used Li-ion batteries often contain various types of cathodes (e.g., $LiNi_xCo_yMn_zO_2$, $LiFePO_4$, $LiMn_2O_4$, $LiCoO_2$, and so on). The majority of researchers focus on the regeneration of a single type of cathode active materials. In contrast, a distinguished route that is capable of handling mixed systems of spent LIBs is rarely discussed. To fulfill the market demands, the mixed system of spent LIBs should be further investigated to develop more efficient regeneration strategies for these complex LIBs systems.

Overall, research on $LiNi_xCo_yMn_zO_2$ cathode regeneration is a prosperous scientific area; however, it requires more attention to develop and investigate novel and simplified $LiNi_xCo_yMn_zO_2$ regeneration processes from the mixed systems of spent LIBs. We hope this paper can accelerate further interest in the development of facile, feasible, effective, eco-friendly, and highly economical $LiNi_xCo_yMn_zO_2$ regeneration strategies to meet the challenge of forthcoming Li-ion battery disposal.

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