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Analysis of Direct Recycling Methods for Retired Lithium-ion Batteries from Electric Vehicles

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Abstract

The rapid expansion of electric vehicle (EV) fleet calls for large number of lithium-ion batteries to be recycled at their end-of-life. Various recycling methods have been developed or under development to recover the high-value materials from retired lithium-ion batteries. Amongst these methods, direct recycling techniques have been developed and reported to recycle battery materials for reuse in new battery manufacturing since the electrochemical properties of the recycled materials can be fully recovered to the same level of pristine materials. In literature, innovative sintering processes have been developed to recover the composition and crystal structure of spent cathode materials; hydrothermal regeneration processes have been reported to regenerate the spent cathode materials in the solvents at a moderate temperature, followed by the high-temperature short annealing process. The regenerated cathode materials show the same specific capacity and cycling performance as those of pristine materials. The electrochemical regeneration method is applied to fully recover the electrochemical performance of cathode material with stable crystal structure. While the direct recycling techniques are still under development, their future applications in industry are still not clear. This study aims to classify and summarize state-of-the-art of the direct recycling methods, and evaluate the regenerated cathode materials' performance and the application potential to be used for manufacturing of new lithium-ion batteries in future. The results will help increase understanding of the direct recycling technologies and facilitate the associated R&D for future industrial scaling-up of direct recycling processes for retired lithium ion batteries from electric vehicles.

Keywords: Spent lithium-ion batteries; Cathode materials recycling methods; Electric vehicles

1. Introduction

Lithium-ion battery, as the power source, is the most important component of an electric vehicle (EV). Since the batteries are with a short life of a few years, a massive amount of lithium-ion batteries is reaching their end of life. By the end of 2020, 17.7 GWh of lithium-ion batteries had reached their end of life, which contains around 20,000 tons of cathode materials. It is estimated that this figure will be increased to more than 140 GWh by 2035. Considering the toxic chemicals in lithium-ion batteries, the disposal of spent lithium-ion batteries will cause harmful impacts to the ecosystem and human health. In addition, the cathode materials accounts for approximately 32.7% of the total cost of lithium-ion batteries [1]. Therefore, recycling and reusing the cathode materials from spent lithium-ion batteries are promising in reducing the total cost of lithium-ion batteries manufacturing and mitigating their environmental impacts. However, current battery recycling efforts offer a low recovery rate of cathode active material while consuming unsustainable energy and metals. By 2021, the recycling rate of the cathode active material was still as low as under 5%.

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Thus, recycling and recovering technologies of cathode active materials are in urgent needs for further reduction of lithium-ion batteries manufacturing cost and rare-earth metals consumption, and environmental impacts mitigation.

Current recycling technologies for spent lithium-ion batteries can be grouped into hydrometallurgy, pyrometallurgy, and direct recycling. Figure 1 shows the flowchart of current recycling methods. The pyrometallurgical recycling method crushes and smelts the end-of-life battery materials to extract precious materials and remove impurities. The useful metals, such as Co, Ni, Mn, and Cu, are recovered and separated, according to their different melting points, through stepwise purification and separation processes [2]. The hydrometallurgical process crushes the spent lithium-ion batteries and dissolves the useful materials using acids. Through adding participants into the solution, the high-valued metals are extracted in the form of sediments of metal compounds, such as Li_2CO_3, $Ni\ (OH)_2$, $CoCO_3$, etc. [3] The pyrometallurgical and hydrometallurgical recycling processes are energy-intensive and consume large amounts of chemicals, generating various gaseous emissions and toxic solutions. Since the product of pyrometallurgical and hydrometallurgical recycling methods are mainly metal alloys or metal compounds, the energy-intensive synthesis process is necessary to reuse the recycled metals and metal compounds in the manufacturing of new lithium-ion batteries.

Different from the pyrometallurgical and hydrometallurgical recycling methods, the direct recycling method extracts the spent cathode materials by physical separation process and recovers the composition and structure of cathode materials from spent lithium-ion batteries without destroying their original structure and hence yields reusable high-value materials to the battery industries. The direct recycling method consumes much less energy and chemicals compared to the pyrometallurgical and hydrometallurgical recycling methods. After the recovering processes and certain treatments, the regenerated cathode materials can possess a high specific capacity, stable long-term cycling performance, and high rate capability close to those of pristine materials. Since the performance of spent cathode materials is directly recovered, the post energy-intensive synthesis process is unnecessary for the direct recycling method.

To replace the usage of pristine cathode materials in the electric vehicles industry, recycled cathode materials should have the same level of electrochemical performance as those of the pristine materials, including capacity, cycling performance, rate capability, thermal stability, etc. Beyond these points, direct recycling methods are also required to be competitive in terms of energy consumption, environmental impact, production efficiency, and commercialization potential. However, so far no study has been reported on the feasibility analysis of reusing the cathode material recycled via various types of direct recycling methods to manufacture new lithium-ion batteries as well as the possibility of commercializing the direct recycling method from lab scale to industrial scale.

In this paper, the current direct recycling methods are classified and summarized with respect to their differences in recycling processes. The performance of recycled cathode materials from each direct recycling method is analyzed and the potential of scaling up the direct recycling method into the industry is investigated. The results will be useful for the further development and application of the direct recycling method on an industrial scale in future.

2. Analysis of current direct recycling methods

The current direct recycling methods can be grouped into three main types: high-temperature relithiation method, hydrothermal relithiation method, and electrochemical relithiation method. The industrial application potential of each type of recycling method needs to be investigated by analyzing the performance of recycled cathode materials, energy consumption, environmental impacts, production efficiency, and scale-up potential [4].

2.1. High-temperature relithiation method

The high-temperature relithiation process is shown in Figure 2A. In the high-temperature relithiation process, lithium sources, such as $LiNO_3$, $LiOH$, and Li_2CO_3, are mixed

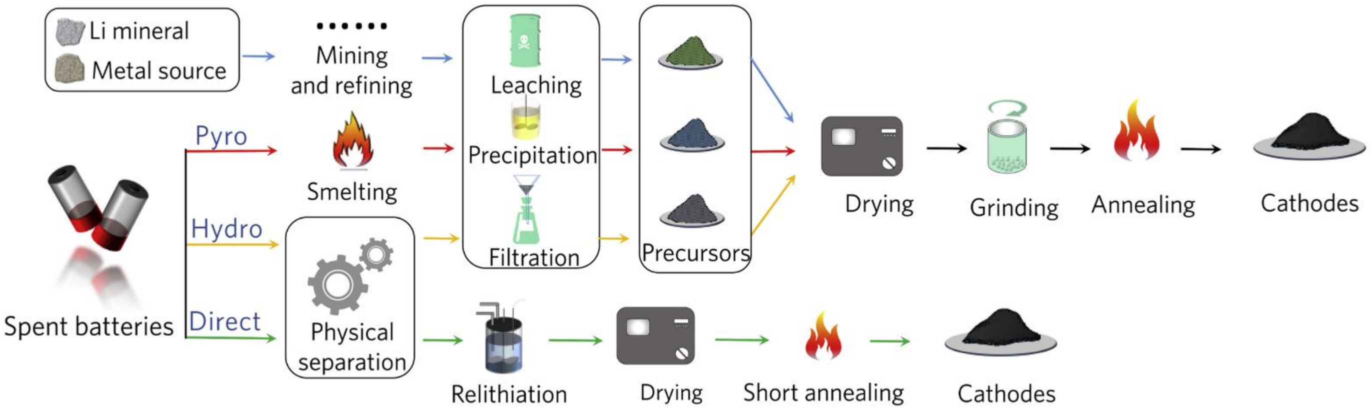

Figure 1 Flowchart of pyrometallurgical, hydrometallurgical, and direct recycling methods [5]

with the degraded cathode materials to compensate for the lithium loss [5] [6]. The lithium intercalates into the degraded cathode materials, to recover the structure and rock-salts layer through a sintering process at moderate temperature, which is validated by the comparison of XRD (X-ray diffraction analysis) results of pristine, degraded, and regenerated NMC523 ($LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$) as shown in Figure 2B. The electrochemical performance and crystal structure are further stabilized in the following short annealing process at a high temperature. Figure 2C and 2D show that the NMC523 regenerated by the high-temperature relithiation method possesses the same or even a higher electrochemical performance compared with that of pristine NMC523.

Recently, a large number of high-temperature relithiation methods have been proposed for various cathode materials with different lithium sources. Shi et al. reported a recycling and recovery method of degraded NMC523 by high-temperature sintering process at 300°C for 2-4h using $LiOH/LiNO_3$ mixture as the lithium source. The recovery of crystal structure and electrochemical performance is shown in Figures 2B, 2C, and 2D, respectively [6]. Li et al. recovered the degraded LFP (LiFePO4) by sintering process at the temperature from 600 to 800°C for 1h under Ar/H_2 flow using Li_2CO_3 as the lithium source [7]. A solid-state relithiation process was designed and proposed by Nie et al. to regenerate spent LCO ($LiCoO_2$). The spent LCO was mixed with excessive Li_2CO_3 and was calcined in air at 850-950°C for 12h [8]. A regenerated LCO with outstanding cycling stability was produced by Chen et al using Li_2CO_3 as the lithium source at 850°C [9]. For further reducing the energy consumption of the relithiation process, a low temperature relithiation method using an eutectic system of lithium compounds was reported by Ji et al [10]. Using this eutectic system, the relithiation temperature can be further reduced to 220°C. All the above-mentioned regenerated cathode materials show the same or a slightly higher electrochemical performance than that of pristine cathode materials, including specific capacity, cycling performance, and rate capability.

The high-temperature relithiation method can fully recover the composition and crystal structure of degraded cathode materials, achieving the same or better electrochemical performance as pristine cathode materials. However, the high-temperature relithiation method is more energy-intensive compared with that of hydrothermal and electrochemical relithiation methods. The temperature required for the sintering process is as high as 950°C. Meanwhile, waste gases are generated due to the decomposition of lithium sources during the sintering process, for example, NO_2 and CO_2. The total regeneration time, including the sintering process and the short annealing, is between 6-10h. Based on the regeneration time, the production efficiency of regenerated cathode materials is relatively high compared to other types of direct recycling methods. However, each batch of spent cathode material needs to be fully mixed with the lithium source before the sintering process. To some extent, the mixing process decreases the production efficiency of the high-temperature relithiation method. The regenerated cathode materials require multiple washing processes to remove the impurities before reusing them in the manufacturing of new lithium-ion batteries. Considering the generation of waste gas during the relithiation process, appropriate treatment of waste gas is also necessary. Therefore, solving the above issues is essential for the application of high-temperature relithiation methods in the industry.

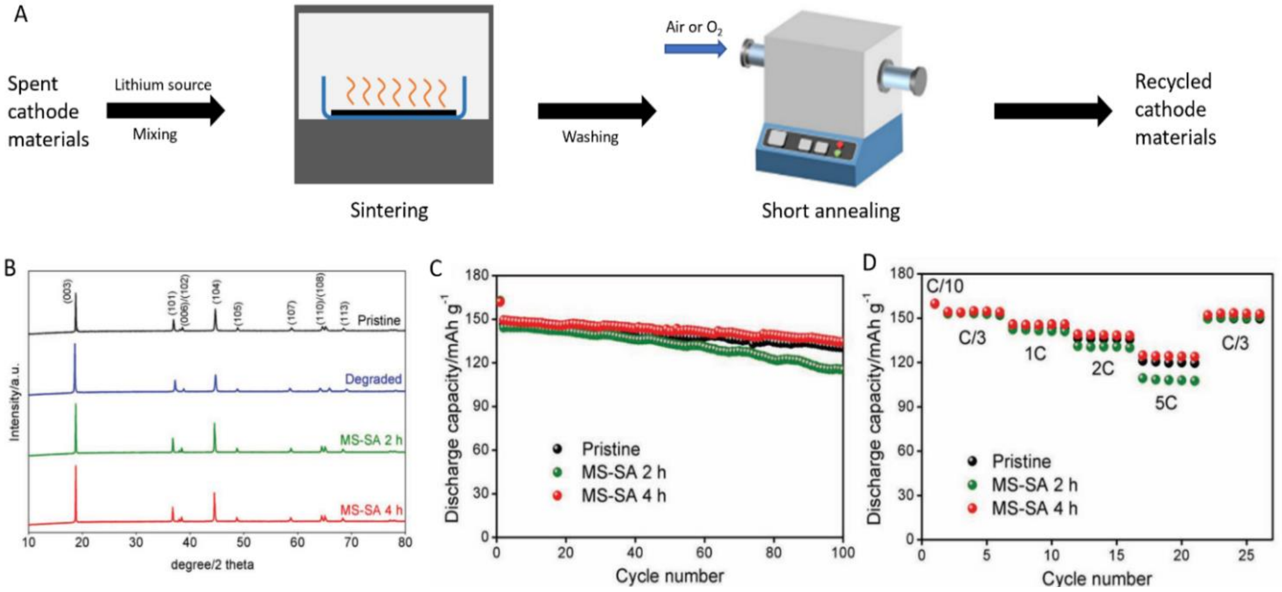

Figure 2. Diagram of high-temperature relithiation process (A), XRD of degraded NMC523, pristine NMC523, and regenerated NMC523 (B), the cycling performance of pristine NMC523, and regenerated NMC 523 at a current density of 1C (C), rate capability of pristine N. (B)(C)(D) are reprinted from [6].

2.2. Hydrothermal relithiation method

Figure 3A shows the hydrothermal relithiation process. The hydrothermal relithiation is typically achieved in conductive solvents, such as water, ionic liquids, etc. Lithium-ion is provided by highly dissolvable lithium compounds, such as LiNO3, and LiOH. The temperature of the hydrothermal relithiation method is below 220°C, which is much lower than that of the high-temperature relithiation method. During the hydrothermal relithiation process, the lithium-ion is inserted into the degraded cathode materials from the solvent, with the crystal structure being recovered at the same time. Figure 3B is the XRD results of degraded, pristine, and regenerated NMC111 ($LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$), showing that the regenerated NMC111 has the same crystal structure as the pristine NMC111. In addition to the crystal structure, the regenerated NMC111 possesses the equivalent cycling performance and rate capability as the pristine material, as shown in figure 3C and 3D. Using certain lithium sources and reaction conditions, the regenerated cathode materials deliver even higher specific capacity and cycling stability compared to the pristine materials.

Several hydrothermal relithiation methods have been proposed in the past few years. Yu et al. proposed a low-temperature hydrothermal relithiation method to regenerate degraded NMC111 and NMC622 ($LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$) using LiOH as the lithium source. This method further reduced the heating temperature from 220°C to 100°C with the addition of green additives in the water, such as ethanol, hydrogen peroxide, and ethylene glycol [11]. Wu et al. reported a chemical relithiation method using Py-Li in DME (Dimethoxyethane) as the lithium source to regenerate the degraded LFP at 80°C [12]. Xu et al. investigated the effect of hydrothermal temperature, duration, and solution composition on the recovery results of degraded LFP [13]. Another low-temperature hydrothermal relithiation has also been proposed by Xu et al. to regenerate the degraded LFP, by adding citric acid to decrease the Gibbs free energy of the relithiation reaction [14]. In addition to the water, ionic liquid with high conductivity and high melting point was also used as the solvent in the hydrothermal relithiation process. Wang et al. have proposed a hydrothermal relithiation method using ionic liquid as the solvent to regenerate degraded NMC111. The electrochemical performance of regenerated cathode materials by hydrothermal relithiation methods is equivalent to that of pristine cathode materials.

The hydrothermal relithiation method can fully recover the composition and crystal structure of degraded cathode materials, to deliver the same electrochemical performance as that of pristine cathode materials. The temperature of the hydrothermal relithiation method is much lower than that of the high-temperature relithiation method, so consuming much less energy. However, the total regeneration time for the hydrothermal relithiation method is over 20h. The production efficiency is low due to the longer regeneration time. Since the regeneration takes place in a liquid, the waste gases generated during the hydrothermal relithiation process can be easily absorbed. After the relithiation process, the solution can be reused in the regeneration of the next batch of degraded cathode materials after the solids are filtered and the lithium concentration is recovered to a certain amount. To scale up the hydrothermal relithiation method to industrial scale, the regeneration time needs to be largely reduced.

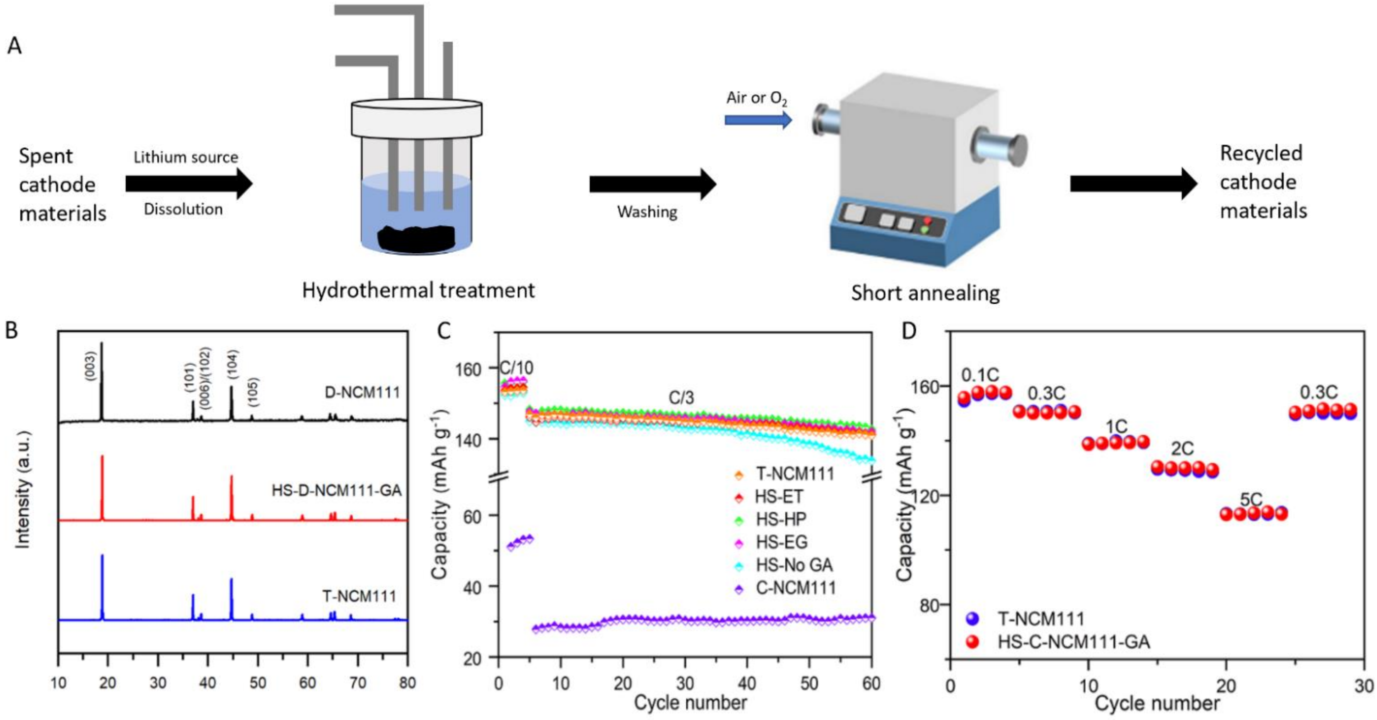

Figure 3 Diagram of hydrothermal relithiation process (A), XRD of degraded NMC111, pristine NMC111, and regenerated NMC111 (B), the cycling performance of pristine NMC111, degraded NMC111and regenerated NMC111 using different green additives (C), rate capability. (B)(C)(D) are reprinted from [11].

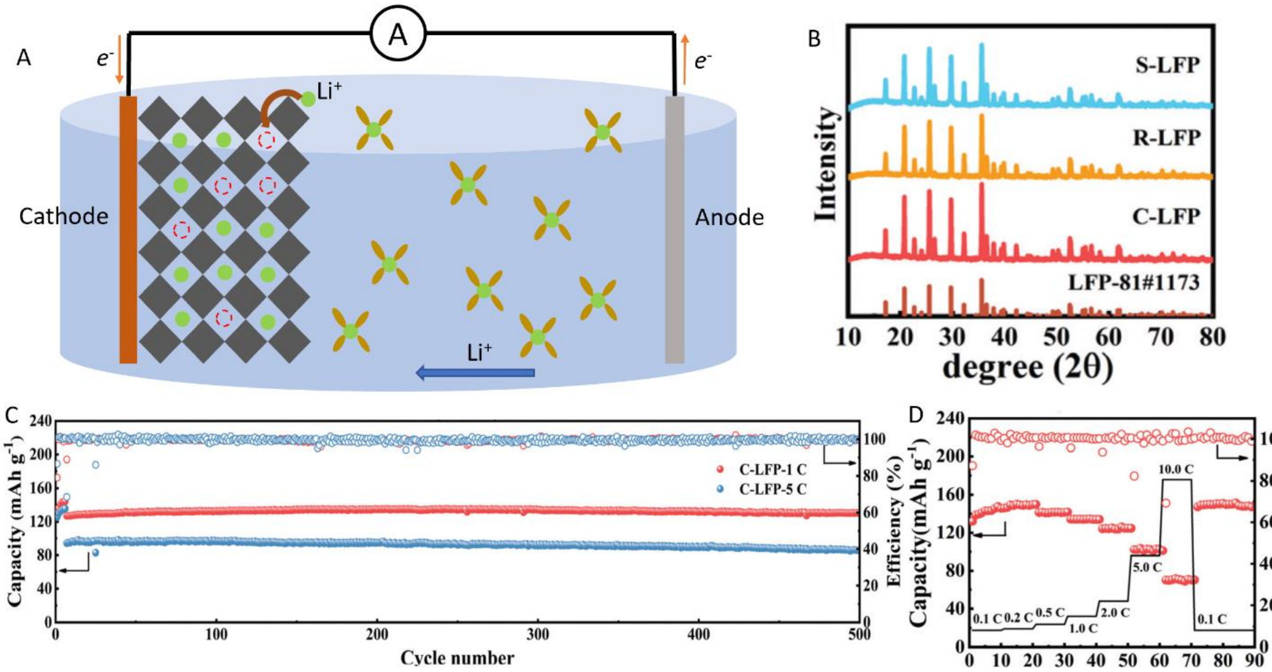

Figure 4 Schematic diagram of electrochemical relithiation process (A), XRD of degraded LFP, pristine LFP, and regenerated LFP (B), the cycling performance of regenerated LFP at 1C and 5C (C), rate capability of regenerated LFP (D). (B)(C)(D) are reprinted from [15].

2.3. Electrochemical relithiation method

The schematic of the electrochemical relithiation method is shown in figure 4A. The electrochemical relithiation method uses the electrolytic cell to regenerate the degraded cathode materials. The cathode electrode is the degraded cathode material, while the reference electrode is the Ag/AgCl. The electrolyte in the electrolytic cell is lithium compounds, such as Li_2SO_4, LiCl, etc. As the current flows, the lithium-ion from the electrolyte is re-inserted into the crystal structure, recovering the composition of degraded cathode materials. Figure 2B is the XRD results of the regenerated and pristine LFP, which shows that the regenerated LFP and pristine LFP have the same crystal structure. The results of long-term cycling performance and rate capability are shown in Figures 2C and 2D, respectively. The regenerated LFP possesses a stable cycling performance and a high rate capability.

Fewer studies have been reported on the electrochemical relithiation method compared to other methods. Peng et al. proposed an electrochemical relithiation method for degraded LFP using Li_2SO_4 as electrolyte and Ag/AgCl as reference electrode [15]. Yang et al. studied the regeneration of degraded LCO using pristine LCO as the lithium source and Li_2SO_4 as the electrolyte [16]. The electrochemical performance of the compared cathode materials is close.

The electrochemical relithiation method can fully recover the composition and electrochemical performance of degraded LFP and LCO. Due to the stable crystal structure of LFP and LCO, the degradation of these two cathode materials is mainly caused by the lithium loss during cycling. After the recovery of lithium content, the regenerated LFP and LCO can deliver equivalent electrochemical performance as the pristine cathode materials. However, for emerging cathode materials, such as NMC and NCA, the crystal structure undergoes severe degradation during cycling. The structure degradation is hard to recover by the electrochemical relithiation method, which can cause a unstable cycling performance and rate capability in long cycles. The electrochemical relithiation method requires at least 15h to fully recover the composition of degraded cathode materials. Due to the low current and voltage for regeneration, the energy consumption of this method is lower. There is no waste gas or solution generated during the reaction. By maintaining the concentration of lithium salts in the solution, the solution can be recycled. However, electrochemical relithiation cannot recover the crystal structure of high-performance materials, hindering its scale-up in real industrial applications.

2.4. Feasibility of direct recycling methods in the industry

Table 1 Summary of three types of recycling methods

	Product performance	Energy consumption	Environmental impact	Production efficiency	Feasibility of scaling-up
Sintering	High	High	High	High	High
Hydrothermal	High	Medium	High	Low	Medium
Electrochemical	Medium	Low	Low	Low	Low

Compared with pristine cathode materials, recycled cathode materials with the same or even a higher electrochemical performance and thermal stability can be directly reused in the manufacturing of new lithium-ion batteries for electric vehicles. In addition, direct recycling methods show advantages in terms of energy consumption, environmental impact, and production efficiency when compared to conventional production of pristine cathode materials. Since direct recycling is still under development at lab-scale, it is crucial to evaluate and compare state-of-the-art direct recycling methods in terms of electrochemical performance, energy consumption, environmental impacts, manufacturing efficiency, and scalability, in order to determine their potential for future commercialization. As summarized in Table 1, sintering and hydrothermal methods can fully recover the electrochemical performance and crystal structure of cathode materials, while electrochemical methods are not suitable for the regeneration of high-capacity cathode materials commonly used in electric vehicles. The high temperature in sintering methods may consume more energy, but it greatly reduces the regeneration time and increases production efficiency. Both sintering and hydrothermal methods generate waste gases during the regeneration process, but these can be easily handled by waste gas treatment systems. Therefore, sintering methods show the highest potential for scale up from a laboratory scale to an industrial scale.

5. Summary and outlook

In summary, direct recycling methods have drawn more and more attention due to their great potential to close the loop of the production of lithium ion batteries for electric vehicles. With direct recycling, the degraded cathode materials can be fully recovered to their original composition and crystal structure, demonstrating the same level of electrochemical performance as that of pristine cathode materials. However, there is still space for further improvement and optimization of direct recycling, to meet the requirements of lithium-ion batteries for EVs as well as to commercialize the direct recycling methods from the lab scale to the industrial scale in future.

Acknowledges

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