

WASTE TO RESOURCE TRANSFORMATION: INNOVATIVE APPROACHES TO RECYCLING CATHODE MATERIALS FROM LITHIUM-ION BATTERIES

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ABSTRACT – The surging use of lithium-ion batteries (LIBs) has precipitated an imperative for sustainable recycling practices to recover valuable cathode materials, ensuring environmental stewardship and resource efficiency. This review delves into recent innovations in cathode material recycling from LIBs, focusing on methodologies that not only reclaim materials but also restore their functionality for reuse. Highlighted are cutting-edge techniques such as an electrochemical relithiation process, which rejuvenates spent cathode materials to equal the performance of new ones. At the forefront of these sustainable practices is the concept of direct regeneration via direct recycling, offering an economically viable and environmentally friendly approach to mend degraded cathodes. Such progress signals a shift away from conventional metallurgical methods toward intelligent regeneration, representing a significant step forward in the sustainable recycling of LIBs. This review provides a brief analysis of these novel recycling processes, illustrating their ability to transform spent batteries into valuable resources, mitigate environmental harm, and foster a circular economy within the realm of energy storage.

Keywords: Lithium-Ion Battery Recycling, Cathode Material, Regeneration, Relithiation, Direct Recycling.

INTRODUCTION

Lithium-ion batteries (LIBs) are extensively used in various applications (electric vehicles, stationary storage, portable electronics, etc.). Given that these batteries generally have a lifespan of 10-15 years, a significant volume of End-of-Life (EOL) batteries will require disposal in the coming years [1]. Furthermore, the recovery of crucial elements like lithium, cobalt, nickel, and manganese, which have substantial economic importance, is essential to maintain the sustainability of the supply chain over the long term [2]. Commonly used cathode materials such as $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$, LiCoO_2 , and LiFePO_4 can be directly regenerated from spent LIBs and reused to produce new batteries, thus forming a sustainable cycle from spent to new cathode materials [3].

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The hydrometallurgical process is noted for its high recovery rate and ability to produce high-purity end products. It is characterized by lower energy consumption and less waste gas production. However, this method generates a significant amount of wastewater and is inherently time-consuming. The principal challenges lie in developing effective wastewater treatment techniques and optimizing the overall process for efficiency. The pyrometallurgical process offers a straightforward operation with a short processing flow and does not necessitate pre-sorting of inputs by categories or sizes. Its high efficiency is a strong advantage. Nonetheless, it does not recover lithium and manganese, entails higher energy consumption, and is less efficient in terms of overall recovery. Moreover, it produces more waste gas, raising concerns about environmental hazards and the cost of waste gas treatment. The key challenges include reducing energy consumption and emissions, mitigating environmental hazards, and ideally, integrating with hydrometallurgical methods to enhance recovery outcomes [4].

Pražanová et al. (2024) compared the cost, energy use, and environmental impact of producing and recycling 1 kg of NMC111 cathode via virgin material production, pyrometallurgy, hydrometallurgy, and direct recycling. Compared to traditional production, pyrometallurgy increases costs by 16%, hydrometallurgy lowers them by 2%, and direct recycling cuts them down by 42%. Energy consumption shows similar trends: pyrometallurgy uses 3% more, hydrometallurgy 11% less, and direct recycling reduces it by 89%. In water use, hydrometallurgy is highest at 55%, followed by pyrometallurgy at 37%, and direct recycling at just 14%. Greenhouse gas emissions are lowest with direct recycling, (9% of traditional levels), while hydrometallurgy reaches 97% and pyrometallurgy 15%. Sulfur oxide emissions are also minimal with direct recycling (1%), compared to 13% for hydrometallurgy and 33% for pyrometallurgy. These data indicate that direct recycling offers significant advantages in terms of reducing costs, energy, and water consumption, as well as reducing emissions of harmful gases.

DIRECT RECYCLING APPROACH

Post-consumption, spent batteries are subjected to direct recycling or material separation. Material separation could involve multiple methods such as hydrometallurgy, pyrometallurgy, and novel processes like electrochemical methods, ionic liquids, and eutectic salts [4].

The concept of "direct recycling" of cathode materials from spent LIBs is an innovative and sustainable approach that aims to recover and regenerate cathode materials which contrasts with traditional recycling methods that typically focus on recovering individual metal constituents. Direct recycling is predicated on the principle of retaining high-value cathode materials in their functional form rather than breaking them down into their elemental components. By doing so, it reduces the need for energy-intensive processes associated with traditional recycling methods, such as smelting and extraction. Furthermore, direct recycling circumvents the economic and environmental costs of synthesizing new cathode materials from scratch [1, 5].

The direct recycling process begins with the collection of EOL batteries, which undergo an initial mechanical treatment to remove the outer casings and isolate the battery cells. Following shredding, the process involves a series of sophisticated

separation techniques that distinguish between the cathode material, the anode, and other metals. Screening ensures the granulation of materials to sizes below 0.5 mm, facilitating separation. The subsequent hydro- and pyrometallurgical processes are crucial for the extraction of valuable metals. In hydro processes, leaching is employed to dissolve specific metals, after which a liquid/solid separation is executed [2].

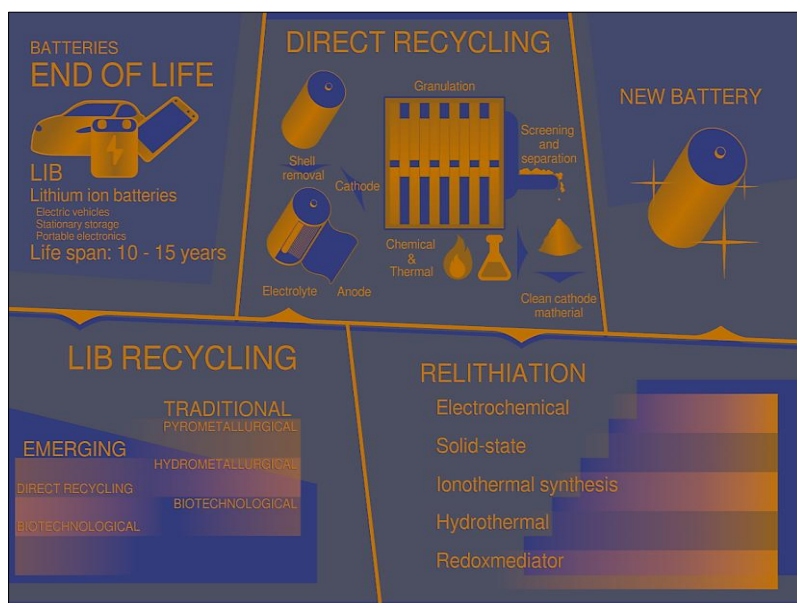


Figure 1 Overview of lithium-ion battery recycling processes: from EOL management to direct recycling and relithiation techniques

The recovery of the electrolyte is another vital step, as it can contain valuable organic compounds and lithium salts. Once the cathode materials are isolated, they undergo treatments to remove any residual carbon black and polyvinylidene fluoride (PVDF) binder. This is typically achieved through chemical or thermal processes. The cleaned cathode materials are then subjected to relithiation, a process where lithium is reintroduced to the cathode material to restore it to a usable state. Upcycling is an additional step that may involve further treatment to improve the performance of the cathode material, possibly surpassing its original specifications [4, 6]. The rejuvenated cathode material can then be directly reused in the manufacturing of new batteries. This "closed-loop" approach presents several advantages: it retains the microstructural and electrochemical properties of the cathode materials, reduces the reliance on raw material extraction, decreases the overall carbon footprint of battery production, and supports the advancement toward a more sustainable and circular economy [4].

Shi et al. (2019), presented the ambient-pressure relithiation process, which involved a novel approach for regenerating degraded LIB cathode materials, specifically $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523), using eutectic Li^+ molten-salt solutions. This method is

designed to restore the lithium composition and crystal structure of the cathode materials at ambient pressure, providing a safer and more environmentally friendly alternative to high-pressure hydrothermal relithiation processes. The process utilizes a eutectic mixture of lithium nitrate (LiNO_3) and lithium hydroxide (LiOH) in a molar ratio of 3:2. This mixture has a low melting point of approximately 176°C , which facilitates the relithiation at relatively low temperatures. Degraded NCM523 cathode particles are mixed with the eutectic Li^+ molten-salt solution. This mixture serves both as a lithium source and a medium for the reaction. The mixture is then heated to 300°C at ambient pressure and maintained at this temperature for 2 to 4 hours. This step allows for sufficient time for lithium ions to diffuse through the cathode particles, ensuring complete relithiation. The mixture is washed with deionized water to remove any residual lithium salts. The relithiated cathode particles are subsequently thermally annealed. This involves sintering the particles with a 5% excess amount of lithium carbonate (Li_2CO_3) at 850°C in an oxygen atmosphere for 4 hours. The excess Li_2CO_3 compensates for any lithium loss that might occur at high temperatures.

This relithiation method not only recovers the lithium content and structural integrity of degraded NCM523 cathode materials but also provides a platform for the application of similar techniques to other cathode materials [7].

Several relithiation methods have been developed and researched in recent years, including ionothermal, hydrothermal, redox mediator relithiation, electrochemical relithiation, solid-state relithiation and eutectic salt relithiation [1, 2]. Advantages and challenges regarding relithiation processes are shown in Table 1.

Among various techniques, the solid-state method is the simplest, involving direct annealing of used cathode materials with lithium sources. Precise control of lithium salt quantity is essential [5]. Ionothermal synthesis uses ionic liquids to enable reactions at lower temperatures, aiding lithium-ion battery cathode recycling. Wang et al. (2020) applied this method using affordable lithium halides and recyclable ionic liquids [8]. The hydrothermal method uses dilute lithium-containing solutions to restore cathode stoichiometry and phase purity. Gao et al. (2020) regenerated LMO cathodes to near-pristine performance, emphasizing the method's environmental and economic advantages [9]. Zhao et al. (2015) indicated that some prelithiation strategies might reduce costs compared to traditional battery manufacturing [10]. The redox mediator in relithiation replenishes lithium via redox reactions between lithium metal and EOL cathode material, though its efficiency may vary with pH [11]. Yang et al. (2019) showed that electrochemical relithiation in aqueous electrolyte followed by heating can restore cathode structure and performance [12].

Relithiation methods continue to evolve, aiming for fast, uniform lithium reintegration [11]. Direct recycling offers benefits like short recovery routes, high recovery rates, and environmental sustainability. However, it also requires complex equipment and may not fully recover all materials. To improve this, research focuses on reducing costs, simplifying material input requirements, and enhancing product quality. These efforts aim to make direct recycling a key solution for sustainable battery production and waste management [4, 12].

Table 1 The advantages and challenges of different direct recycling technologies [2]

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, etc.; 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

CONCLUSION

Direct recycling is a highly promising method, efficiently restoring degraded cathodes without breaking them down into base components. It cuts energy use by up to 89% and lowers both water consumption and greenhouse gas emissions. Economically, it reduces costs by 42% compared to producing virgin materials.

Electrochemical relithiation helps recover the lithium stoichiometry in cathodes, improving recycled materials to match or exceed original performance. When combined with methods like ionothermal synthesis and redox mediator strategies, it enables effective reintegration of valuable materials, supporting the circular economy.

The challenges ahead include reducing operational costs and addressing technical complexities in material recovery. Successful industrial integration will depend on scalability and environmental impact.

In conclusion, the advancement of recycling technologies for LIB cathode materials is not only a technical necessity but also an environmental imperative. As the demand for LIBs continues to escalate, driven by the global push towards electrification and renewable energy sources, the ability to efficiently reclaim and reuse valuable materials from spent batteries will be crucial. The ongoing development of these recycling processes promises to reduce reliance on virgin resources, decrease production costs, and diminish environmental degradation, thereby supporting the sustainability goals of the modern world.

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