Research Progress on Economical, Environmentally Friendly, and Efficient Lithium Recycling Processes for Ternary Lithium-Ion Battery Cathode Materials

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Abstract. With the rapid development of the electric vehicle industry, the volume of retired nickel-cobalt-manganese (NCM) ternary batteries has surged. As a critical strategic resource within their cathode materials, lithium faces challenges in current recycling processes, including high subsequent recovery losses, significant energy consumption, and substantial pollution. This paper systematically reviews research progress in lithium recovery from NCM cathode materials. First, it outlines the composition characteristics of NCM batteries and core recycling requirements, analyzing the principles and limitations of mainstream technologies such as pyrometallurgy, hydrometallurgy, and direct repair. It then focuses on novel lithium-preferential recovery processes, including hydrometallurgy-pyrometallurgy hybrid systems, deep eutectic solvents (DES), and electrochemical leaching, detailing their technical pathways, case study outcomes, and advantages. Finally, it summarizes current challenges, including technological maturity, lithium loss control, and large-scale application, while outlining future directions such as AI optimization, closed-loop processes, and technology integration. Research indicates that developing low-energy, low-pollution, and highly selective lithium recovery processes is crucial for ensuring lithium resource security and advancing the carbon peaking and carbon neutrality goals.

Keywords: spent NCM ternary batteries, lithium recovery, pyrometallurgy, hydrometallurgy, deep eutectic solvents.

1. Introduction

Currently, lithium-ion batteries are widely used in applications such as power batteries and energy storage. Among these, nickel-cobalt-manganese ternary lithium batteries (NCM batteries) have become one of the mainstream choices for electric vehicle power batteries due to their high energy density and excellent long-cycle life. However, with the continuous increase in electric vehicle production, the volume of retired NCM batteries is growing rapidly. If not properly managed, the heavy metals (such as cobalt and nickel) and organic electrolytes contained in the cathode materials of retired NCM batteries pose severe environmental pollution risks to soil and water bodies. Simultaneously, lithium—a critical strategic resource—often suffers from high loss rates and low recovery rates in current recycling processes due to "downstream recycling." This issue poses a significant challenge to the sustainable supply of lithium resources.

At present, the mainstream technological approaches in lithium battery recycling encompass hydrometallurgy, pyrometallurgy, and direct repair technology. Among these, direct repair technology remains in the laboratory R&D phase, constrained by demanding reaction conditions and challenges in scaling up for practical application [1]. Traditional pyrometallurgical techniques face challenges of high carbon emissions and energy consumption, with lithium elements prone to loss through slag and waste streams, leading to significant resource wastage. While hydrometallurgy offers advantages in selective metal separation, its core drawbacks lie in the discharge and treatment of waste liquids during acid-base leaching processes [2]. Furthermore, if lithium is positioned in later stages of the leaching sequence, its recovery rate significantly declines. Furthermore, current technical approaches prioritizing lithium recovery are generally constrained by high reagent costs and stringent reaction conditions, directly limiting improvements in lithium recovery and reuse rates [3].

Therefore, integrating the economies of scale offered by pyrometallurgy with the high selectivity advantages of hydrometallurgy to develop an economical, environmentally friendly, and efficient lithium-preferential recovery process has become an urgent priority in the lithium battery recycling field.

This paper aims to summarize the recovery concepts and processes for NCM battery cathode materials. By leveraging the strengths of existing techniques while addressing their limitations, it seeks to provide innovative approaches for optimizing current recovery workflows and developing novel, cost-effective, and efficient lithium element recovery processes.

2. Overview of NCM Recycling

2.1. NCM Material Composition and Core Recycling Requirements

The chemical formula for NCM cathode materials is LiNixCoyMn1-x-yO2. Based on the atomic ratio of Ni, Co, and Mn, they can be classified into types such as NCM111 (1:1:1), NCM523 (5:2:3), NCM622 (6:2:2), and NCM811 (8:1:1). ——Higher Ni content yields greater energy density (NCM811 achieves 280 Wh/kg), but compromises structural stability and increases recycling complexity.

The core requirements for NCM recycling focus on three key areas: high lithium recovery rate (target ≥95%), full recovery of heavy metals (Co, Ni, Mn recovery rate ≥99% to minimize resource waste), and zero discharge of waste liquids/slag (reducing acid-base consumption and solid waste disposal costs). Among these, prioritizing lithium recovery is critical. Early lithium separation reduces reagent consumption in subsequent metal extraction, lowering overall process costs by over 20% [4].

2.2. Industrial Recycling Process for NCM Batteries

The current universal front-end pretreatment process for NCM battery recycling is as follows:

As shown in Figure 1, the characteristics of each stage and the associated lithium loss risks are as follows:

The discharge process employs either saltwater immersion or low-current discharge to prevent short circuits and fires during disassembly. No lithium loss occurs during this stage； The disassembly stage involves disassembling the cell casing, electrolyte, and positive/negative electrode sheets. The electrode pre-treatment must be recovered separately (containing lithium salts such as $LiPF_6$) to prevent lithium from being discarded with the waste liquid. Pre-metallurgical losses of lithium primarily occur during electrode sheet pretreatment, where calcination (removing PVDF binder) or physical stripping separates the cathode active material from the aluminum foil. This step is prone to Li_2CO_3 dust loss due to electrode sheet breakage, resulting in lithium losses of 5%–8%. The metallurgical processing stage—the core control point for lithium recovery rate—is the primary focus of this article. It employs pyrometallurgical, hydrometallurgical, or combined processes to extract metals. Finally, the product processing stage involves purifying lithium salts (e.g., Li_2CO_3) and transition metal alloys/salts to meet requirements for power battery remanufacturing.

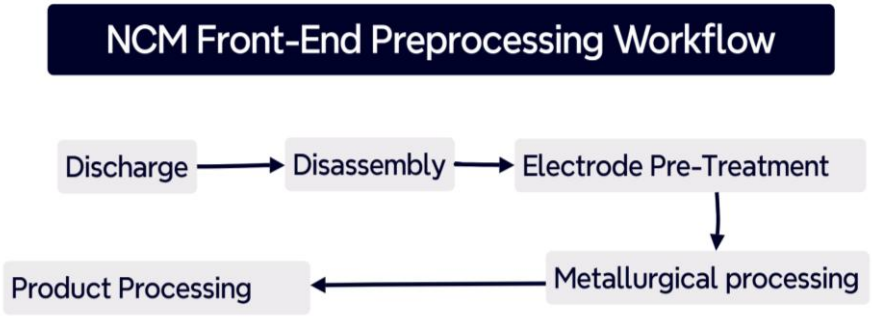

Figure 1. NCM Front-End Preprocessing Workflow

3. Existing mainstream recycling technologies

3.1. Pyrometallurgy

At high temperatures (typically 1000–1500°C), key metal oxides are reduced to their elemental forms using reducing agents such as coke or CO. Nickel, cobalt, and manganese—due to their similar atomic sizes—mutually dissolve at high temperatures to form Ni-Co-Mn alloys. Most other components form molten slag, which has a lower density than the metal alloys. Consequently, the upper layer of the product consists of slag, while the lower layer comprises the metal alloys. This process offers advantages of high processing efficiency and simplified operation, making it suitable for large-scale industrial recycling. However, a significant portion of lithium (Li) exists as Li_2O within the upper slag layer, making it difficult to recover and resulting in substantial waste of Li. Secondly, pyrometallurgical processes consume substantial energy and readily generate large quantities of greenhouse gases and toxic emissions (such as HF), causing significant environmental pollution. This approach is incompatible with current demands for economically viable and environmentally sustainable recycling.

3.2. Hydrometallurgy

Acids dissolve cathode materials, converting metals into soluble metal ions. Reducing agents (such as oxalic acid or sodium sulfite) then reduce these high-valent metal ions. Finally, extraction and precipitation methods separate and purify the metal ions. Compared to pyrometallurgy, hydrometallurgy achieves higher lithium recovery rates, reaching up to 95%. Recovery rates for other critical metals can exceed 99%, with significantly reduced energy consumption. However, its lengthy industrial chain, challenging waste liquid treatment, and frequent anti-corrosion maintenance requirements for equipment pose substantial challenges to both environmental sustainability and process costs.

Equations should be centred and should be numbered with the number on the right-hand side.

4. New Lithium Element Recovery Process

4.1. Combined Hydrometallurgical and Pyrometallurgical Processes

Given the current maturity and broad applicability of hydrometallurgical and pyrometallurgical processes, optimizing the lithium recovery methodology hinges on refining the process chain by integrating the fundamental steps of both approaches while leveraging their respective strengths. Current hydrometallurgical processes are widely applied to recover key metals (such as lithium, nickel, cobalt, and manganese) from pretreated NCM battery cathode materials. Integrating hydrometallurgy with pyrometallurgy provides an effective pathway for efficient lithium recovery. Based on extensive research summarized by Guo et al. [5], hydrometallurgical processes can be summarized into two main steps: The first step is metal enrichment, where leaching agents (currently predominantly acids or ammonium salts) convert solid cathode materials into various ionic forms of metal ions. The second step is metal extraction, employing chemical principles such as extraction and ion exchange to sequentially recover metal ions from leachate and leaching residues. Final metal enrichment is achieved through refining and secondary leaching operations. In combined hydrometallurgical and pyrometallurgical approaches, the core pyrometallurgical step is calcination. This involves oxidizing or reducing specific metal elements within the cathode material under controlled temperature and oxygen conditions (primarily reduction in NCM to lower the valence state of certain metals). This achieves targeted, efficient extraction of key metals (particularly effective and widely applied in Li recovery). The primary principle behind efficient Li recovery in combined hydrometallurgical-pyrometallurgical processes is reducing the valence state of Li in NCM cathode materials under specific conditions (optimal calcination temperature, oxygen content, and duration). Subsequently, suitable extractants selectively extract the reduction products of Li, prioritizing Li

recovery while minimizing its dispersion, thereby achieving high-efficiency recovery. For instance, when incorporating pre-roasting into hydrometallurgical processes, Li^+ in layered NCM reacts with atmospheric CO_2 at elevated temperatures to form Li_2CO_3. While Li_2CO_3 exhibits lower solubility in water than LiOH, its solubility is two orders of magnitude higher than that of crystalline Li. A 10-minute water leaching step can recover 60–70% of the lithium, thereby reducing the subsequent acid leaching load.

4.1.1. Carbon-Heat Reduction Method

The NCM cathode material to be treated is processed together with carbon-based materials such as graphite (obtainable from waste NCM anode material), lignite, or coke as reducing agents. This reduces the Li elements in the cathode material to lower valence states (e.g., alloys or intermediate-valent compounds), thereby enabling preferential leaching. For instance, Liu employed the sodium bicarbonate extraction method [6], utilizing carbon as a reducing agent to achieve highly efficient Li extraction. Since the reducing agent can be directly extracted from waste NCM cathode materials and its carbon emissions are lower than conventional pyrometallurgical processes, this method balances economic viability with environmental sustainability.

4.1.2. Chlorination Roasting Method

By adding chlorinating agents (such as NH_4Cl, NaCl, etc.), Li elements are chlorinated into Li^+, enhancing their extraction efficiency and priority. For instance, Yu et al.'s thermodynamic analysis indicates that Li readily forms LiCl [7], while Ni, Co, and Mn tend to form oxides. Therefore, Yu et al. roasted at 600°C for 60 minutes using a 2:1 molar ratio of NH_4Cl to Li, converting Li into water-soluble LiCl while transforming Ni, Co, and Mn into water-insoluble oxides (e.g., NiO, $MnCo_2O_4$). The final Li leaching rate reached 97.81%; while the leaching rates of other impurity metals (e.g., Ni, Co, Mn) were all below 1%, demonstrating high selectivity. This method requires no strong acids, features low energy consumption, and is simple to operate.

4.1.3. Sulfurization Reduction Method

Sulfurizing agents can promote Li extraction due to their auxiliary additive properties, such as using sodium sulfite to assist calcination, or directly calcining under SO_2 conditions. For instance, Wu et al. achieved a Li leaching rate of 99.6% by combining SO_2 roasting (roasting cathode materials at 800°C for two hours in an atmosphere containing over 99% sulfur dioxide) with water leaching followed by acid leaching [8]. However, additional costs are incurred to install alkali washing purification equipment to treat the residual SO_2.

4.2. Deep Eutectic Solvent Extraction (DES)

Beyond combined hydrometallurgical and pyrometallurgical processes, several promising recovery methods warrant attention, with the DES method being one of them. DES refers to a class of low-melting-point liquid mixtures formed by blending hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) in specific molar ratios. The principle behind its efficient lithium recovery lies in its typical composition: quaternary ammonium salts (e.g., choline chloride) as hydrogen bond acceptors (HBAs) and polyols, carboxylic acids, or amides as hydrogen bond donors (HBDs). During recovery, anions in the DES system (e.g., Cl^-) and functional groups of HBDs (e.g., -OH, -COOH) in the DES system can form stable coordination complexes with lithium ions in spent cathode materials. Due to the small ionic radius and high charge density of lithium ions, the material lattice is readily attacked by H^+ ions, leading to preferential extraction. The binding affinity of lithium ions with the coordinating groups in DES is significantly stronger than that of transition metal ions (Ni^{2+}, Co^{2+}, Mn^{2+}) with larger ionic radii and relatively lower charge densities. This differential coordination ability is central to achieving selective leaching. Zhang et al. have already achieved highly efficient recovery of multiple key metals, including lithium, from NCM using a DES method based on TEAC (tetraethylammonium chloride, as HBA) and LAA (lactic acid, as HBD) [9]. The DES method features readily available raw materials, low equipment investment and energy costs,

minimal requirement for strong acids or bases in the process chain, and extremely low waste liquid and residue discharge. Metal ion leaching can be controlled by adjusting the HBA-to-HBD ratio and reaction temperature. The process chain enables solvent recycling since the DES itself is not significantly consumed after metal leaching. After ratio adjustment, the solvent can be directly recovered using physical methods such as distillation or water evaporation. This approach aligns perfectly with the current demand for economical, environmentally friendly, and efficient lithium recovery processes.

4.3. Electrochemical Leaching

Electrochemical leaching is a hydrometallurgical process that applies an electric current to target materials by measuring potential, enabling specific metals within the material to selectively dissolve into the solution. This achieves the goal of directional, efficient leaching. In electrolytic leaching experiments conducted by Chen Min et al., no acids or alkalis were required as leaching agents [10]. Under conditions of 4% binder content, 1.5V voltage, 30°C temperature, and a 3-hour leaching duration, the selectivity for Li leaching in sodium carbonate solution approached 100%. This leaching method generates minimal waste discharge due to the absence of acids or bases. Its mild conditions also result in low energy consumption, providing a novel experimental model for direct repair technologies. However, significant limitations remain: the electrode preparation process is cumbersome, lithium leaching efficiency is low, and applicability has only been confirmed for NCM systems. These shortcomings indicate substantial room for process improvement.

5. Challenges and Outlook

5.1. Challenges

First, for the aforementioned processes, lithium loss does not occur exclusively in a single step but rather across multiple stages within the process chain. Taking the liquid-phase extraction process as an example: during pretreatment, dismantling and pre-calcination cause lithium to be easily lost as Li_2CO_3 dust; in metallurgical processing, residual Li^+ in waste liquids remains a critical step warranting attention for lithium recovery.

Second, the DES method holds significant potential for prioritizing lithium extraction with broad industrial prospects. However, its lengthy process cycle (ranging from 1 to 10 hours) poses challenges. While accelerating leaching times with microwave equipment could be considered, this approach incurs substantial additional costs. Furthermore, since some solvent adheres to material surfaces or undergoes decomposition losses, even when DES is recoverable, its recovery rate remains around 90%. These limitations make the process inadequate for large-scale NCM cathode material recovery.

Finally, while hydrometallurgical-pyrometallurgical integration is relatively mature with continuously improving recovery techniques, persistent challenges remain: difficulty in controlling leaching conditions, waste liquid and gas discharge, residue treatment, substantial energy consumption compared to other methods, and incomplete waste liquid and byproduct recovery chains. These issues require long-term improvement and resolution.

5.2. Outlook

During the pretreatment stage, lithium loss primarily occurs in the form of Li_2CO_3 dust. Therefore, adding appropriate binding agents during battery disassembly to adhere the dust to material surfaces could be considered. Meanwhile, the Li element in waste liquids exists as a small amount of Li^+ ions. In this scenario, electrochemical leaching (EL) can be employed to selectively extract lithium from the waste liquid. This approach is feasible because, among the key metal ions present, Li^+ possesses the smallest ionic radius. Using electrode materials with appropriately sized interstitial spaces enables selective incorporation of lithium ions, followed by extraction from the electrodes.

The challenges hindering the large-scale implementation of the DES method include its lengthy process cycle and low recovery rates due to DES solvent adhesion to material surfaces. To address

the extended DES cycle time, novel, cost-effective microwave-catalyzed modes and catalysts can be developed to accelerate DES leaching. Additionally, optimizing and developing new hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) within DES that enable efficient, rapid Li leaching, while appropriately adjusting catalyst ratios and reaction temperatures, is another viable approach. To address DES solvent adhesion to material surfaces, contrary to measures reducing pre-treatment Li content, suitable diluents and DES meeting low-viscosity and low-boiling-point criteria should be identified. Physical separation and recovery methods under specific conditions can then be employed. The initial application results of novel processes like DES are outstanding, providing significant confidence for developing further recovery technologies. Research has demonstrated promising outcomes using biomass-derived reducing agents and metallurgical recovery processes based on molten salt technology [11][12]. The aforementioned processes may also draw inspiration from these methodologies, exploring the application of their reagents to enhance recovery efficiency.

Given the established scale and industrial foundation of pyrometallurgical and hydrometallurgical processes, optimizing their recovery chains remains the primary consideration and choice until novel methods like DES reach maturity. First, to address issues like Li loss and waste liquid discharge caused by difficulties in controlling temperature and reagent conditions, efforts should focus on developing more intelligent and automated process chains. For instance, employing specialized reaction vessels that reflect the internal state of the system being processed, combined with AI-optimized control algorithms to regulate optimal reaction conditions, can ensure precise reagent dosing for cost savings while providing feedback on waste liquid composition. Secondly, regarding significant energy consumption and the discharge of waste liquids and gases, as auxiliary equipment and overall purification system costs decrease in the future, combined pyrometallurgy and hydrometallurgy will enter a new phase characterized by high efficiency, high automation, high intelligence, low emissions, low energy consumption, and low costs.

While the current new energy device industry faces tight supply for lithium metal, other critical metallic elements also hold significant recycling value. Moreover, batteries other than NCM still hold a substantial market share in lithium-ion batteries. For instance, in the first half of 2025, LPF batteries (lithium iron phosphate power batteries) accounted for 55.1% of global installations. The recycling of various critical metals, including lithium, from these power batteries is also becoming urgent. Therefore, in the near future, extending the technology for prioritizing lithium recovery from NCM cathode materials to other critical metals and other lithium-ion battery types will become a key research focus in lithium-ion battery recycling.

6. Conclusion

This study reviews prior research to elucidate advancements in economically viable and environmentally efficient lithium recovery processes for ternary cathode materials in lithium batteries.

Compared to previous work, this research focuses specifically on NCM materials and prioritizes lithium recovery, highlighting existing challenges and shortcomings in current recycling technologies. Based on others' experimental analyses, it evaluates the advantages, disadvantages, and application prospects of novel processes, proposing hypotheses for optimizing procedures through different methods. This contributes to future research and development directions for lithium battery recycling.

Overall, this study offers new perspectives on economically viable, environmentally friendly, and efficient lithium recovery from NCM batteries. It provides guidance for advancing the lithium battery industry and ensuring lithium resource security, while enhancing the scientific theoretical framework for achieving the carbon peaking and carbon neutrality goals.

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