Direct Recycling of End-of-Life Lithium-Ion Batteries by Electrochemical Route

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Keywords: Direct Recycling, Lithium-Ion Batteries, Electrochemical re-lithiation
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In the search for new renewable energy solutions, Lithium-Ion Batteries (LIBs) are one of the most promising solutions in recent decades, offering high energy density, long life and multidisciplinary applications. Thanks to these advantages, LIBs have been perfectly integrated into energy storage, both for stationary use in homes and industry, and for powering the electric motors of heavy vehicles or light personal transport. The scientific community's intense research into the vagaries of lithium-ion chemistry has catalysed remarkable innovation and presented numerous paradigms to elucidate the fundamentals of LIB technologies in their ever-evolving permutations.

Inside LIBs there is an interplay of cathode and anode materials, electrolytes and separators. This ensemble allows lithium ions to move effectively and reversibly between the anode and cathode during charging and discharging. However, new electrode materials, electrolyte formulations and manufacturing processes have been required for the next generation of LIBs to improve performance and sustainability. As is continued to unravel the complex web of LIBs technology, researchers face a myriad of issues ranging from capacity degradation to safety and the environmental footprint of raw materials. In response, their efforts are increasingly focused on not only addressing these concerns, but also integrating sustainability across the entire battery lifecycle. From advanced recycling technologies that recover valuable materials from spent batteries to the search for environmentally friendly alternatives in manufacturing, these solutions underscore the scientific community's commitment to creating a sustainable and circular LIBs value chain, where advances in design, materials and recycling technology converge to deliver minimal environmental impact and maximum resource efficiency.

The end-of-life (EoL) management of LIBs is a critical mainstream consideration as a major secondary source of valuable materials such as cobalt, nickel, manganese, lithium and graphite, among others. Their recycling is currently a headache, solved by non-100% green technologies such as pyrometallurgy or inorganic acid leaching (hydrometallurgy), which do not reduce the battery footprint and produce secondary wastewater, respectively. However, achieve good recovery rates per critical raw material, depending on the type of LIB. Recently, there has been a move away from the conventional and destructive acid leaching process. Pyrometallurgy is a high-temperature melting process that includes thermal treatment and chemical separation. The hydrometallurgical process involves the solubilisation of target metallic elements from black mass of LIBs in a leaching solution and reclaiming the metals via the further stage of separation and purification. Direct recycling stands out as a method of regenerating degraded cathode material without compromising its original structure. This approach represents a significant advancement, with various techniques such as electrochemical relithiation (Yang, 2020; Zhang, 2020), solid-state synthesis (Nie, 2015; Gao, 2020), and hydrothermal relithiation (Xu, 2021; Sloop, 2019) gaining prominence for their enhanced sustainability and reduced environmental impact. Thus, direct recycling is becoming more attractive to researchers and recycling stakeholders due to its high recovery rate and improved sustainability, but large-scale developments are not yet underway.

The battery recycling market is growing rapidly due to the need for critical raw materials and new European policies to reduce material dependency from other countries outside the European Union, however, currently the amount of industrial battery recycling facilities is not enough established to cover the significant volumes of first generation EoL LIBs from electric vehicles for the next decade. Considering that global battery demand is expected to grow by 25% per year to reach 2,600 GWh in 2030 (Fleischmann, 2023), the need for efficient industrial recycling solutions are critical. With this in mind, research projects worldwide are exploring cutting-edge technologies to enhance recycling rates and diminish the environmental impact of the battery industry.

Direct recycling process is divided in two well-defined steps such as fine disassembly and separation, and the relithiation step. This study aimed to directly recycle NMC-622 cathode electrode from the EoL LIB of an electric vehicle (EV), through prior efficient cell disassembly in order to achieve cathode electrodes of LGX E63B pouch cells. This NMC chemistry of LIBs currently dominates the market and is a typical layered Li transition metal oxide cathode material. Long-term use (charge-discharge) can lead to various component and structural

failures such as loss of active lithium, dissolution of transition metal ions, mixing of nickel and lithium, or dendrite formation over the anode, among others, which significantly degrade the performance of the NMC cathode material (Kang, 2021; Jiang, 2021; Yin, 2021).

Fine disassembly and separation step were achieved after the deactivation process. Before the manipulation of the pouch cells, deep discharging was achieved to reduce electrical risks during cell disassembly, followed by a second safety measure of freezing to -18ºC for 24h prior to manual cell opening, which was performed in a fume hood to separate casing, anode, cathode and separator. A vacuum oven was then used to evaporate and condense the electrolyte. The re-lithiation step was carried out in a electrochemical cell formed by free-electrolyte cathode electrode which was employed as working electrode (WE), an Ag/AgCl with saturated KCl solution as reference electrode (RE) and Pt as counter electrode (CE). All three electrodes were immersed in a lithium solution. The influence of different lithium solutions such as Li_2SO_4 and LiOH at different concentrations (0.2–1M) and variation of cathodic current density (between -0.4 and -1 mA/cm^2) was investigated. Once the electrochemical insertion of Li^+ into the spent cathode electrode was completed, the cathode electrode was annealed in a muffle at 800ºC during 2h to reach the healed cathode active material (CAM) for the electrochemical performance. To check the viability of the recycling process, the CAM was tested in half-cell using a Celgard 2400 separator and $LiPF_6$ DEC: EC electrolyte in the voltage range 2.7 - 4.2 V vs Li metal. Figure 1 shows how this direct recycling route fits inside the LIBs value chain.

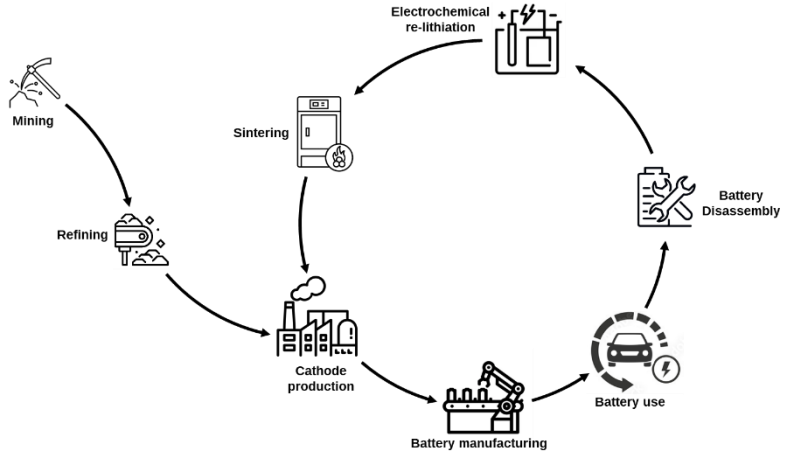

Figure 1. Integration of direct recycling through electrochemical route inside battery value chain.

The regenerated NMC-622 cathode material demonstrates a discharge capacity of 150 mAh/g at 0.05C during activation and 100 mAh/g at 0.1C with a capacity retention of 80% after 100 cycles. These electrochemical results align with state-of-the-art NMC622 cathode materials that are commercially available. The recycling approach outlined in this study is not only straightforward but also scalable, offering a potential avenue to tackle the environmental issues associated with large quantities of end-of-life lithium-ion batteries (EoL LIBs).

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