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Unlocking the Recycling Strategies: A Review on challenges, Potential, and approaches

Farshad Boorboor Ajdari[1*], **Ali Hassan-nejad**[1], **Fereshteh Abbasi**[1], **Mohadeseh Jafari**[1], **Parnaz Asghari**[1]

[1] Department of Applied Chemistry, Faculty of Chemistry, University of Kashan, Kashan, Iran.

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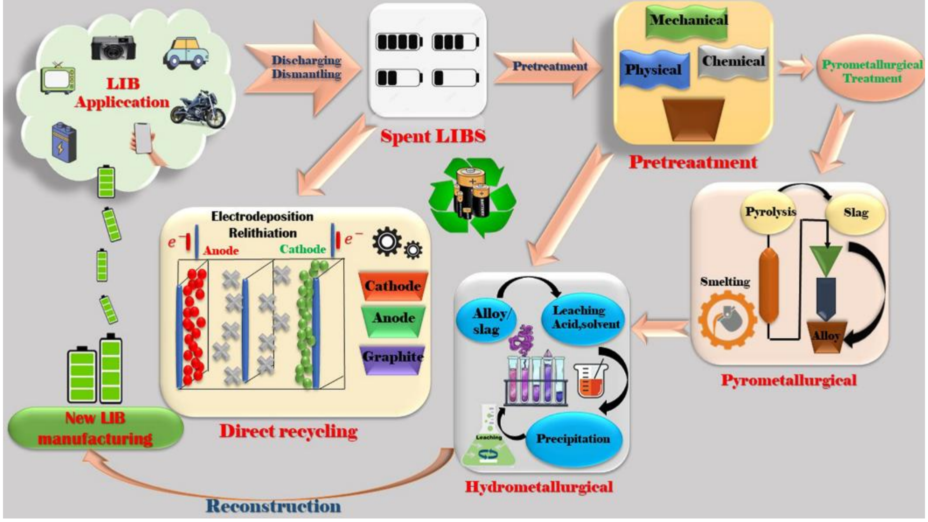
ABSTRACT

Today, the utilization of lithium-ion batteries (LIBs) has significantly increased as an energy storage technology. In recent years, the high demand for lithium for LIB has resulted in a significant increase in the consumption of lithium-containing materials. It is anticipated that the reduction of lithium due to the limited reserves of lithium will be one of the considerable challenges in the future. The lithium-ion battery industry's primary component is lithium, extracted from natural minerals and saline water. However, the extraction of lithium from natural minerals and saline water is a complex process requiring significant energy. Conversely, the number of batteries approaching the end of their lifespan is unavoidably increasing alarmingly. To address the obstacles that the lithium battery supply chain encounters, it is imperative that a variety of recycling technologies and methodologies be further developed. This article concentrates on technologies that can recycle lithium compounds from LIB through distinct processes and procedures. These stages are further divided into two pre-treatment phases and a lithium extraction stage. The lithium extraction stage is divided into three primary methods: pyrometallurgy, hydrometallurgy, and Direct. This review article quantitatively compares and analyzes each recycling method's processes, advantages, disadvantages, efficiency, price, environmental contamination, and degree of commercialization. This review can offer a suitable perspective to enhance this path.

Graphical Abstract



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[*] Farshad Boorboor Ajdari
Email Address: f.boorboor@kashanu.ac.ir, farshadborbor.2009@gmail.com
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1. Introduction

The number of used batteries has significantly increased as a result of the growing use of lithium-ion batteries (LIBs) in many industries, most notably in electric vehicles (EVs) and renewable energy storage [1,2]. There are prospects for resource recovery and environmental challenges due to the increase in battery trash. Sustainable development depends on the efficient recycling of LIBs since it recovers significant resources like nickel, cobalt, and lithium while also reducing environmental pollutants [3–5].

Despite the promising ideas, relatively little attention has been paid to the stable disposal and maintenance of LIBs beyond their end of life [6,7]. Many LIBs in electric vehicles are past their useful life, with an average lifespan of 8–10 years. Critical metals found in LIBs are limited and unequally distributed around the world. For example, the Democratic Republic of the Congo supplies around 70% of cobalt. Recycling can aid in the recovery of these commodities, decreasing the adverse effects of mining on the environment and lowering reliance on virgin resources [8,9]. Also, improper LIB disposal might result in hazardous waste, like flammable electrolytes and poisonous metals. Recycling aids in keeping ecosystems and landfills free of harmful pollutants.

LIB recycling has the potential to be profitable. By 2024, the global battery industry is expected to grow to a value of about 50$ billion. By reusing resources, efficient recycling procedures can establish a circular economy and lower the expenses of acquiring raw materials.

LIB recycling can be divided into three main categories, as illustrated in Figure 1:

1. Pyrometallurgical Recycling: Metals are recovered by smelting waste batteries at a high temperature. Although it works well for some materials, it uses a lot of energy and can produce a lot of pollutants.
2. Hydrometallurgical Recycling: Metals are extracted from battery components using chemical solutions. Despite its great recovery rates, it produces a lot of effluent and necessitates careful chemical agent management.
3. Direct Recycling: Direct recycling is a viable substitute that aims to revitalize used electrode materials without disassembling them into their parts. Because it produces less trash and requires less chemical processing, this approach is said to be more ecologically friendly and energy-efficient [10–14].

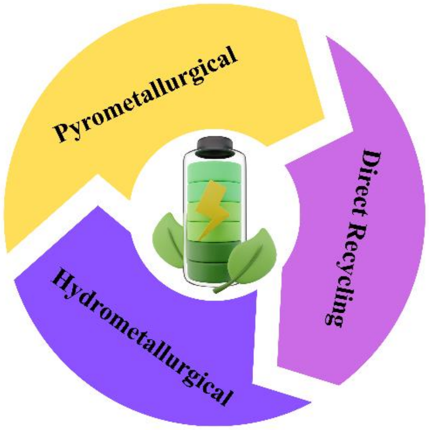

Figure 1: LIB recycling can be divided into three main categories.

Although recycling technology has advanced, there are still some obstacles to overcome, and the high expense of recycling procedures may discourage investment and adoption. Additionally, the development of adequate recycling infrastructures may be hampered by the absence of uniform legislation and incentives for recycling, and present recycling processes frequently encounter difficulties in processing a variety of battery chemistries and obtaining high purity in recovered materials, creating novel techniques that minimize the shortcomings of current strategies while combining their advantages. For example, combining direct recycling with pre-treatment procedures may

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increase productivity and lower expenses. Identifying the most sustainable practices by thoroughly analyzing the financial and environmental effects of various recycling techniques. Raising consumer and producer awareness of the value of recycling LIBs can encourage recycling program participation and increase collection rates. Recycling lithium-ion batteries is essential to environmental preservation and sustainable resource management. Addressing the difficulties in recycling LIBs will be crucial to establishing a circular economy and reducing the environmental impact of battery technologies as the market for these batteries grows. This review first explains the pre-lithiation approach for the LIB recycling process. Next, it looks at the metal extraction process, which includes direct recycling, pyrometallurgy, and hydrometallurgy. Finally, it discusses the future and prospects for efficient recycling [15–17].

2. Pre-lithiation approach for the LIB Recycling Process from Discharge to Material Exfoliation

When LIBs reach the end of their useful life, they can retain a negligible quantity of charge [18–20] . A mechanical disturbance or physical impact in the shredder in the presence of oxygen during the recycling process, which is caused by the oxidation of radicals during the production of lithium metal, produces sparks and explosions. The efficacy of hydrometallurgy and pyrometallurgy, as well as direct recycling, will be restricted by the complex and dense structure of LIBs. Consequently, the batteries are initially discharged, opened, and prepared for the primary recycling process. Batteries are frequently discharged before shredding to prevent battery explosions and flames. Typically, LIBs are discharged by immersing them in sodium chloride salt. The schematic of the ideal and practical technique of recycling battery materials is illustrated in Figure 2 [12].

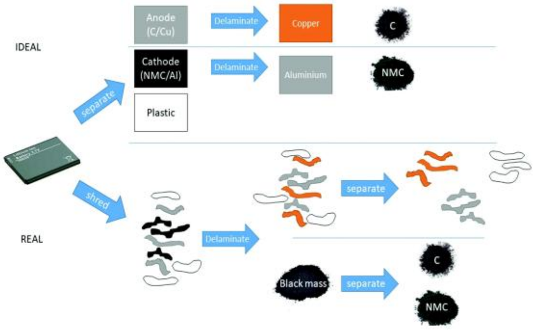

Figure 2: Schematic comparison of the ideal and practical method of recycling battery materials [12].

The initial step in battery recycling is electrolyte recovery or recycling. The leftover electrolyte in the conventional recycling process is typically calcined, which raises the amount of solid/gas waste and carbon pollution produced during recycling. For LIBs to grow environmentally friendly and sustainably, electrolyte recycling is crucial. Because of the instability of the lithium salt, the volatility of the solvent, and the high capital requirements, recycling and reusing electrolytes remains difficult. It is nevertheless imperative that electrolyte recovery and recycling continue to advance.

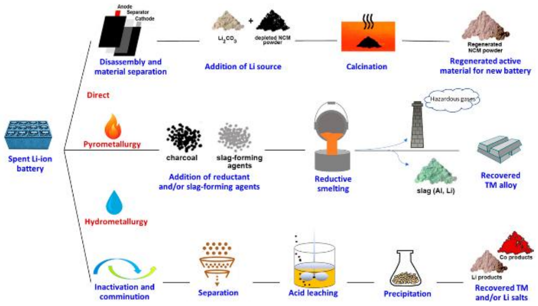

Figure 3: Steps of battery recycling [14]

Dry batteries are crushed after the electrolytes are removed, and the resulting solid mixture is then put through some separation procedures to separate the metals, polymers, cathodes, and anodes. The residual electrode portions are primarily made up of anodic active materials on copper foil and cathode active materials on aluminum foil after the battery has been crushed and components like plastic, silicon coating, and

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magnetic metals have been separated. Recycling metals and renewing materials depend on the efficient exfoliation of active materials from current collectors (copper and aluminum foil). The steps involved in battery recycling are outlined in Figure 3 [21,22].

2.1. A technique for dissolving solvents

LIB recycling was established as a lab process. Using an NMP solution at ten degrees Celsius, the anode and cathode are separated from the aluminum and copper foil in this procedure. This technique allows copper and aluminum foil to be successfully separated from the cathode and graphite powder. The copper and aluminum foils don't show any signs of surface corrosion and maintain their appearance. Dimethyl formaldehyde (DMF) was used by Zhou et al. to dissolve PVDF and extract cathode components from aluminum foil [23]. They proved that, at 60 degrees Celsius, 1176 g/L of PVDF is soluble in DMF. However, the separation of cathodes that are attached to aluminum foil using a PTFE binder is not suitable for this organic solvent. Trifluoroacetate (TFA) was used in the development of a unique technique to separate cathode materials from aluminum foil in LIBs with PTFE binder to address this problem [24]. This solvent can effectively and favorably separate the cathode granules and aluminum foil. However, the articles rarely consider PTFE-based cathodes in their methodology and instead focus on PVDF binder cathodes. In addition, the separation process's solvents are costly, highly toxic, and regarded as hazardous to human health and the environment.

A green solvent separation procedure separated the electrode materials and current collectors (copper and aluminum foil) (e.g., ethylene glycol and Cyrene). Cathodic coatings can be removed entirely from metal sheets in seconds without heat. This process does not affect the crystal structure or microstructure of the recycled battery products, especially the NMC cathodes. They also demonstrated electrochemical performance on par with pure commercial cathode powder. It is possible to recover the PVDF binder and use the solvent indefinitely. Furthermore, reclaimed aluminum metal foils are impervious to rust. Water-soluble SBR/CMC binder is a substance that is widely utilized in the anodic sector [25–27].

2.2. Technique of dissolving Hydroxide

An NaOH solution separated the aluminum foil and cathode powder during the cathode material recovery process. With a solid-to-liquid ratio of 100 g/L, a reaction time of five hours at room temperature, and a sodium hydroxide solution with a 10% by-weight concentration, approximately 98% of the aluminum foil was dissolved. This method's high separation efficiency and simplicity of use are its advantages. However, recovering aluminum is difficult due to its ionic state and the environmentally dangerous character of alkaline wastewater [28].

2.3. Thermal recovery strategy

In the thermal recovery strategy, the adhesion force is decreased using binders that decompose at high temperatures [29–31]. After that, sieving makes it easy to separate the cathode components. PVDF binders are usually said to break down at temperatures higher than 350 degrees Celsius. On the other hand, materials currently in use, such as conductive carbon and acetylene black, will disintegrate at temperatures higher than 60 degrees Celsius. Sun and Q presented an innovative method of using vacuum heating to separate cathode materials [32]. This process breaks down the electrolyte and binder, lowering the adhesion of the aluminum foil and cathode material. Reaching a temperature of 500 to 600 degrees Celsius improves the effectiveness of the separation process. However, at temperatures beyond 600°C, the aluminum foil becomes brittle and dried, making it challenging to remove the cathode powder. It was suggested that aluminum foil and cathode powder be extracted using the reduction heat treatment approach. The cathode materials are suitably separated from the aluminum foils by regulating the temperature of the reduction reaction. The procedure of regenerative heat treatment is simple and has several advantages. Nevertheless, during heat treatment, the binder decomposes and releases harmful vapors. Even though the cathode powder can be liberated by pyrolysis or thermal treatment of the PVDF binder, the cathode microstructure may be disrupted [33].

2.4. Mechanical processes

Mechanical methods, including pulverizing, screening, and magnetic separation, can separate cathode powder from aluminum foil in lithium batteries. The primary drawback of mechanical methods is that the components of pulverized batteries are not entirely segregated, and the environment is deemed hazardous due to the decomposition of $LiPF_6$ and dimethyl carbonate during the mechanical process.

3. The procedure of extracting metal

Direct, hydrometallurgy, and pyrometallurgy are the three main techniques used in the extraction process. This section looks into these approaches.

3.1. Pyrometallurgy

The recovery of valuable metals from used LIBs is frequently achieved through high-temperature reduction smelting, a pyrometallurgical process. Following this process, the precious metals are regenerated and recovered as alloys. For instance, Umicore Company developed a recycling process that incorporates hydrometallurgical and pyrometallurgical techniques [33]. Pretreatment is not necessary to place used batteries directly in the melting furnace. Heat is generated by the plastic, organic solvent, and graphite in batteries during combustion, while the metal components are regenerated and converted into alloys. Cobalt oxides and nickel hydroxides are obtained by purifying the alloys using sulfuric acid scouring and solvent extraction. Despite the absence of pre-treatment, this process results in lithium loss. Researchers have developed a novel method combining hydrometallurgy and pyrometallurgy to extract precious metals from LIBs that have been used up, intending to minimize lithium loss during recovery. The reductive melting method was employed to extract precious metals from LIBs that have been used up. These valuable metals, such as iron, nickel, cobalt, and manganese, are transformed into alloys. The alloy is acid-washed and subsequently converted into pure lithium with the assistance of sulfuric acid [34].

In a nitrogen atmosphere, the $LiCoO_2$ cathode particles and graphite were heated to 1000 degrees Celsius for 30 minutes. Products that have been cleaned (cleaning is the process of heating metal that contains sulfide in the presence of oxygen) endure partial oxidation, resulting in the formation of sulfur dioxide. The cleansing reaction is conducted in furnaces with a fluid bed at 500 to 700 degrees Celsius. After being purified, the carbon, cobalt, and lithium carbonate were dissolved in water and separated by magnetic separation. The lithium concentration in the lithium-rich solution was only 337.4 mg/L, making lithium recovery difficult. [35].

Ho et al. proposed a novel approach to recovering used LIBs, which was informed by their previous research. This method was implemented in an argon atmosphere and low-temperature purification. Lithium carbonate was extracted from the rinsed product by washing it. The results indicated that the cleansed products contained cobalt, nickel, lithium carbonate, and manganese oxide. After cleaning, the items were dissolved in water, and CO_2 was added. 19% carbon was used to renew the cathode materials for three hours at 650 degrees Celsius. Insoluble Li_2CO_3 is transformed into $LiHCO_3$ as a consequence of this mechanism. Lithium carbonate will be extracted from the solution by concentration, crystallization, and recovery. The solution had a solid-to-liquid ratio of 100 g/L, a lithium concentration of 4.36 g/L, a carbon dioxide flow rate of 20 ml/min, and a washing period of two hours [36–39]. Furthermore, the recycling procedure results in the loss of lithium, which is a disadvantage of pyrometallurgical recycling that must be rectified.

3.2. Hydrometallurgy

The powder separated from the aluminum foil is removed during the pre-treatment phase of the hydrometallurgical technique to recover metals from old LIBs. This makes it easier to recover the metals by acid washing. Inorganic and organic acids are this process's most frequently employed

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cleansing agents. Hydrochloric acid [40–43], sulfuric acid [44,45], nitric acid [46], and phosphoric acid [47,48] are the most common mineral acids employed as cleansing agents to extract metals from batteries. Spent LIBs are utilized. Sodium bisulfite [49], glucose [50], cobalt, and manganese will be reduced by their higher capacity in the solid phase, causing either Co^{2+} or Mn^{2+} to dissolve readily with the aid of reducing agents such as hydrogen peroxide [51,52]. The acid-washing process is affected by temperature, reaction duration, acid concentration, solid-to-liquid ratio, and reducing agent concentration. Nitric acid, hydrochloric acid, and sulfuric acid were used to wash the NCA cathode particles. The results indicate that the acid type significantly influences the metals' cleansing rate. The most effective conditions for acid cleansing are a concentration of 4 mol/L of hydrochloric acid and a solid-to-liquid ratio of 50 g/L at 90°C for 18 hours. Approximately all-important metals in laboratory settings are soluble in cathode powder [41]. Without reducing agents and converting Co^{2+} to Co^{3+}, it is often difficult to remove the Co^{2+} from the NCA cathode material. Consequently, the solubility of metals is increased, and the washing efficiency is more appropriate when not using a reducing agent. Hydrochloric acid, nitric acid, and sulfuric acid are washing agents. This is due to the chlorine ions in hydrochloric acid. The process will follow equation 1 when hydrochloric acid is employed as a washing agent and $LiCoO_2$ is used as a primary material.

$$2\mathrm{LiCoO_2} + 8\mathrm{HCl} \rightarrow 2\mathrm{LiCl} + 2\mathrm{CoCl_2} + 4\mathrm{H_2O} + \mathrm{Cl_2} \quad (1)$$

Many environmental issues are caused by chlorine production during the cleansing process, as indicated by Equation 1. Consequently, some researchers employ nitric or sulfuric acid instead of hydrochloric acid to clean the $LiCoO_2$ cathode powder. For instance, the $LiCoO_2$ cathode was recovered at 75°C using 1 mol/L hydrogen peroxide and nitric acid. In the absence of hydrogen peroxide, the cleansing efficiency of lithium and cobalt was determined to be 75% and 40%, respectively. When 1.7 volume percent of hydrogen peroxide was employed in this procedure, the washing efficiency of lithium and cobalt increased to over 99%. The primary cause of this increase is the reduction of Co^{3+} to Co^{2+} in the presence of hydrogen peroxide [46]. Cobalt oxalate (CoC_2O_4) was recovered from previously used LIBs using hydrometallurgical techniques such as alkaline washing, acid washing, solvent extraction, and chemical precipitation. Sulfuric acid was used as a cleaning agent and hydrogen peroxide as an oxidizing agent. The findings showed that at 85 degrees Celsius, 100 g/L solid-to-liquid ratio, 120 minutes of exposure to 4 mol/L sulfuric acid, and a 10-volume percent hydrogen peroxide solution, the washing efficiency of cobalt and lithium is 95% and 96%, respectively. The pH is adjusted to the ideal level to get ions to precipitate out of the solution, and cobalt will be extracted using the P_5O_7 extractor. Afterward, ammonium oxalate precipitates cobalt oxalate, resulting in a purity of over 99%. Optimizing metal metabolism in mineral acids is effortless. Nevertheless, mineral acids generate acidic effluents of SO_2, Cl_2, NO_x, and other hazardous gases, contributing to environmental pollution. Conversely, the industrial application of organic acids is not feasible due to their exorbitant expense. Sulfuric acid is typically employed as a washing agent in the recycling procedure.

Compared to the waste produced during the LIBs' cathode manufacturing process, the products that result from the lithium battery recycling process are more intricate and contain a more significant number of metal impurities (such as iron and aluminum) that are introduced into the cathode powder during the pre-purification stage. When used to cleanse cathode materials, the acid-washing solution does not exhibit optimal selectivity for metal recovery. This is due to various metal ions, which complicates product separation and purification. The two primary methods for recovering metals from LIBs are hydrometallurgy and pyrometallurgy. Nevertheless, pyrometallurgical recycling results in substantial energy consumption and metal loss. Conversely, the hydrometallurgical recycling procedure

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necessitates extensive chemical consumption. Consequently, hydrometallurgy and pyrometallurgy are incompatible with the environment. The current economic and infrastructural challenges in used battery processing offer little incentive to lithium battery recyclers to recycle them correctly. Although conventional pyrometallurgy and hydrometallurgy methods have been employed in the commercial recycling of LIBs, inefficient processes and high quantities of corrosive chemicals result in secondary pollution with significant CO_2 emissions. A procedure that destroys used batteries' energy or economic value will be inherently inefficient [53], as they still retain 80% of their initial capacity [54]. The overall battery recycling rate is reduced as a function of the total cell due to the primary concentration of recyclers on the recovery of valuable materials, such as cobalt. In this regard, direct recycling technology has been proposed as a viable substitute for traditional recycling.

3.3. Direct recycling

In contrast to hydrometallurgy and pyrometallurgy, direct recycling is an environmentally friendly and relatively gentle procedure that does not necessitate using energy or chemicals. In addition to preventing the discharge of environmental pollutants, this straightforward process also prevents excessive waste and water pollution. Furthermore, by retaining a significant amount of the energy in the materials from the primary manufacturing process, direct recycling immediately recovers or renews the deteriorated electrode materials and avoids destroying old battery materials. This process cannot produce precursor products from hydrometallurgy and pyrometallurgy, including transition metal compounds or hydroxides. However, it can yield cathode materials that are both highly valuable and entirely suitable for immediate use in the development of novel LIBs. According to previous product life cycle analysis assessments, the elemental products recovered through pyrometallurgical and hydrometallurgical recycling procedures are not as valuable as cathode materials regenerated through direct recycling.

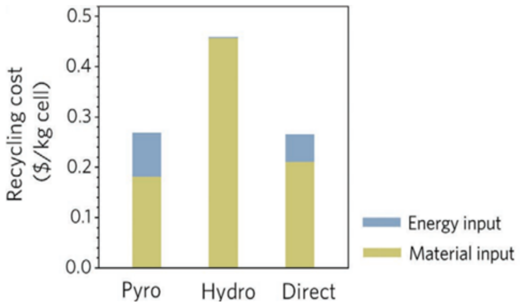

Figure 4: Chart of recycling cost in terms of input materials and energy for each method [55]

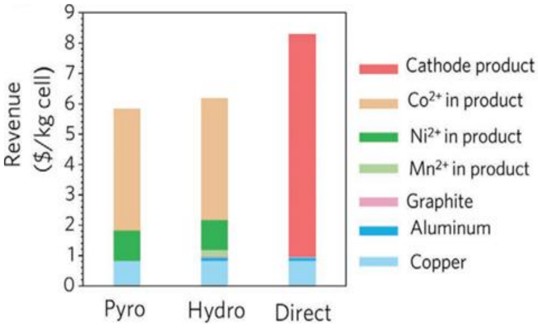

Figure 5: Chart according to various materials [55]

This is primarily because the products do not require resynthesis and can be directly used to generate new LIBs. Furthermore, direct recycling eliminates the use of hazardous and toxic compounds and processes with high energy consumption, reducing greenhouse gas emissions and energy consumption. The analysis of the recycling cycle of LIBs has demonstrated that direct recycling will substantially reduce the costs of energy and chemical consumption in comparison to conventional pyrometallurgy and hydrometallurgy processes (as illustrated in Figures 4 and 5).

Generally speaking, the loss of Li^+ in the crystal structure is the main reason for compositional and structural flaws in damaged cathode materials after extended electrochemical cycles. Consequently, the related issues can be resolved through direct recycling based on effective lithium filling, which can regenerate the cathode material to meet the same quality standards as commercial pure cathode powder. The process of electrochemical relithiation (ECR) replenishes

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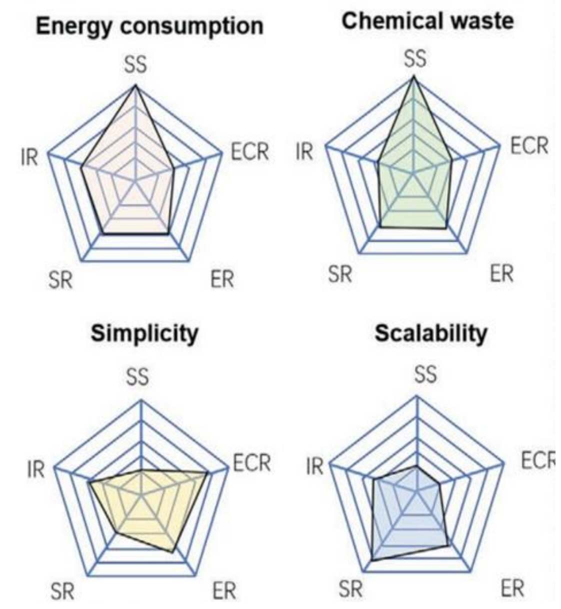

Figure 6: Comparison of different re-lithiation methods [56]

the lithium concentration of cathode materials in lithium-ion batteries via electrochemical processes; the second technique is thermal ion relithiation (IR), a direct recycling technique that may clean damaged lithium-ion batteries of impurities, the third method is solid state regeneration (SS), which attempts to keep the electrode material in its original condition and lessen the need for intensive reprocessing by removing and simultaneously rebuilding their structure and lithium content, the fourth is eutectic relithiation(ER), which recycles by using green eutectic solvent. Solution re-lithiation (SR) is the most recent method of lithiation (Figure 6 compares these methods).

In particular, the copper and aluminum foils in the battery cells are first separated from one another, and the battery cells are opened for each battery that contains cathode powder with a distinct chemical formula. The cathode and graphite materials on copper and aluminum foil are separated, and copper and aluminum fragments are collected. The separated cathode powder is subjected to the regeneration process, which includes aqueous lithiation and short sintering. Ultimately, the cathode material that has been regenerated is employed to generate new cells. The inherent physical and chemical properties and degradation mechanisms in the cathode powder of lithium batteries with different chemical formulas are distinct, necessitating that the specific conditions of direct regeneration for each material be adjusted accordingly. These conditions include the concentration of lithium solutions, reaction temperature, and pressure, as well as the heating operation's temperature, duration, and atmosphere. The following are a few examples of processes.

3.3.1. Direct recycling of olivine cathode material of the $LiFePO_4$ type

Because of its remarkable thermal stability, cheap cost, and long cycle life, $LiFePO_4$ (LFP) is crucial in the LIB industry, especially in electric tools, electric cars, and network energy storage [57–59]. Cell surface engineering and optimization developments have allowed advanced LFP batteries to achieve energy densities of more than 175 Wh/kg per cell surface. This development has made them a promising option for future electric vehicles [60]. Nevertheless, the economic incentive to recycle with conventional methods is minimal due to the nonexistence of essential metals (e.g., Cobalt and Nickel) in LFP. In this scenario, direct recycling can substantially reduce recycling costs while simultaneously producing higher-value products, as it does not require large quantities of corrosive chemicals or energy-intensive processes. A comprehensive understanding of the degradation process is crucial for formulating efficient direct recycling methods. In a study, the microstructure of $LiFePO_4$ was examined at the atomic scale, and 40% of the lithium was extracted through chemical separation [61]. The stoichiometry of $Li_{1.0}FeO_4$ is maintained by most of the particle, as illustrated in Figure 7, and the rare Li regions are primarily located near the surface. This is under the core shrinkage model that was previously reported [62]. It is essential to mention that the aggregate surface of the particle exhibits a stable atomic arrangement, which suggests that the olivine structure has been effectively preserved even after separation.

The microstructure of LFP, subjected to electrochemical use for 500 cycles, was analyzed. The primary source of capacity decrease in damaged LFP may be inferred as the loss of

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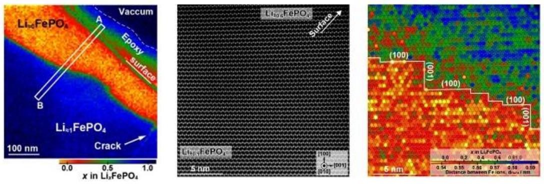

Figure 7: Investigation of $LiFePO_4$ cathode level [61]

lithium inside the crystal structure [63,64].The regeneration of LFP depends on the effective incorporation of lithium ions into the crystal structure. Lithium sources include inorganic lithium compounds (e.g., Li_2CO_3 and LiOH), lithium halides (e.g., LiI and LiBr), and organic lithium salts (polycyclic aryl-lithium compounds). The regeneration process is given by Equation 2.

$$FePO_4 + \; Li^+ + e^- \rightarrow LiFePO_4 \quad (2)$$

3.3.1.1. Regeneration of solid states

To replenish the Li^+ lost in the cathode during re-cycling, the lithium-containing salt mixture and decomposed cathodes are heated to a relatively high temperature in the fundamental concept of solid-state regeneration in LFP. The restoration of consumed LFP will be affected by the difficulties associated with completely removing conductive carbon and PVDF binder from nano-sized LFP particles while maintaining structural integrity. The investigation used PVDF binder and conductive agents as carbon sources for in-situ LFP coating. Li_2CO_3 and LFP were directly combined in a 1:1 molar ratio, and the resulting mixture was annealed at 700 °C for 3 hours in a N_2 atmosphere (Figure 8) [65].

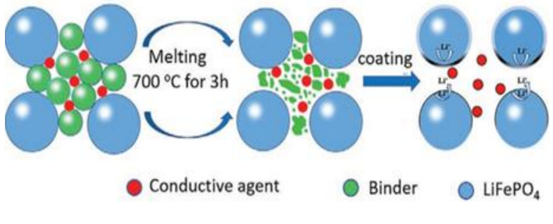

Figure 8: Schematic of the method of using binder and conductive materials as a carbon source [65]

During the annealing process, the PVDF binder decomposes into amorphous carbon, which is deposited on the surface of the LFP cathode particles. The reaction between LFP and HF derived from PVDF decomposition will result in an unwanted loss of Li^+, although the electrochemical efficacy of the regenerated LFP was enhanced. Before annealing the exhausted LFP mixture, the PVDF and conductive agent were calcined at a low temperature of 450°C for 2 hours in an air atmosphere to mitigate the effects of PVDF binder decomposition. The supplementary lithium salt was also eradicated. This study asserted that the crystal structure of LFP was not affected by the pre-elimination phase. The capacity was restored from 98 to 132 mAh at 0.2C due to the regeneration process [66]. This performance must be further improved to obtain a performance comparable to that of advanced commercial materials (150-165 mAh/g [21]). Intriguingly, Shi's research [67] revealed that cyclic LFP contained impurities Li_3PO_4, P_2O_5, and Fe_2O_3, in addition to the primary olivine phases of LFP and $FePO_4$. This finding starkly contrasts previous reports [62–64]. As mentioned above, the mixture was employed directly as a precursor for synthesizing new LFP without adding any additional lithium source. Although a pure LFP phase could be attained below 350 °C, the yield remained inadequate. To obtain optimal electrochemical performance and increase crystallinity, temperatures exceeding 650°C are necessary. Nevertheless, additional research should be conducted to determine the degradation mechanism associated with the composition of the LFP consumed due to the identification of various impurities in prior reports [67]. These impurities may be the result of varying degrees of battery degradation. Solid-state recycling is straightforward; however, it is difficult to guarantee the integrity of the reconstituted LFP. This is because LFP is easily decomposed during the pre-heating stage of the oxide or in the post-sintering process. The research has shown that the reduced product is highly susceptible to the sintering atmosphere, temperature, duration, and quantity of Li^+ that is introduced. To prevent LFP oxidation, it is generally recommended to use an inert or reducing atmosphere. The degradation of LFP before complete amplification is achieved is likely to occur at higher temperatures or for extended periods, resulting in a low-purity final

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product [65,66]. Sintering for an insufficient time does not guarantee complete lithiation, and a time of more than 3 hours leads to the presence of P_2O_5 impurity phases [65]. Also, the decomposition of LFP was observed at a temperature higher than 650 °C. In addition, the electrochemical performance of the regenerated cathode materials is significantly impaired by the formation of Fe_3P and Li_2O impurities due to excess Li_2CO_3 [68]. Consequently, it is imperative to maintain a suitable equilibrium of processing conditions to produce a high-quality reconstructed LFP.

3.3.1.2. Electrochemical regeneration

Another technique for regenerating depleted LFP cathode materials is electrochemical lithiation. The electrode used for the sample was LFP. An Ag/AgCl reference electrode and an auxiliary electrode made of platinum mesh were attached to the cathode. Li_2SO_4 solution was used as a Li source and electrolyte. A spontaneous and sequential electro-lithiation process was used to finish the repair. A fraction of Li^+ may spontaneously diffuse into Li-deficient LFP, primarily when no current is supplied and the Li to Fe ratio is between 0.67 and 0.89. When a steady cathodic current is provided, the excess Li^+ that remains in unoccupied capacity eventually restores the stoichiometric composition of LFP. The regenerated LFP showed a remarkable retention capacity of 95.3% after 500 cycles and a discharge capacity of 135.2 mAh/g at 1C following the sintering procedure. Although the electrochemical characteristics of the regenerated LFP are similar to those of commercial materials, using liquid electrolytes with a three-electrode system may limit its size, and the separated electrodes must be reduced to a standard dimension. To couple cells with deteriorated LFP, Guo et al. used pre-lithiated graphite as a novel anode. They used electrochemical pre-lithiation to store the Li source in the graphite anode.

During the discharge process, Li^+, which is pre-stored on the graphite side, may go to the cathode and transform $FePO_4$ into LFPs. Additionally, separator pre-lithiation was used. A commercial separator was coated with a thin coating of $Li_2C_2O_4$. This substance breaks down at a specific applied voltage to compensate for the lack of lithium in the cathode and releases more Li^+. Eliminating steps like slurry preparation and coating before cell assembly and using in-situ electrochemical regeneration methods that use pre-coated graphite anodes or separator chemical repair techniques may lower recycling costs.

3.3.1.3. Restoration that is solution-based

Although damaged cathode materials may be repaired via solid-state regeneration and electrochemical re-lithiation, assessing the state of health (SOH) of a sizable percentage of used cells from various sources might be difficult. Furthermore, the recovery of depleted lithium is the focus of most studies. In practice, a tiny proportion of Fe ions may move to Li sites, where they might produce Fe/Li antisite defects. According to reports, the obstruction of lithium-ion diffusion paths can result in a 5% reduction in capacity and collapse due to only 0.1% of antisite defects. However, it is equally crucial to eliminate Fe/Li antisite defects to regain full functionality during regeneration. Chen's team found that the employed LFP cathode materials had 47.1% lithium vacancy defects and 4.81% Fe/Li antisite faults in batteries with a 50% capacity decrease.

The high activation energy (approximately 1.4 eV) required for Fe^{2+} to occupy the Li site and relocate to the original position of M2 results from the intense electrostatic repulsion of the surrounding Fe^{3+}.

LiOH was mixed with citric acid (CA) to reduce energy consumption (Figure 9) [21]. Fe^{3+} electrons may lessen electrostatic repulsion forces by efficiently absorbing energy. At room temperature, this reaction is thermodynamically advantageous. After brief annealing, the regenerated LFP exhibited a regular crystal structure and good cycle stability at high speeds to fix structural flaws.

Compared to pyrometallurgical and hydrometallurgical recycling routes, regeneration can be conducted under mild conditions (ambient pressure and 60°C). This process provides high

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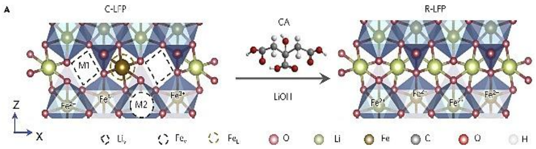

Figure 9: Schematic of the use of citric acid as a reducing agent [49]

Economic efficacy and reduces energy consumption and greenhouse gas emissions (GHG). Furthermore, to support the future development of direct recycling technology, it is essential to have a fundamental understanding of the atomic-scale processes of LFP degradation and regeneration. Similarly, to recover LFP that was lost during the hydrothermal process, Li et al. used Na_2SO_3 as a reducing agent in LiOH solution. They found that the electrochemical performance of the regenerated LFP was also hampered at a very high process temperature of 180 °C and that the capacity of the depleted LFP could not be recovered at a comparatively low process temperature of 120 °C. The optimal temperature was 150 degrees Celsius. Wang and associates substituted hydrazine ($N_2H_4.H_2O$) for the reducing agent during the hydrothermal regeneration process.

They discovered that the stoichiometric amount and equivalent Li^+ defects in the spent LFP could effectively regenerate the materials. Due to the excess Li^+ in the solution, the final product's composition did not exhibit any discernible distinctions.

In contrast to the solid-state sintering recycling process, this example demonstrates the self-saturation feature of solution-based re-lithiation techniques. Additionally, raising the hydrothermal temperature from 120°C to 200°C can increase the capacity of regenerated LFP from 135 to 139 mAh/g (Figure 10) [69].

Cheng's team used CH_3COOLi as the source of lithium and ethanol as the primary medium and reducing agent. In addition to these molecules, PVP was added to the solution as a nitrogen source. LFP covered with N-doped carbon was produced by relithiation and sintering. The interaction between nitrogen and iron inhibited the creation of Fe/Li anti-site defects during cycling, and the regenerated LFP outperformed the commercial one.

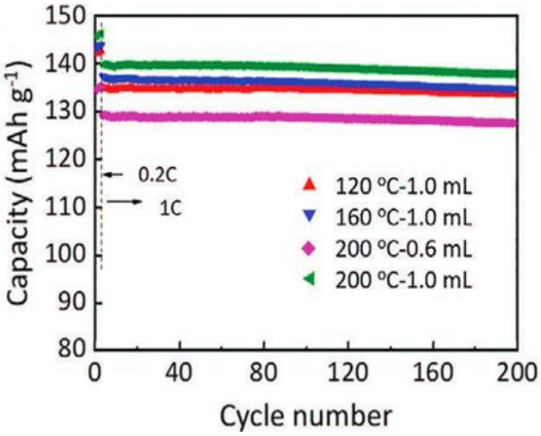

Figure 10: The effect of temperature on the recycling process [50]

3.3.1.4. Eutectic restoration

A eutectic solution comprises a certain percentage of mixed lithium compounds that melt at a low enough temperature to provide strong ionic conductivity and decreased viscosity. This liquid system is a medium that contains lithium and has great potential for re-lithiation. However, when heated in an air environment, LFP olivine is susceptible to oxidation even at modest temperatures. Xia and colleagues created a reaction system consisting of $LiNO_3.FeC_2O_4$. The reducing agent used was sucrose, which was used to stop LFP from oxidizing. The battery's composition and functionality were fully recovered after re-lithiation at 300 °C and baking at 650 °C.

3.3.2. Recycling utilizes layered oxides directly $Li_{1-x}CoO_2(0<x<1)$

The principal compound of the $LiMO_2$ family, $LiCoO_2$ (LCO), has a broad range of applications in portable electronic equipment. In addition to lithium shortages in the bulk crystal structure, which was previously noted in the particles participating in the LFP battery cycle, deteriorated spinel phases (formed from the layered structure) were also seen on the surface of the cathode particles in the degraded LCO.

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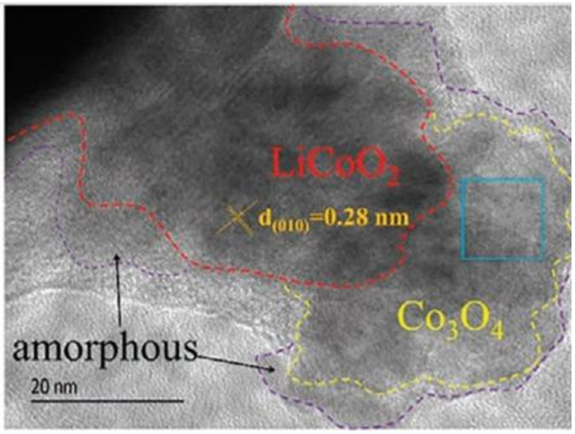

Figure 11: Improving the crystal structure [70]

In addition to enhancing the lithium deficiency in the spinel phase, the LCO crystal (primarily Co_3O_4) should transform its original stratified structure (Figure 11). The initial stage of re-lithiation can be completed in either aqueous or solid environments. The subsequent stage is typically conducted during a brief annealing phase that contains approximately 5% excess Li_2CO_3. Equations 3 illustrate the pertinent reactions.

In addition to enhancing the structure, the spinel phase (primarily Co_3O_4) should be converted to the original stratified structure (Figures 12) due to the absence of lithium in the LCO crystal [70].

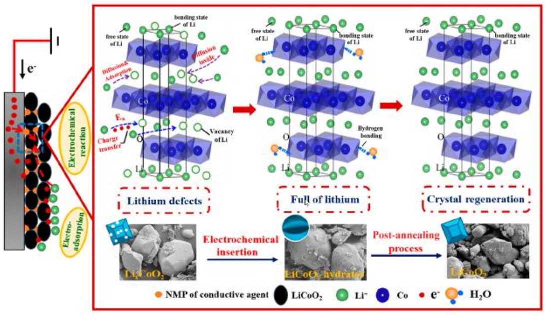

Figure 12: Schematic of electrochemical regeneration of LCO [71]

The initial stage of re-lithiation can be completed in either aqueous or solid environments. The subsequent stage is typically conducted during a brief annealing phase that contains approximately 5% excess Li_2CO_3. Equations 3 and 4 illustrate the reactions that are pertinent.

$$Li_{1-x}CoO_2 + xLi^+ + xe^- \rightarrow LiCoO_2 \qquad (3)$$

$$Co_3O_4 + 6Li_2CO_3 + O_2 \rightarrow 12LiCoO_2CO_2 \quad (4)$$

3.3.2.1. Lithium-Ion Battery Spent Cobalt Oxide Cathode Regeneration Using Solid-State Direct Regeneration

To solve compositional and structural flaws and regenerate LCO, several studies have directly mixed the recycled LCO cathode with solid lithium sources (such as Li_2CO_3 and LiOH) and annealed the combination at 800°C to 950°C. Wu et al. found that the Co_3O_4 contaminant phase in the LCO cathode material would persist even after cycling until the Li/Co ratio hit 1.0. Li_2O impurities are present, and the final electrochemical performance decreases as the ratio rises over 1.2. Chen et al. found that the regenerated LCO with a 5% surplus lithium supply exhibits the best LIB performance. Except for the main difficulty in figuring out the exact amount of surplus lithium salt, the solid-state approach works well, and LCO is more thermally stable than LFP.

3.3.2.2. Electrochemical-based regeneration

The electrochemical re-lithiation approach also investigated the regeneration of faulty or Li-deficient LCO. He and his colleagues used an Ag/AgCl reference electrode, a platinum counter electrode plate, and an LCO electrode derived from a depleted lithium-ion battery with a 20% failure or capacity decrease as the sample electrode. When the cathodic current is constant throughout the discharge procedure, Li^+ in the Li_2SO_4 electrolyte can penetrate the damaged LCO cathode and restore Li deficits. The counter electrode released O_2 concurrently. After annealing, the whole cathode structure was restored. Figure 12 provides a crude illustration of the electrochemical regeneration process of LCO [71].

However, during the electrochemical re-lithiation process, the Al foil corrodes due to the electrolyte becoming more acidic due to water oxidation on the counter electrode. Li et al. used a novel LCO electrode instead of the platinum

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counter electrode as an electron donor. The Li_2SO_4 electrolyte stayed almost neutral during the electrochemical relithiation process, and the symmetric relithiation procedure showed no bubbles. Furthermore, the operating electrode showed no signs of aluminum corrosion. The capacity and cycle performance of the LCO electrode were identical to those of the improved commercial sample after a brief annealing process. Even still, the whole manufacturing process was highly complex because the regenerated materials still require purification and exfoliation steps to be used in producing new LIBs. For the direct regeneration of spent cathode materials in situ, electrochemical re-lithiation in cycle batteries is the best option because it doesn't require any further separation steps. Moreover, applying electrochemical re-lithiation widely in aqueous systems is impossible. For instance, protons in the solution can potentially damage multilayer NCM cathode materials.

3.3.2.3. Solution-based restoration

For the first time, spent LCO was successfully regenerated in 2004 by Lee's group [72]. The regeneration process was conducted in a 5 M LiOH solution at 200 °C for 20 hours. After 40 cycles, the regenerated LCO demonstrated 92.2% stability and a 144 mAh/g capacity. This study provided satisfactory verification of the effectiveness of hydrothermal re-lithiation. However, a thorough understanding of the microstructure development in consumed and deteriorated materials is lacking. After closely examining the crystal structure of exhausted LCO, Chen's group [73] discovered that the LCO surface created the Co_3O_4 phase. After hydrothermal re-lithiation, the impurity Co_3O_4 phase was transformed into a stratified LCO phase by a granulation or agglomeration stage.

Furthermore, after a careful examination of several temperatures and times, the ideal condition was found to be hydrothermal relithiation at 180°C followed by thermal annealing at 800°C (Figures 13) [73].

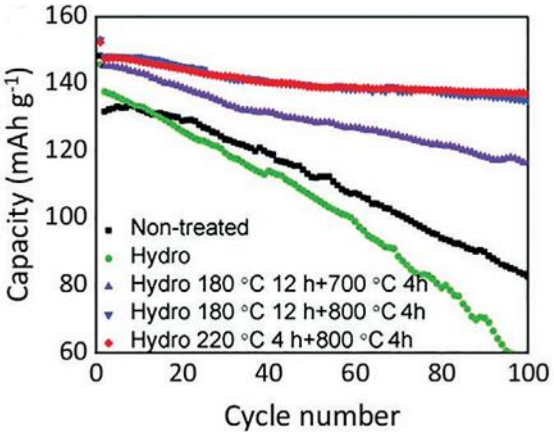

Figure 13: The effect of temperature and time on capacity [73]

Even if extra Li is used in the solution re-lithiation process in the direct recycling based on hydrothermal re-lithiation, the filling of lithium vacancies in the crystal structure ends spontaneously when the stoichiometric composition is attained. However, there is still much to learn about the kinetics and thermodynamics of the lithium-loading process in aqueous solution. More investigation is needed to find out how high pressure and temperature affect the re-lithiation process. It is beneficial to keep conditions relatively temperate to mitigate safety risks during operation and save on recycling costs.

3.3.2.4. Reconstruction based on eutectic mixture

Eutectic solvent exhibits significant and advantageous characteristics, including exceptional solubility, low cost, environmental tolerance, and nontoxicity. To regenerate depleted LCO directly, Cheng et al. developed a $LiCl$-CH_4N_2O eutectic system. By altering the molar ratio between LiCl and CH_4N_2O, the eutectic point may be lowered to less than 120 °C, below the temperature of many hydrothermal regeneration methods used today.

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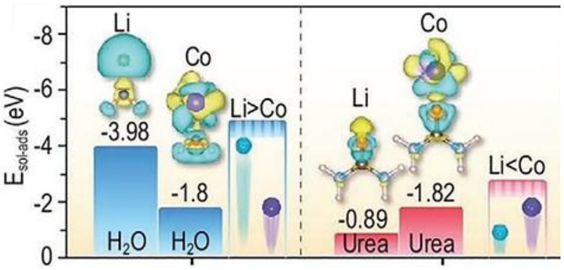

Figure 14: Eutectic system energy diagram [74]

Additionally, they discovered that the loss of Co is a significant factor in the loss of Li^+ in LCO. In their lithiation system, CO2+ diffuses from the incomplete crystal structure more preferentially than Li+ because CO^{2+} has a greater affinity for urea molecules than Li^+ does. Figure 14 illustrates the energy diagrams for the adsorption and dissolution of these materials.

Consequently, the Li/Co ratio is higher in the sample obtained in the LiCl aqueous solution. It was demonstrated in this study that the recycling of eutectic salts can enhance economic efficacy by reducing the cost of raw materials. The cycle of eutectic use and recycling is illustrated in Figure 15 [74].

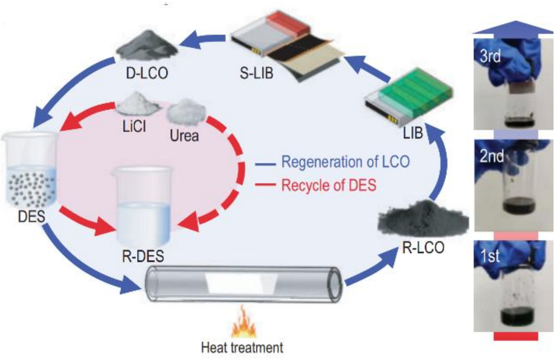

Figure 15: Eutectic solvent use cycle [74]

4. Perspectives

The successful recycling approach promotes the sustainable development of energy storage technology, which mitigates the environmental concerns associated with exhausted LIBs. Compared to commercial hydrometallurgical and pyrometallurgical recycling processes, direct recycling has shown significant benefits in ease of processing, low energy consumption, reduced secondary pollution, and greater economic effectiveness. There has been some success with directly recycling various cathode and anode materials; however, it is currently in the laboratory-scale operational phase. The discarded cathode and anode powders gathered after manual separation have an unusually high purity, forming the basis of the direct regeneration process. However, there are still significant barriers to the practical application of this technology [56].

In particular, the current industrial-scale preprocessing process involves crushing batteries from electric vehicles after discharge. Thus, the final result is a blend of cathode and anode components, conductive agents, PVDF binder, and any remaining impurities (Al, Cu, the like). The section that follows covers the technological difficulties and possibilities involved in creating a scalable direct regeneration procedure.

4.1. A look at the separation of graphite anode and cathodes in lithium-ion battery

Each component must be separated from the others for direct recycling to provide high-quality cathode and anode. Subsequently, they undergo additional purification. Water is typically employed as a foaming agent in flotation, an exceptional method for distinguishing the anode and cathode. Nevertheless, the protons diffuse throughout the crystal structure of the cathode and eliminate Li^+. Furthermore, the foam maker's efficacy has not been optimal thus far, resulting in graphite residues in the used cathode powders. In the same vein, gravity separation has been investigated by forming a suspension in a solvent (e.g., water), resulting in an incomplete separation. Additional research is required to investigate the side effects of proton exchange and graphite impurity indirect regeneration.

4.2. Eliminating the PVDF binder and conductive agent

Impurities included in the binder and conductive particles (e.g., lowering of capacitance state, induction of oxygen loss, creation of thick LiF coating, etc.) also contribute to the degradation of the regenerated active materials. Removing the conductive agent, which is the process of particles attaching through

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surface melting due to heat, with or without pressure, so that they become solid pieces, usually requires a pre-sintering procedure at a low temperature. However, the end outcome is permanently damaged cathode materials with high levels of lithium deficits and poor thermal stability. Furthermore, the reaction between the cathode particles and HF generated by the thermal breakdown of PVDF might further damage the cathode structure. In another way, NMP washing also works well to eradicate them, but it limits the toxicity and expense of overuse. Furthermore, the complete removal of PVDF that has been merged with nanoscale LFP particles is challenging.

4.3. Aluminum and Copper scraps

Al and Cu residues can be eliminated using precise materials in laboratory and small-scale settings. Nevertheless, Al and Cu residues in black powder pose a significant challenge for direct recycling. However, sieving can remove large metals in concentrated reactions and large-scale processing. Metal impurities do not significantly impact the regeneration process; however, they are present in the final products when used to manufacture batteries. It raises significant concerns. Because of the limitations of existing separation methods, the collected wasted cathode and anode powders (also known as "black mass") may not be pure enough. Regardless of the re-lithiation process, metal impurities, copper and aluminum foils, and PVDF binder are sustainability and quality issues for regenerated materials that provide acceptable attributes and remanufactured batteries. Furthermore, the cathode materials of the NCM family possess similar properties, rendering it nearly impossible to separate them after combining. Consequently, it is imperative to employ advanced separation techniques to enhance the integrity of used electrode materials for the regeneration of battery materials that have reached the end of their useful life in recent years.

The production chain will need significant improvements and the cooperation of manufacturers, governments, and researchers in the future to ensure the sustainability of battery development. First, battery components and formats should be standardized and designated using the Global Battery Identity Passport (BIGP). This tag, which recognizes the battery chemistry on a digital chip, can significantly improve the separation of batteries with different cathode powders. Second, the prior idea can be used to protect recycling operators, lower expenses, and ease safety issues while facilitating the robotic separation of batteries with different cathode particles. Third, it is advised to swap out the outdated NMP-based PVDF binder for a fresh one that is soluble in alcohol or water. This is essential for the efficient and environmentally friendly removal of binder contaminants and the active material peeling from aluminum sheets that are currently in use. It also provides the opportunity to obtain highly pure powdered waste electrode material. As a result, the previously described advancements greatly simplify the process of separation and regeneration and optimize the supply chain of minerals required for LIBs. Apart from the difficulties related to pre-treatment, the subsequent facets of innovative regeneration methods necessitate additional investigation and refinement:

The rapidly changing market is a significant obstacle for direct regeneration methods available today. The majority of electric vehicle batteries manufactured in the last ten years use NMC111. However, the use of compounds rich in nickel, including NCA and NMC622, has been more widespread. Recycling techniques must keep up with the battery's technological advancements. For the development of next-generation LIB cathode materials and beyond LIB chemistry, such as all-solid-state batteries and sodium-ion batteries, it is essential to develop direct recycling technology. The substantial worry and society's need for energy storage devices with a high density of LIBs means that the conventional LMO and NCM111 cannot meet the needs of consumers. This suggests that the recycled cathode is probably made using an outdated recipe, which will limit its marketability. Techniques for recycling and converting obsolete materials into more sophisticated cathode compositions must be developed and assessed. It would be more advantageous to create technologies that employ NCM111 as the primary raw material to make NCM622 (or perhaps NCM811) [70].

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However, recycling garbage into goods that include high-density battery components is a viable substitute approach [75]. The three techniques of direct, hydrometallurgy, and pyrometallurgy are contrasted in the following section. Each method's benefits, drawbacks, profit, and loss have been compared [68].

5. Conclusions

In conclusion, the recycling practices of common cathode materials, such as LFP, LCO, and NCM, were the main emphasis of this review research. Advanced recycling methods appropriate for each electrode material were thoroughly examined from a materials viewpoint since various electrode materials' physical and molecular properties govern specific recycling conditions. The possibilities of each technique, as well as the challenges to its industrial use, were covered. Future opportunities for LIB recycling design and manufacturing were proposed to facilitate LIB recycling better. The repurposing of used batteries and cathode materials into next-generation cathodes and the mineral supply cycle, the development of universal direct recycling technology for a variety of electrode materials, the prerequisites for additional direct recycling optimization, and the potential industrial applications of direct recycling are all highlighted in this review.

Declaration of Conflicting Interests

The authors declared no potential conflicts of interest regarding the research, authorship, and/or publication of this article.

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References

[1] F. Boorboor-Ajdari, F. Abbasi, A. Fathollahi Zonouz, A. Heydari, H. Shokoui Mehrabani, The Role of Dopamine Additive Toward Enhancing Performance of LFP-based Li-ion Battery, Appl. Chem. Today 19 (2024) 225–248.

[2] P. Zhao, G. Kuang, R. Qiao, K. Liu, F. Boorboor Ajdari, K. Sun, C. Bao, M. Salavati-Niasari, J. Song, Regulating Lithium Ion Transport by a Highly Stretchable Interface for Dendrite-Free Lithium Metal Batteries, ACS Appl. Energy Mater. 5 (2022) 10141–10148.

[3] J. Tan, Z. Wang, G. Li, H. Hu, J. Li, R. Han, D. Zhang, Electrochemically driven phase transition in $LiCoO_2$ cathode, Materials (Basel). 14 (2021) 1–10. https://doi.org/10.3390/ma14020242.

[4] A. Pražanová, Z. Plachý, J. Kočí, M. Fridrich, V. Knap, Direct Recycling Technology for Spent Lithium-Ion Batteries: Limitations of Current Implementation, Batteries 10 (2024). https://doi.org/10.3390/batteries10030081.

[5] P. Xu, D.H.S. Tan, B. Jiao, H. Gao, X. Yu, Z. Chen, A Materials Perspective on Direct Recycling of Lithium-Ion Batteries: Principles, Challenges and Opportunities, Adv. Funct. Mater. 33 (2023) 1–63. https://doi.org/10.1002/adfm.202213168.

[6] A.M. Aghdam, N.M. Chahartagh, S. Namvar, M. Ershadi, F.B. Ajdari, E. Delfani, Improving the performance of a SnS_2 cathode with interspace layer engineering using a Na^+ insertion/extraction method for aqueous zinc ion batteries, J. Mater. Chem. A 12 (2024) 1047–1057.

[7] Q. Nie, W. Luo, Y. Li, C. Yang, H. Pei, R. Guo, W. Wang, F.B. Ajdari, J. Song, Research Progress of Liquid Electrolytes for Lithium Metal Batteries at High Temperatures, Small 19 (2023) 2302690.

[8] G. Lombardo, B. Ebin, B.-M. Steenari, M. Alemrajabi, I. Karlsson, M. Petranikova, Comparison of the effects of incineration,

[DOI: 10.22068/ase.2024.690]

vacuum pyrolysis and dynamic pyrolysis on the composition of NMC-lithium battery cathode-material production scraps and separation of the current collector, Resour. Conserv. Recycl. 164 (2021) 105142.

[9] M. Petranikova, P.L. Naharro, N. Vieceli, G. Lombardo, B. Ebin, Recovery of critical metals from EV batteries via thermal treatment and leaching with sulphuric acid at ambient temperature, Waste Manag. 140 (2022) 164–172.

[10] J. Wang, Q. Zhang, J. Sheng, Z. Liang, Y. Chen, G. Zhou, H. Cheng, in lithium-ion batteries, (2023).

[11] Q. Jing, J. Zhang, Y. Liu, W. Zhang, Y. Chen, C. Wang, Direct Regeneration of Spent LiFePO4Cathode Material by a Green and Efficient One-Step Hydrothermal Method, ACS Sustain. Chem. Eng. 8 (2020) 17622–17628. https://doi.org/10.1021/acssuschemeng.0c07166.

[12] D.L. Thompson, J.M. Hartley, S.M. Lambert, M. Shiref, G.D.J. Harper, E. Kendrick, P. Anderson, K.S. Ryder, L. Gaines, A.P. Abbott, The importance of design in lithium ion battery recycling–a critical review, Green Chem. 22 (2020) 7585–7603.

[13] Z.J. Baum, R.E. Bird, X. Yu, J. Ma, Lithium-Ion Battery Recycling─Overview of Techniques and Trends, ACS Energy Lett. 7 (2022) 712–719. https://doi.org/10.1021/acsenergylett.1c02602.

[14] B.K. Biswal, B. Zhang, P. Thi Minh Tran, J. Zhang, R. Balasubramanian, Recycling of spent lithium-ion batteries for a sustainable future: recent advancements, Chem. Soc. Rev. 53 (2024) 5552–5592. https://doi.org/10.1039/d3cs00898c.

[15] N. Lingappan, W. Lee, S. Passerini, M. Pecht, A comprehensive review of separator membranes in lithium-ion batteries, Renew. Sustain. Energy Rev. 187 (2023) 113726. https://doi.org/10.1016/j.rser.2023.113726.

[16] P.M. Tembo, C. Dyer, V. Subramanian, Lithium-ion battery recycling—a review of the material supply and policy infrastructure, NPG Asia Mater. 16 (2024). https://doi.org/10.1038/s41427-024-00562-8.

[17] W. Liu, M. Liu, F. Ma, M. Qin, W. Zhong, X. Chen, Z. Zeng, S. Cheng, J. Xie, Direct lithium extraction from spent batteries for efficient lithium recycling, Sci. Bull. 69 (2024) 1697–1705. https://doi.org/10.1016/j.scib.2024.02.034.

[18] B. Mosallanejad, S.S. Malek, M. Ershadi, A.A. Daryakenari, Q. Cao, F.B. Ajdari, S. Ramakrishna, Cycling degradation and safety issues in sodium-ion batteries: Promises of electrolyte additives, J. Electroanal. Chem. 895 (2021) 115505.

[19] F. Boorboor Ajdari, A. Fathollahi Zonouz, A. Heydari, H. Shokoui Mehrabani, M. Shakourian-Fard, G. Kamath, F. Ghasemi, M. Kahrizi, Exploring the Effects of Dopamine and DMMP Additives on Improving the Cycle Boosting and Nonflammability of Electrolytes in Full-Cell Lithium-Ion Batteries (18650), J. Phys. Chem. C 127 (2023) 8195–8207.

[20] F. Boorboor Ajdari, P. Asghari, A. Molaei Aghdam, F. Abbasi, R.P. Rao, A. Abbasi, F. Ghasemi, S. Ramakrishna, N. Mikaeili Chahartagh, Silicon Solid State Battery: The Solid-State Compatibility, Particle Size, and Carbon Compositing for High Energy Density, Adv. Funct. Mater. n/a (2024) 2314822. https://doi.org/https://doi.org/10.1002/adfm.202314822.

[21] P. Xu, Q. Dai, H. Gao, H. Liu, M. Zhang, M. Li, Y. Chen, K. An, Y.S. Meng, P. Liu, Efficient direct recycling of lithium-ion battery cathodes by targeted healing, Joule 4 (2020) 2609–2626.

[22] M. Contestabile, S. Panero, Bjj. Scrosati,

[DOI: 10.22068/ase.2024.690]

A laboratory-scale lithium-ion battery recycling process, J. Power Sources 92 (2001) 65–69.

[23] X. Zhou, W. He, G. Li, X. Zhang, J. Huang, S. Zhu, Recycling of electrode materials from spent lithium-ion batteries, in: 2010 4th Int. Conf. Bioinforma. Biomed. Eng., IEEE, 2010: pp. 1–4.

[24] X. Zhang, Y. Xie, H. Cao, F. Nawaz, Y. Zhang, A novel process for recycling and resynthesizing $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ from the cathode scraps intended for lithium-ion batteries, Waste Manag. 34 (2014) 1715–1724.

[25] D. Marchese, C. Giosuè, A. Staffolani, M. Conti, S. Orcioni, F. Soavi, M. Cavalletti, P. Stipa, An overview of the sustainable recycling processes used for lithium-ion batteries, Batteries 10 (2024) 27.

[26] M.K. Tran, M.-T.F. Rodrigues, K. Kato, G. Babu, P.M. Ajayan, Deep eutectic solvents for cathode recycling of Li-ion batteries, Nat. Energy 4 (2019) 339–345.

[27] Y. Bai, N. Muralidharan, J. Li, R. Essehli, I. Belharouak, Sustainable direct recycling of lithium-ion batteries via solvent recovery of electrode materials, ChemSusChem 13 (2020) 5664–5670.

[28] J. Nan, D. Han, X. Zuo, Recovery of metal values from spent lithium-ion batteries with chemical deposition and solvent extraction, J. Power Sources 152 (2005) 278–284.

[29] Y. Sun, H. Yang, J. Li, J. Li, X. Zhuge, Y. Ren, Z. Ding, A large volume and low energy consumption recycling strategy for $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ from spent ternary lithium-ion batteries, J. Power Sources 602 (2024) 234407.

[30] P.G. Schiavi, A.G. Marrani, O. Russina, L. D’Annibale, F. Amato, F. Pagnanelli, P. Altimari, Aqueous electrochemical delithiation of cathode materials as a strategy to selectively recover lithium from waste lithium-ion batteries, J. Energy Chem. 88 (2024) 144–153.

[31] L. Yang, H. Zhang, F. Luo, Y. Huang, T. Liu, X. Tao, G. Yang, X. Luo, P. Shao, Minimized carbon emissions to recycle lithium from spent ternary lithium-ion batteries via sulfation roasting, Resour. Conserv. Recycl. 203 (2024) 107460.

[32] L. Sun, K. Qiu, Vacuum pyrolysis and hydrometallurgical process for the recovery of valuable metals from spent lithium-ion batteries, J. Hazard. Mater. 194 (2011) 378–384.

[33] Y. Yang, G. Huang, S. Xu, Y. He, X. Liu, Thermal treatment process for the recovery of valuable metals from spent lithium-ion batteries, Hydrometallurgy 165 (2016) 390–396.

[34] T. Georgi-Maschler, B. Friedrich, R. Weyhe, H. Heegn, M. Rutz, Development of a recycling process for Li-ion batteries, J. Power Sources 207 (2012) 173–182.

[35] J. Li, G. Wang, Z. Xu, Environmentally-friendly oxygen-free roasting/wet magnetic separation technology for in situ recycling cobalt, lithium carbonate and graphite from spent $LiCoO_2$/graphite lithium batteries, J. Hazard. Mater. 302 (2016) 97–104.

[36] M.-M. Wang, C.-C. Zhang, F.-S. Zhang, Recycling of spent lithium-ion battery with polyvinyl chloride by mechanochemical process, Waste Manag. 67 (2017) 232–239.

[37] R. Golmohammadzadeh, F. Rashchi, E. Vahidi, Recovery of lithium and cobalt from spent lithium-ion batteries using organic acids: Process optimization and kinetic aspects, Waste Manag. 64 (2017) 244–254.

[38] I.L. Santana, T.F.M. Moreira, M.F.F. Lelis, M. Freitas, Photocatalytic properties of Co_3O_4/$LiCoO_2$ recycled from spent lithium-ion batteries using citric acid as leaching agent, Mater. Chem. Phys. 190 (2017) 38–44.

[39] X. Zheng, W. Gao, X. Zhang, M. He, X. Lin, H. Cao, Y. Zhang, Z. Sun, Spent lithium-ion battery recycling–Reductive

[DOI: 10.22068/ase.2024.690]

ammonia leaching of metals from cathode scrap by sodium sulphite, Waste Manag. 60 (2017) 680–688.

[40] S.P. Barik, G. Prabaharan, L. Kumar, Leaching and separation of Co and Mn from electrode materials of spent lithium-ion batteries using hydrochloric acid: Laboratory and pilot scale study, J. Clean. Prod. 147 (2017) 37–43.

[41] M. Joulié, R. Laucournet, E. Billy, Hydrometallurgical process for the recovery of high value metals from spent lithium nickel cobalt aluminum oxide based lithium-ion batteries, J. Power Sources 247 (2014) 551–555.

[42] P. Zhang, T. Yokoyama, O. Itabashi, T.M. Suzuki, K. Inoue, Hydrometallurgical process for recovery of metal values from spent lithium-ion secondary batteries, Hydrometallurgy 47 (1998) 259–271.

[43] Z. Takacova, T. Havlik, F. Kukurugya, D. Orac, Cobalt and lithium recovery from active mass of spent Li-ion batteries: Theoretical and experimental approach, Hydrometallurgy 163 (2016) 9–17.

[44] D.A. Ferreira, L.M.Z. Prados, D. Majuste, M.B. Mansur, Hydrometallurgical separation of aluminium, cobalt, copper and lithium from spent Li-ion batteries, J. Power Sources 187 (2009) 238–246.

[45] G. Dorella, M.B. Mansur, A study of the separation of cobalt from spent Li-ion battery residues, J. Power Sources 170 (2007) 210–215.

[46] C.K. Lee, K.-I. Rhee, Preparation of $LiCoO_2$ from spent lithium-ion batteries, J. Power Sources 109 (2002) 17–21.

[47] E.G. Pinna, M.C. Ruiz, M.W. Ojeda, M.H. Rodriguez, Cathodes of spent Li-ion batteries: Dissolution with phosphoric acid and recovery of lithium and cobalt from leach liquors, Hydrometallurgy 167 (2017) 66–71.

[48] X. Chen, H. Ma, C. Luo, T. Zhou, Recovery of valuable metals from waste cathode materials of spent lithium-ion batteries using mild phosphoric acid, J. Hazard. Mater. 326 (2017) 77–86.

[49] P. Meshram, B.D. Pandey, T.R. Mankhand, Hydrometallurgical processing of spent lithium ion batteries (LIBs) in the presence of a reducing agent with emphasis on kinetics of leaching, Chem. Eng. J. 281 (2015) 418–427.

[50] F. Pagnanelli, E. Moscardini, G. Granata, S. Cerbelli, L. Agosta, A. Fieramosca, L. Toro, Acid reducing leaching of cathodic powder from spent lithium ion batteries: Glucose oxidative pathways and particle area evolution, J. Ind. Eng. Chem. 20 (2014) 3201–3207.

[51] J. Li, X. Li, Q. Hu, Z. Wang, J. Zheng, L. Wu, L. Zhang, Study of extraction and purification of Ni, Co and Mn from spent battery material, Hydrometallurgy 99 (2009) 7–12.

[52] J. Kang, G. Senanayake, J. Sohn, S.M. Shin, Recovery of cobalt sulfate from spent lithium ion batteries by reductive leaching and solvent extraction with Cyanex 272, Hydrometallurgy 100 (2010) 168–171.

[53] J. Heelan, E. Gratz, Z. Zheng, Q. Wang, M. Chen, D. Apelian, Y. Wang, Current and prospective Li-ion battery recycling and recovery processes, Jom 68 (2016) 2632–2638.

[54] C. Xu, Q. Dai, L. Gaines, M. Hu, A. Tukker, B. Steubing, Future material demand for automotive lithium-based batteries, Commun. Mater. 1 (2020) 99.

[55] R.E. Ciez, J.F. Whitacre, Examining different recycling processes for lithium-ion batteries, Nat. Sustain. 2 (2019) 148–156.

[56] P. Xu, D.H.S. Tan, B. Jiao, H. Gao, X. Yu, Z. Chen, A materials perspective on direct recycling of lithium-ion batteries: principles, challenges and opportunities, Adv. Funct. Mater. 33 (2023) 2213168.

[57] C. Qi, T. Yao, W. Zhai, M. Zhang, J. He, L. Song, Advances in degradation

[DOI: 10.22068/ase.2024.690]

mechanism and sustainable recycling of $LiFePO_4$-type lithium-ion batteries, Energy Storage Mater. (2024) 103623.

[58] A. Amarray, A. Boutahar, H. El Fallah, K.T. Silvère, A.E.L. Bendali, L. Boutajanouit, M. Aqil, J. Alami, M. Dahbi, Recovery of lithium from spent LFP and NCA batteries by electro-oxidation process and synthesis of cathode material from recycled precursors, J. Energy Storage 102 (2024) 114001.

[59] P. Jenis, T. Zhang, B. Ramasubramanian, S. Lin, P.R. Rayavarapu, J. Yu, S. Ramakrishna, Recent progress and hurdles in cathode recycling for Li-ion batteries, Circ. Econ. 3 (2024) 100087.

[60] J. Li, Z.-F. Ma, Past and present of LiFePO4: from fundamental research to industrial applications, Chem 5 (2019) 3–6.

[61] S. Kobayashi, A. Kuwabara, C.A.J. Fisher, Y. Ikuhara, Atomic-scale analysis of biphasic boundaries in the lithium-ion battery cathode material LiFePO4, ACS Appl. Energy Mater. 3 (2020) 8009–8016.

[62] J. Wang, X. Sun, Olivine LiFePO 4: the remaining challenges for future energy storage, Energy Environ. Sci. 8 (2015) 1110–1138.

[63] N. Paul, J. Wandt, S. Seidlmayer, S. Schebesta, M.J. Mühlbauer, O. Dolotko, H.A. Gasteiger, R. Gilles, Aging behavior of lithium iron phosphate based 18650-type cells studied by in situ neutron diffraction, J. Power Sources 345 (2017) 85–96.

[64] E. Fan, L. Li, Z. Wang, J. Lin, Y. Huang, Y. Yao, R. Chen, F. Wu, Sustainable recycling technology for Li-ion batteries and beyond: challenges and future prospects, Chem. Rev. 120 (2020) 7020–7063.

[65] J. Li, Y. Wang, L. Wang, B. Liu, H. Zhou, A facile recycling and regeneration process for spent $LiFePO_4$ batteries, J. Mater. Sci. Mater. Electron. 30 (2019) 14580–14588.

[66] Q. Liang, H. Yue, S. Wang, S. Yang, K. Lam, X. Hou, Recycling and crystal regeneration of commercial used $LiFePO_4$ cathode materials, Electrochim. Acta 330 (2020) 135323.

[67] J. Chen, Q. Li, J. Song, D. Song, L. Zhang, X. Shi, Environmentally friendly recycling and effective repairing of cathode powders from spent $LiFePO_4$ batteries, Green Chem. 18 (2016) 2500–2506.

[68] X. Li, J. Zhang, D. Song, J. Song, L. Zhang, Direct regeneration of recycled cathode material mixture from scrapped LiFePO4 batteries, J. Power Sources 345 (2017) 78–84.

[69] Q. Jing, J. Zhang, Y. Liu, W. Zhang, Y. Chen, C. Wang, Direct regeneration of spent LiFePO4 cathode material by a green and efficient one-step hydrothermal method, ACS Sustain. Chem. Eng. 8 (2020) 17622–17628.

[70] J. Tan, Z. Wang, G. Li, H. Hu, J. Li, R. Han, D. Zhang, Electrochemically driven phase transition in $LiCoO_2$ cathode, Materials (Basel). 14 (2021) 242.

[71] L. Zhang, Z. Xu, Z. He, Electrochemical relithiation for direct regeneration of $LiCoO_2$ materials from spent lithium-ion battery electrodes, ACS Sustain. Chem. Eng. 8 (2020) 11596–11605.

[72] D.-S. Kim, J.-S. Sohn, C.-K. Lee, J.-H. Lee, K.-S. Han, Y.-I. Lee, Simultaneous separation and renovation of lithium cobalt oxide from the cathode of spent lithium ion rechargeable batteries, J. Power Sources 132 (2004) 145–149.

[73] Y. Shi, G. Chen, Z. Chen, Effective regeneration of $LiCoO_2$ from spent lithium-ion batteries: a direct approach towards high-performance active particles, Green Chem. 20 (2018) 851–862.

[74] J. Wang, Q. Zhang, J. Sheng, Z. Liang, J. Ma, Y. Chen, G. Zhou, H.-M. Cheng,

[DOI: 10.22068/ase.2024.690]

Direct and green repairing of degraded $LiCoO_2$ for reuse in lithium-ion batteries, Natl. Sci. Rev. 9 (2022) nwac097.

[75] X. Ma, J. Hou, P. Vanaphuti, Z. Yao, J. Fu, L. Azhari, Y. Liu, Y. Wang, Direct upcycling of mixed Ni-lean polycrystals to single-crystal Ni-rich cathode materials, Chem 8 (2022) 1944–1955.

[DOI: 10.22068/ase.2024.690]