



Review article

## Recycling methods for different cathode chemistries – A critical review

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## ABSTRACT

Lithium-ion batteries (LIBs) have been gathering increasing attention worldwide as they are being widely used in portable devices and implemented in electric vehicles. With the increasing volume of LIBs poured into the market, the recycling of LIBs is becoming essential because the elements being currently used in LIBs, such as, Li and Co, have limited deposits in the world. In this paper, various recycling approaches, which are now prevalent or have the potential to become dominant in the near future are reviewed. Recycled materials reuse performance is included to exhibit the feasibility of these recycling technologies. Furthermore, emerging cathode chemistries are also introduced and possible recycling strategies for them are discussed.

### 1. Introduction

Portable electronic devices (PEDs) play an essential part of people's daily life. These devices are required to work long hours and get rapidly recharged as well as being light in weight. Lithium-ion batteries (LIB) have been dominating the market of PEDs because of their high voltage and high energy density, low self-discharge and no memory effect [1]. While some researches aim at transferring carbon dioxide into useful chemicals to achieve carbon neutrality [2,3], electric vehicles are another solution of carbon neutrality which decreases the emissions at the very beginning [4]. The United Kingdom is one of the pioneers in attempt to substitute internal combustion engine cars with EVs, and in 2020, it was declared to ban all diesel and petrol vehicles by 2030 [5]. Besides the UK, Germany [6], France [7] and some other countries have also proclaimed similar plans for banning traditional fossil fuel vehicles. LIBs are nowadays one of the most satisfactory options as EV power source owing to the aforementioned merits [8]. Consequently, the overall global LIBs market reached over 30 billion USD in 2019 and it has been predicted that this market will expand at a rate of 13 % per year from 2020 to 2027 [9]. Currently, the total worldwide car sale for the year 2020 was around 60 million while the total EV sale was just around 3 million. Once the previously mentioned ban is officially issued, the sale for EVs is expected to increase sharply to ten times over the present market volume. It has been predicted that EV stock would boost to the

billion magnitude, while the annual sale of EVs would experience a drastic rise to hundreds of millions in 2050 [10].

As essential elements for LIBs, lithium, cobalt, manganese and nickel are drawing great attention because of the enormous demand of energy storage systems in the near future. In 2019, the worldwide mine production of lithium was around 90,000 mt and approximately 65 % of the production was for the battery market [11]. The numbers for cobalt, manganese and nickel were 140,000 mt, 19,000 mt and 2,700,000 mt, respectively. Such tremendous collection of resources, with a predictable upward trend, is pouring into the battery industry which would definitely cause relevant environment-related issues if they are not treated following the appropriate approach [11–13] at the end of the battery life. Apart from the harm to the environment caused throughout the pristine material production, LIBs also pose menaces to waste sorters when they are retired from EVs and PEDs as they are extremely combustible if the casing is damaged. It was reported by the Environmental Services Association that LIBs were responsible for 38 % of all fires at recycling centers in 2019 [14] and the proportion can keep increasing with the accelerated commercialization of LIBs.

For the purpose of decreasing the mining of natural reserves and managing the threatens of LIB to people's lives, the waste of lithium-ion battery (WLIB), which contains all the necessary elements for producing new batteries, needs to be better taken care of. Different authorities around the world have introduced policies and regulations for LIB waste.

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China was the front runner in the LIB supply chain in 2020 [15], had its first political guidance for WLIB in 1996 and it has been updated with the footage of time [16]. In 2020, the MANAGEMENT OF THE STAGED APPLICATION OF GREEN CARS BATTERIES was published and solicit opinions from the society [17]. It encourages the reuse of WLIB, which stimulated the cooperation between the re-users and the EV industry. However, China is still falling behind due to the lack of waste sorting and collecting system, which just started in past two years. As the first region which recognized the importance of battery recycling [18], the European Union (EU) passed their first legal document for batteries in 2006, the DIRECTIVE 2006/66/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL [19]. The latest regulation, the REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL [20], was proposed on the 10th Dec 2020, aiming at guaranteeing the sustainability and safety of batteries in their cycle life. It also emphasized that the present framework of recycling is not satisfactory enough to diminish the dependence of raw materials, which could result in severe crises of supply chain. EU is now focusing on how to utilize new technologies, boost profits in related industries and attract investment for an expansion. However, as different EU members have their own specific economic conditions and implementation schemes, there would be some inevitable controversies amid them, causing additional difficulties when it comes to the practical application level. As a pioneer in the management of wasted lead acid batteries, the United States succeeded to reclaim 99 % of lead for the years 2014 to 2018 [21]. The complete and efficient battery recycle system made it relatively straightforward for the USA to handle LIBs. In 2021, many companies with clean, profitable and competent technologies are trying to take the control of this market [22].

Fig. 1 compares the basic technologies adopted by several battery recycling companies, where the capability stands for the weight of LIBs that can be treated annually. It can be noticed that hydrometallurgical and pyrometallurgical methods are dominating in the industry because of their maturity as battery recycling strategies for decades. Mechanical methods are less popular due to their low selectivity towards those metals, such as Co and Ni. The direct recycling although promising

requires more time and effort to achieve profitable industrialization. The Umicore method, which is widely known for its battery recycling, is briefly introduced below to provide a general view of the industry.

The Umicore approach is based on the use of a shaft furnace that can be divided into three different zones (listed from the top to the bottom of the furnace): the preheating zone, the plastics pyrolyzing zone and the smelting and reducing zone [26]. The raw materials of this method consist of coke, slag formers as well as Co or Ni based dead batterie in a certain weight ratio. The weight ratio of the batteries should not be <30 %, preferably 50 %, to ensure the profitability of this method. Meanwhile, the ratio determines the selectivity of this process as it affects the redox potential in the furnace [27]. Raw materials are first fed into the preheating zone, where the temperature slowly raises up towards 300 °C, aiming at evaporating the electrolyte to avoid any explosion. Subsequently, the materials are heated to 700 °C in the plastics pyrolyzing zone to melt the plastic components from the batteries. The smelting of plastics can offer energy for the gases generated during the process, so they do not condense in the furnace. At last, a flow of pre-heated oxygen-enriched air is introduced into the smelting and reducing zone (1200 to 1450 °C) via tuyeres at the bottom of the furnace, resulting in a slag and an alloy of mainly Co and Ni [27]. There are three products from this particular process: gases, slag and alloy. The gases would be post-treated in a combustion chamber at above 1150 °C and then cooled down to <300 °C, avoiding the formation of halogenated organic compounds and the formation of dioxins and furans [26]. The slag can be used as substitute for the gravel in the concrete while the alloy is then treated by hydrometallurgical methods to refine valuable elements.

This process is relatively simple and flexible with the feedings, as it does not need to pre-treat the batteries. The vertical design of the shaft furnace greatly reduces the cost, compared with the more traditional two-furnaces treatment. Furthermore, the recovery rate of valuable metals is considerably high for industrial application. However, this method aims at recycling Co and Ni instead of Li, and it requires a huge amount of energy and depends highly on the prices of Co and Ni [26,27].

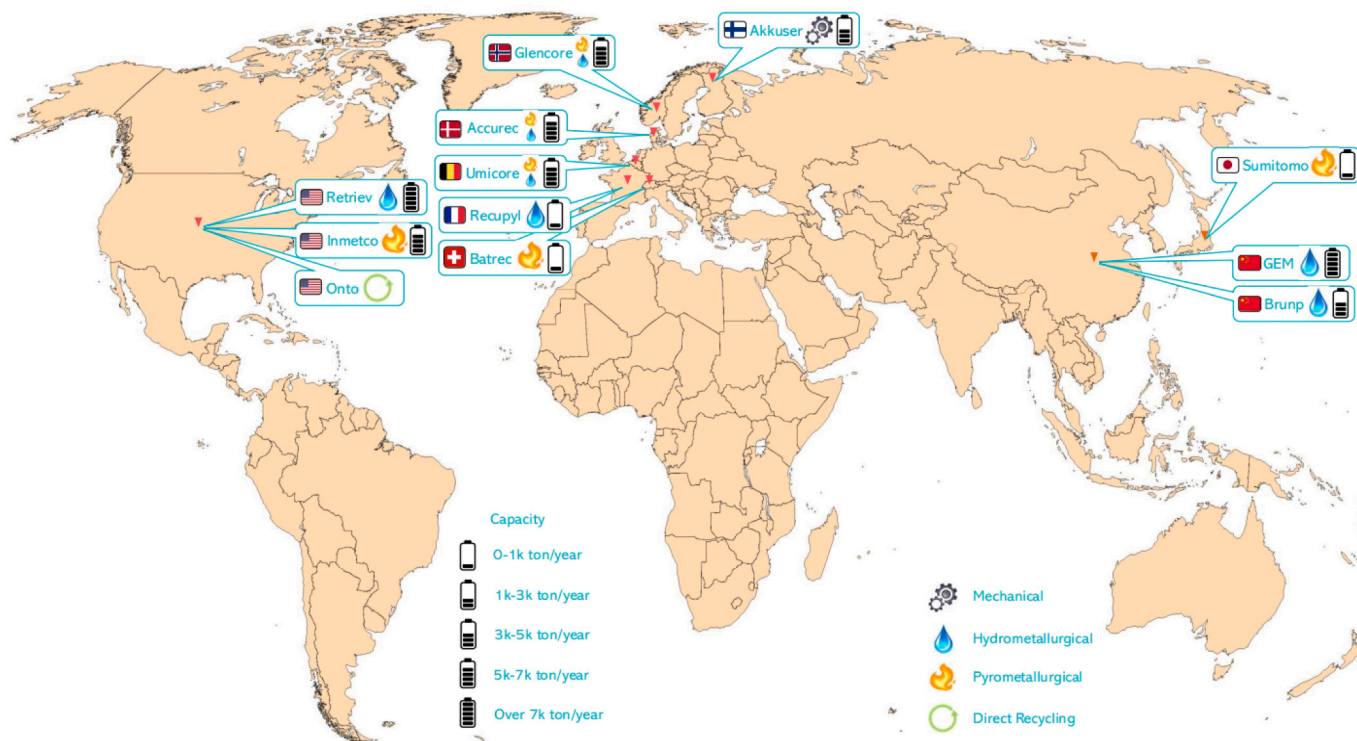


Fig. 1. Overview of different LIB recycling companies(Data of this figure is from [1,23–25]).

### 1.1. Main components of LIBs

In order to recycle LIBs, it is mandatory to have the knowledge of their main components and the risks when disassembling them. In LIBs, Li ions can intercalate in and out certain structures (ex. Layer, Spinel, Olivine [28]) of the cathode and anode, thus generating currents for the devices to operate. Besides, the electrolyte, which links electrodes by moving Li ions from one electrode to the other, also contributes to the performance of LIBs. The basic concept of LIBs can be represented in Fig. 2.

As a big family with various members, LIBs are typically categorized by the cathode material, as the anode material is graphite for most cases [29]. Lithium cobalt(III) oxide ( $\text{LiCoO}_2$ , LCO) batteries, which were demonstrated by Goodenough [30] in 1979 [31], were initially issued by SONY for commercial application in 1991 [32] and it has been the most successful LIB product then. However, due to the high price of cobalt and the low thermal stability of LCO [33], there were continuous attempts to substitute Co with other elements, such as Mn. Consequently, lithium manganese(III) oxide ( $\text{LiMnO}_2$ , LMO) was introduced by Thackeray et al. [34]. Besides, lithium iron(II) phosphate ( $\text{LiFePO}_4$ , LFP), with improved thermal stability, was investigated by Padhi et al. [35] in 1997 and now is widely used in the EV industry [36]. Moreover, lithium nickel manganese cobalt oxide ( $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ , NMC), another candidate in the market which was studied in the 1990s [31], can tune its energy properties by changing the concentration of Ni, Co and Mn, which guarantees its competence in different situations [37]. Fig. 3 shows a brief summary of different characteristics of popular LIBs.

Efforts were also devoted in discovering novel anodes [38,39] and electrolytes [40,41] with improved performances for LIBs. More specifically, for anodes, graphite is still commercially dominating because of its high cost-efficiency, abundance in nature, stable electrochemical properties and minor difference between real and theoretical specific capacity. Nevertheless, the main drawback of graphite is the insufficient specific capacity, which confines its opportunities for the forthcoming LIBs to power EVs or even electric planes. Therefore, several anode alternatives were proposed to serve the future batteries, and the examples are Si-based [42,43], nanostructured carbon-based [44], transition metal-based [45] and even anode-free LIBs [46].

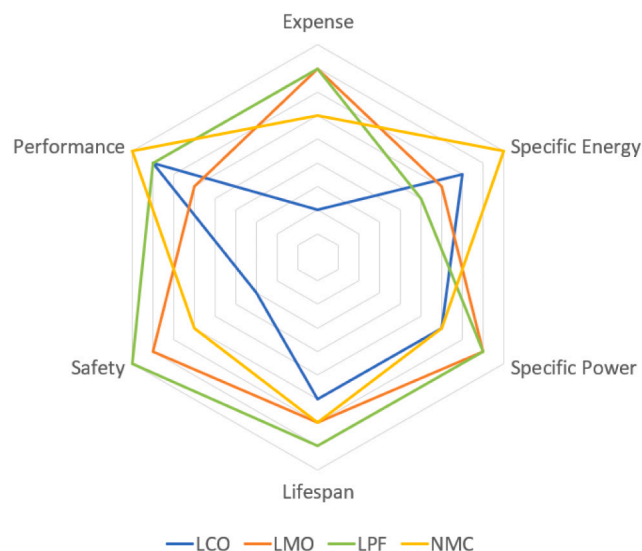


Fig. 3. A brief summary of LIBs with different cathodes (Data of this figure is from [28]).

### 1.2. Recycling methods

Recycling is regarded as the third choice in the waste management hierarchy [47], where prevention and reuse are preferred as the first and second options, respectively. However, prevention, also called redesign, requires countless efforts and even some luck to discover a new method of storing or transferring energy, which is strongly time-consuming as well, making it more like a guiding strategy than a practical solution. As for reuse, retired LIBs from EVs can be treated and serve for stationary energy storage which could tolerate lower power density [48]. Nonetheless, when the degradation of reused LIBs reaches a certain level that leads to the disability of empowering as a qualified energy storage cell, they have to be recycled and this seems to be the ultimate destination for LIBs. The present work will introduce in the following the current prevalent approaches of recycling, in particular for recycling the more

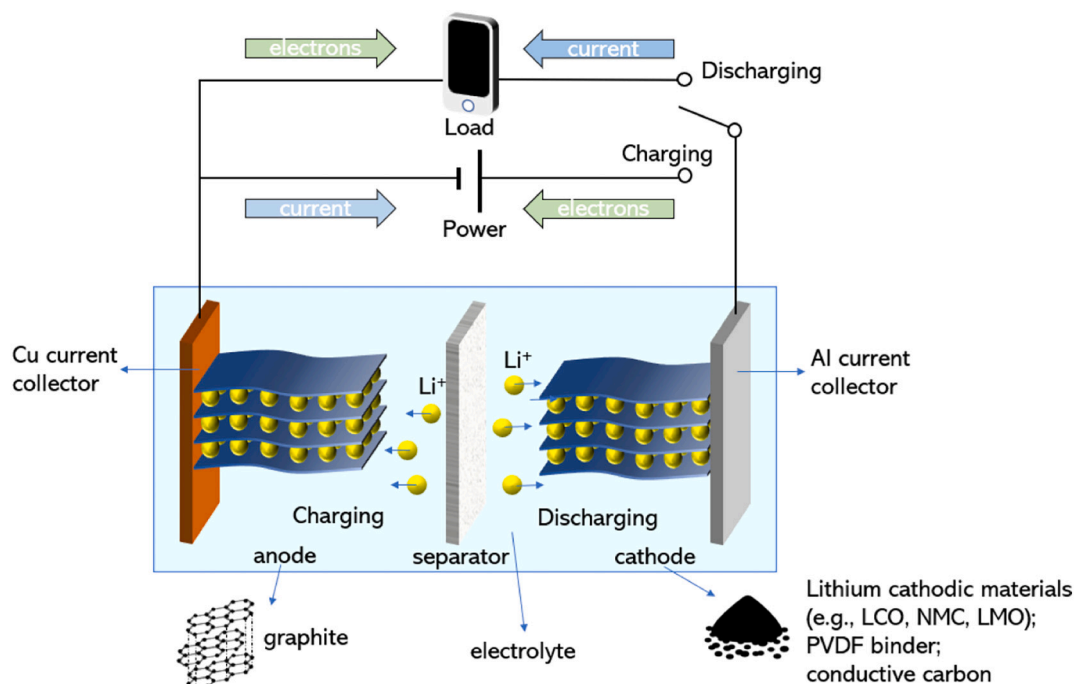


Fig. 2. Charging and discharging mechanisms of LIBs(Color needed for print).

valuable cathode materials rather than the carbon anode or the separators.

Recycling methods can generally be categorized into four different main groups, as shown in Fig. 4. Some methods, such as bioleaching and mechanochemical methods [49,50], are not included in the figure because they are just used at the lab scale. Reasons are that bioleaching shows a low leaching efficiency towards valuable metals like cobalt [51], while mechanochemical method has low selectivity. However, they are briefly introduced in this chapter to provide a broader view of battery recycling.

As per the temperature used in pyrometallurgical methods, they can be further divided into pyrolysis & incineration, roasting and smelting. Pyrometallurgical methods focus on various thermal treatments to recycle or recover WLIBs. Pyrometallurgy is based on vigorous chemical reactions in a furnace and, when compared with other approaches, it is highly efficient, relatively simple to operate, and can deal with many batches of materials simultaneously. Besides, it can manage almost all categories of LIBs, such as LCO, LMO, LPF and NMC, which guarantees its application in real industry. Examples of applying industrial pyro-recycling techniques are Umicore battery recycling in Belgium and Sony and Sumitomo in Japan [52]. However, these techniques are also facing the problems of toxic gas emissions, massive consumption of energy and imperative additional purifying processes in order to get valuable products.

In Fig. 4, hydrometallurgical methods are categorized by the leaching reagent, which is the most critical variable in this case. Hydro-extraction is based on chemical reactions which could help to recycle valuable elements from WLIB. It consumes less energy and requires less capital investment than pyro-recycling methods, making it a reasonable choice for real industrial application [24]. Generally, hydrometallurgy involves two stages: 1. Dissolving cathode materials into a solvent; 2. Extracting the dissolved ions via precipitation and filtration or

electrodeposition. Fig. 5 illustrates the most common procedures of a hydrometallurgical approach to recycle WLIBs [23].

Mechanical methods can be divided into destroying (crushing, grinding and milling) and separation (sieving and screening) (Fig. 4), which are the two main steps to follow in the mechanical operations. Mechanical methods take advantage of different properties of the materials, such as the density, electrical conductivity as well as magnetic properties, to achieve the separation of the WLIBs [53]. These approaches can reduce the size of the WLIBs while dividing and concentrating the components of LIBs, making them advantageous over the other methods [53]. However, the safety of the mechanical processes is a major concern when dealing with the removal of the electrolyte and the breaking of the batteries [1]. Besides, the selectivity of mechanical approaches is another disadvantage which limits their applications.

Direct recycling can be categorized according to the nature of the lithium source used in the re-lithiation process: lithium salt powder or a lithium saturated solution. Direct recycling aims at curing or healing the cathode without chemically transforming cathodic materials into substituent substances like in hydrometallurgical methods, which makes it more efficient as well as cheaper [26,54,55]. The main concept of this recycling method is to compensate the lithium lost in the operation of LIBs by combining the retired cathode material with a lithium source such as  $\text{LiCO}_3$  powder [55] or a saturated lithium solution [54]. However, in order to obtain the cathode powder of the WLIBs for further re-lithiation, discharging, dismantling, removing of PVDF (Polyvinylidene fluoride) and some thermal treatments are still mandatory, making it not as direct as the name of the process indicates [56]. Moreover, the performance of regenerated cathodes still needs an improvement when compared with pristine cathodic materials.

As previously mentioned, biotechnology is also utilized as a leaching method in battery recycling. This process involves the use of some specific microbes which can generate leaching reagents such as acids. It



Fig. 4. General categorization of typical LIB recycling methods.



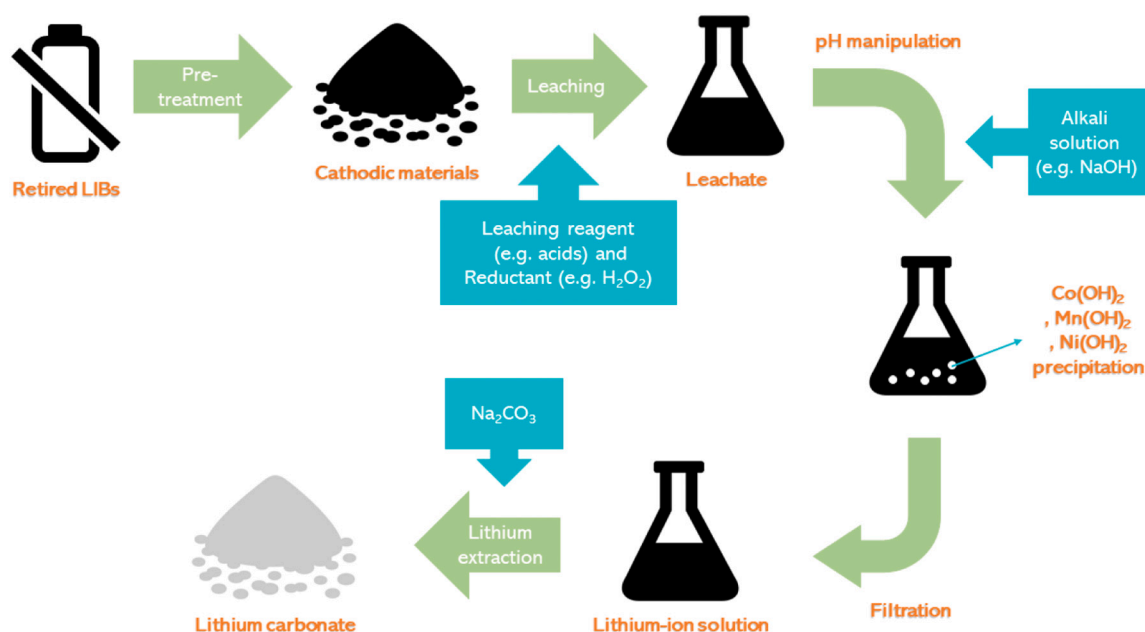


Fig. 5. Flowchart of a typical hydrometallurgical method.

is widely investigated due to its low cost and environmentally friendly processing. Typical microbes are chemo lithotrophic prokaryotes, heterotrophic bacteria, and fungi [51]. The challenges of bioleaching are the low leaching efficiency and the toxicity of the metals towards microbes. Therefore, the main concern of bioleaching is to find microorganisms with high tolerance towards the metals to be recycled.

Mechanochemical methods take advantage of mechanical energy, instead of heating or applying pressure, to facilitate the chemical reaction. By changing the reagents during the reactive milling or grinding, batteries with different chemistries can all be dealt with. For instance, Al was added as reducing reagent for LCO to obtain metallic cobalt [49] and  $\text{Na}_2\text{S}_2\text{O}_8$  was mixed with spent LFP cathodes to achieve selective recycling [50]. However, just like in mechanical methods, subsequent refining processes are mandatory to achieve high purity products. The present work introduces recycling methods for different cathode chemistries, as the cathode is the most valuable part of spent batteries. The difficulty of the recycling process, emission issues and the performance of recycled materials are included. Procedure conditions of the most recent works are summarized at the end of Section 2. Herein, Table 1 compares the different recycling methods through their pros and cons. Potential recycling methods and perspectives are also given as a reference for those willing to investigate in this topic (Tables 2–4).

## 2. Recycling strategies for different cathodes

Before recycling WLIB, there are several common pre-treatments to finish for all recycling methods: discharging, dismantling and cathodic material harvest. Discharging, usually is immersing batteries in NaCl solution for hours, can avoid potential shortcut during the dismantling process. However, the discharging process can vary significantly with the different solutions utilized. Halide salts can be very corrosive and can penetrate the outer case of LIBs as shown in Fig. 6, while carbonates and phosphates present a non-corrosive discharging. Still, sodium nitrite solution is the most recommended option, with a relatively fast discharging as well as a negligible corrosion effect [102]. However, to destroy spent batteries which are already physically damaged, halide salts may be a better choice due to the ultrafast discharging and abundance of the salts.

Dismantling is to uncurl the batteries and separate cathode, separator and anode. This is mostly done by hand while sometimes by

Table 1

Brief comparison of different LIB recycling methods.

Recycling method	Pros	Cons
Pyrometallurgical	<ul style="list-style-type: none"> <li>Capable of dealing with different types of batteries simultaneously</li> <li>Pre-treatment not needed</li> <li>High recovery rate</li> </ul>	<ul style="list-style-type: none"> <li>Huge capital investment</li> <li>High energy consumption</li> <li>Refining process required</li> <li>Toxic gas emission</li> </ul>
Hydrometallurgical	<ul style="list-style-type: none"> <li>High recovery rate and purity</li> <li>Processes adjustable for different battery chemistry</li> <li>Energy-saving</li> </ul>	<ul style="list-style-type: none"> <li>Pre-treatment needed</li> <li>Used chemical compounds need to be post-treated</li> <li>Lower efficiency</li> </ul>
Mechanical	<ul style="list-style-type: none"> <li>Capable of dealing with different types of batteries simultaneously</li> <li>Straightforward process</li> </ul>	<ul style="list-style-type: none"> <li>Organic compounds decomposed to toxic materials.</li> <li>High energy consumption</li> </ul>
Direct recycling	<ul style="list-style-type: none"> <li>Cheap and efficient</li> <li>More environmentally benign compared to pyro- and hydro- methods</li> </ul>	<ul style="list-style-type: none"> <li>Insufficient selectivity</li> <li>Pre-treatment needed</li> <li>Improvement needed for the performance of harvested cathode material</li> <li>High energy consumption (if furnace is used)</li> </ul>

grinding and crushing. A direct and precise disassembly process was investigated by Zhao et al. [103] without the need for discharging. This non-destructive dismantling method takes advantage of the rolling structure of batteries to control the exposure of spent batteries to water and enables the full recycling of all the components from a spent battery.

As for cathodic material harvest, it is to liberate the black mass from the Al current collector. Popular harvesting methods are: 1. Dissolving PVDF binder with NMP(N-Methylpyrrolidone) solution; 2. Dissolving Al collector with NaOH solution; 3. Thermal treatment—incineration which burns the PVDF binder in oxygen environment; 4. Thermal treatment—pyrolysis which decomposes PVDF in vacuum or inert gases; 5. Grinding and sieving which separates by sieving pore size. After all these pre-treatments have been done, the obtained cathodic materials are then being processed to recover valuable elements.

**Table 2**  
Review of the main characteristics of current pyrometallurgical recycling methods.

Battery type	Additive	Thermal Process conditions	Atmosphere	Subsequent treatment	Final product	Recycling efficiency	Reference
LCO	HNO <sub>3</sub> (75 °C, 5 h)	250 °C, 60 min	Air	Water leaching (25 °C, S/L 2:1)	LiCO <sub>3</sub>	93 % for Li	[56]
LCO	NH <sub>4</sub> Cl	350 °C, 20 min	Air	Water leaching (S/L 100 g/L)	LiCO <sub>3</sub> , CoC <sub>2</sub> O <sub>4</sub>	99 % for Li and Co	[57]
LCO	Graphite, NaOH	520 °C, 180 min	Ar	Water leaching	LiCO <sub>3</sub> , CoO	93 % for Li	[58]
LCO	Al foil	600 °C, 60 min	Ar	Alkaline leaching (NaOH)	LiOH, CoSO <sub>4</sub>	93.67 % for Li	[59]
LMO	Graphite	800 °C, 45 min	Oxygen-free	Water leaching (20–30 min)	LiCO <sub>3</sub> , MnO	91.3 % for Li	[60]
NMC	Graphite	500 W(microwave power), 30 min	N <sub>2</sub>	Acid leaching (HCl)	N/A	95.11 % for Mn 97 % for Ni, Co, Mn	[61]
LCO	Graphite	1000 °C, 30 min	N <sub>2</sub>	Wet magnetic separation	LiCO <sub>3</sub> , Co	99 % for Li 95.75 % for Co 98.93 % for Li	[62]
LiCoNiO <sub>2</sub>	Copper slag	1450 °C, 30 min	Air	Grinding of alloy and slag	Co-Ni-Cu-Fe Alloy	98.83 % for Co 98.39 % for Ni	[63]

**Table 3**  
Main processing parameters and leaching efficiency of current hydrometallurgical methods for Li-ion battery cathodes.

Group	Raw material	Leaching reagent	Reductant	Temperature & Time	Leaching efficiency (%)		Reference
					Li	Co	
Inorganic	LCO	2 M HCl	N/A	60–80 °C, 90 min	100	100	[65]
Inorganic	LCO/LMO/NMC	4 M HCl	N/A	80 °C, 60 min	100	100	[66]
Inorganic	LCO	1 M HNO <sub>3</sub>	1.7 vol% H <sub>2</sub> O <sub>2</sub>	75 °C, 60 min	85	85	[67]
Inorganic	LCO	1 M HNO <sub>3</sub>	1 vol% H <sub>2</sub> O <sub>2</sub>	80 °C, 60 min	100	100	[68]
Inorganic	LCO	2 M H <sub>2</sub> SO <sub>4</sub>	5 vol% H <sub>2</sub> O <sub>2</sub>	80 °C, 60 min	99	99	[69]
Inorganic	LCO	4 vol% H <sub>2</sub> SO <sub>4</sub>	1 vol% H <sub>2</sub> O <sub>2</sub>	40 °C, 60 min	100	97	[70]
Inorganic	Mixed LIBs	2 M H <sub>2</sub> SO <sub>4</sub>	4 vol% H <sub>2</sub> O <sub>2</sub>	70 °C, 120 min	98.8	99.6	[71]
Inorganic	LCO	6 vol% H <sub>2</sub> SO <sub>4</sub>	1 vol% H <sub>2</sub> O <sub>2</sub>	65 °C, 60 min	95	72	[72]
Inorganic	LCO	4 M H <sub>2</sub> SO <sub>4</sub>	10 vol% H <sub>2</sub> O <sub>2</sub>	65 °C, 120 min	96	95	[73]
Inorganic	LCO	2 M H <sub>2</sub> SO <sub>4</sub>	6 vol% H <sub>2</sub> O <sub>2</sub>	60 °C, 60 min	97	98	[74]
Inorganic	LCO	2 M H <sub>2</sub> SO <sub>4</sub>	15 vol% H <sub>2</sub> O <sub>2</sub>	75 °C, 10 min	100	100	[75]
Inorganic	LCO	2 M H <sub>2</sub> SO <sub>4</sub>	2 vol% H <sub>2</sub> O <sub>2</sub>	60 °C, 120 min	87.5	96.3	[76]
Inorganic	LCO	2 M H <sub>2</sub> SO <sub>4</sub>	5 vol% H <sub>2</sub> O <sub>2</sub>	75 °C, 30 min	94	93	[77]
Inorganic	LCO	3 M H <sub>2</sub> SO <sub>4</sub>	3 wt% H <sub>2</sub> O <sub>2</sub>	70 °C, 300 min	90	90	[78]
Inorganic	NMC	2 M H <sub>2</sub> SO <sub>4</sub>	10 vol% H <sub>2</sub> O <sub>2</sub>	70 °C, 90 min	94	91.6	[79]
Inorganic	NMC	3 M H <sub>2</sub> SO <sub>4</sub>	3 vol% H <sub>2</sub> O <sub>2</sub>	80 °C, 60 min	97.8	96.5	[80]
Inorganic	NMC	1.25 M H <sub>2</sub> SO <sub>4</sub>	0.1 M Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	60 °C, 60 min	>80	>80	[81]
Inorganic	LCO	2 M H <sub>2</sub> SO <sub>4</sub>	0.11 ascorbic acid	80 °C, 90 min	95.7	93.8	[82]
Inorganic	LCO	2 g*g <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub>	50%exc glucose	90 °C, 180 min	98	97	[83]
Inorganic	NMC	0.2 M H <sub>3</sub> PO <sub>4</sub>	0.4 citric acid	90 °C, 30 min	100	91.63	[84]
Inorganic	LCO	0.7 M H <sub>3</sub> PO <sub>4</sub>	4 vol% H <sub>2</sub> O <sub>2</sub>	40 °C, 60 min	99	99	[85]
Organic	LCO	1 M Oxalic acid	N/A	80 °C, 120 min	98	98	[86]
Organic	LCO	1.5 M DL-malic acid	3 vol% H <sub>2</sub> O <sub>2</sub>	80 °C, 25 min	98.13	98.86	[87]
Organic	LCO	1.5 M malic acid	0.6 g/g grape seed	80 °C, 180 min	99	92	[88]
Organic	LCO	1.25 M malic acid	0.3 M glucose	80 °C, 180 min	100	99.87	[89]
Organic	LCO	1.25 M ascorbic acid	N/A	70 °C, 20 min	98.5	94.8	[90]
Organic	NMC	1.5 M citric acid	2 vol% H <sub>2</sub> O <sub>2</sub>	95 °C, 30 min	97	95	[91]
Organic	NMC	0.5 M citric acid	N/A	90 °C, 80 min	91	90	[92]
DES	LCO	Choline chloride: ethylene glycol (1:2)	N/A	220 °C, 24 h	99.3	99.3	[93]
DES	Ni-MH	Choline chloride: Urea (1:2)	N/A	95 °C, 24 h	N/A	53.3	[94]
DES	LCO	polyethylene glycol: thiourea (2:1)	N/A	160 °C, 24 h	N/A	60.2	[95]

## 2.1. LiCoO<sub>2</sub>

LCO is the most often used cathode in LIBs and therefore, it is also a target compound that researchers investigate novel recycling methods of WLIB, probably due to its relatively easy chemistry composition to deal with. Co is the key element to collect because of its high price and Li is sometimes ignored, especially in some pyrometallurgical methods where Li is in the flue dust after thermal treatment which requires much effort to recycle.

Hydrometallurgical leaching methods are very popular in recycling LCO [23,77], as there are only Li and Co to deal with and they can be easily separated by precipitation. The main challenge for leaching LCO is to find an appropriate leaching reagent which is cost-effective, eco-friendly as well as beneficial for subsequent separation. Inorganic acids, such as H<sub>2</sub>SO<sub>4</sub> [69,70], HCl [65,66], HNO<sub>3</sub> [67,68] and H<sub>3</sub>PO<sub>4</sub> [85], were first investigated, due to their high leachability and availability. They did perform well in dissolving the cathodic LCO, but it was found that the addition of a reductant, such as H<sub>2</sub>O<sub>2</sub> [72,73], ascorbic acid [82]

and glucose [83], can further facilitate the leaching of Co by reducing Co<sup>3+</sup> to Co<sup>2+</sup>, which is more soluble in water. Different from the other inorganic acids which can only dissolve the cathodic LCO, H<sub>3</sub>PO<sub>4</sub> can also precipitate over 99 % Co as Co<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> with a purity of 97.1 % after leaching [85]. The lithium will be stored in the solution as ions, and normally Li<sup>+</sup> will be precipitated as Li<sub>2</sub>CO<sub>3</sub> with addition of saturated Na<sub>2</sub>CO<sub>3</sub> solution. However, as lithium carbonate has a solubility of 1.29 g/100 mL in water at room temperature, it is difficult to recover all the lithium with this approach.

During leaching process which always involves heating the solution, inorganic acids emit harmful gases, such as SO<sub>2</sub>, Cl<sub>2</sub>, calling for eco-friendlier substitute leaching reagent. Thus, organic compounds began to draw more attention for LCO leaching. Examples are oxalate [86], malic acid [87,88] and ascorbic acid [90]. Oxalate here seems to be a promising option, as it can both leach and precipitate the cobalt in LCO which simplifies the process. Although the precipitating efficiency is around 98 %, the leaching efficiency is not reported [86]. For organic acids, Golmohammadzadeh et al. [104] studied the differences between

**Table 4**  
Main process parameters, conditions and characteristics of current direct recycling approaches.

Reference	Pre-treatment	Process details	Achievements	Significance
Sloop et al. [54]	<ol style="list-style-type: none"> <li>1. Batteries discharged via sodium bicarbonate brine solution</li> <li>2. Electrolyte removed by liquid CO<sub>2</sub> system</li> <li>3. Batteries shredded into smaller pieces</li> </ol>	<ol style="list-style-type: none"> <li>1. Black mass immersed and then heated in a saturated Lithium solution</li> <li>2. Cathodic materials separated via floatation</li> <li>3. Cathodic materials heated under air with a ramp rate of 5 °C min<sup>-1</sup> for 9 h and then cooled down to room temperature</li> <li>4. Cathodic materials rinsed with 0.25 M nitric acid and then deionized water</li> <li>5. Cathodic materials dried at 120 °C in vacuum and then heated at 500 °C under nitrogen</li> </ol>	The full cell made of the regenerated cathode demonstrated useful capacity.	It can minimize the environmental and safety hazards and process costs.
Gao et al. [55]	<ol style="list-style-type: none"> <li>1. Discharging and disassembling</li> <li>2. Cathode soaked in N,N-dimethylacetamide (DMAC) for 24 h to dissolve binders</li> <li>3. Black mass heated at 120 °C for 12 h to remove DMAC</li> <li>4. Black mass ground into fine powder</li> </ol>	<ol style="list-style-type: none"> <li>1. Cathode materials mixed with LiOH·H<sub>2</sub>O powder and then ball milled for 3 h at 250 rpm</li> <li>2. Mixture calcinated at 800 °C for 8 h (heating rate 5 °C min<sup>-1</sup>)</li> <li>3. Al<sub>2</sub>O<sub>3</sub> powder added to the mixture and then ball milled for 3 h at 250 rpm</li> <li>4. Al<sub>2</sub>O<sub>3</sub>-coated cathode heated at 800 °C for 5 h in air then naturally cooled</li> </ol>	Discharge specific capacity for the Al <sub>2</sub> O <sub>3</sub> -coated regenerated LCO is 136.8 mAh g <sup>-1</sup> , and it remains at 90.1 % after 100 cycles.	Great formation of a layered structure in the LCO. Al <sub>2</sub> O <sub>3</sub> coating enhanced the electrochemical properties of the LCO.
Gao et al. [96]	<ol style="list-style-type: none"> <li>1. Discharging and disassembling</li> <li>2. Batteries immersed in NMP at 50 °C for 6 h to dissolve PVDF</li> <li>3. Centrifuging to get cathodic materials and then dried at 80 °C overnight under vacuum</li> </ol>	<ol style="list-style-type: none"> <li>1. The powder soaked in 0.1 M LiOH solution and then heated in an autoclave at 180 °C for 12 h</li> <li>2. Powder washed with deionized water and dried at 80 °C overnight</li> </ol>	Discharge capacity of 111 mAh g <sup>-1</sup> and 98 mAh g <sup>-1</sup> after 100 cycles at 0.5C rate.	A simple one-step hydrothermal direct recycling method. Regenerated LMO with high capacity and great cycling stability as well as high-rate performance
Shi et al. [97]	<ol style="list-style-type: none"> <li>1. New batteries cycled, discharged and disassembled</li> <li>2. Cathode strip immersed in NMP to remove PVDF for 30 min and then 20 min sonication</li> <li>3. Black mass centrifuged, separated and dried</li> </ol>	<p>Method 1: Black mass immersed in LiOH and then heated in a tube furnace. Powder washed, dried and then annealed.</p> <p>Method 2: Measure composition via ICP-OES. Powder mixed with Li<sub>2</sub>CO<sub>3</sub> and then sintered.</p>	91.2 % capacity retention after 100 cycles at 1C 141.9 mAh g <sup>-1</sup> at 2C 130.3 mAh g <sup>-1</sup> at 5C	A simple and efficient non-destructive recycling approach. It can fully recover the specific capacity and cycling stability of LCO. (method 1) Different cathodes can be treated together.
Shi et al. [98]	<ol style="list-style-type: none"> <li>1. Commercial and homemade batteries were used as raw materials</li> </ol>	Hydrothermal treatment combined with a short annealing step in controlled atmospheres (hydrothermal treatment at 220 °C for 4 h, post-annealing at 850 °C in oxygen for 4 h) Regenerated materials were made into new coin cells to characterize the properties.	NMC 111: discharge capacity 158.4 mAh g <sup>-1</sup> at 1C and 122.6 mAh g <sup>-1</sup> after 100 cycles NMC 532: discharge capacity 128.3 mAh g <sup>-1</sup> after 100 cycles	A more efficient and non-destructive process to recycle NMC cathodes. The electrochemical properties of the regenerated NMC cathode can reach the virgin commercial materials' level.
Song et al. [99]	<ol style="list-style-type: none"> <li>1. Discharging and dismantling</li> <li>2. Cathode plates was cut into pieces and immersed in organic solvents to remove PVDF</li> </ol>	<ol style="list-style-type: none"> <li>1. Spent cathode heated in a tube furnace under N<sub>2</sub></li> <li>2. Solid phase sintered for 8 h with the doping of new LPF powder</li> </ol>	Specific capacity: 144 mAh g <sup>-1</sup> at 0.1C and 135 mAh g <sup>-1</sup> after 100 cycles	The regenerated LPF cathode materials can meet the basic requirement for reuse. 800 °C sintering behaved worse than 600 °C and 700 °C.
Li et al. [100]	<ol style="list-style-type: none"> <li>1. Discharging and dismantling</li> <li>2. Immersed in NaOH solution and then washed and centrifuged</li> <li>3. Dried and ball milled and sieved</li> </ol>	Solid phase heat treatment at 650 °C for an hour under Ar/H <sub>2</sub> Li <sub>2</sub> CO <sub>3</sub> as lithium supplement	First-discharge capacity of 147.3 mAh g <sup>-1</sup> and of 140.4 mAh g <sup>-1</sup> after 100 cycles at 0.2C rate, while capacity retention is 95.32 %	A more ecological approach of direct recycling LPF without any second pollution. 650 °C appeared to be the optimum sintering temperature for LPF.
Ganter et al. [101]	<ol style="list-style-type: none"> <li>1. Batteries are cycled, discharged and dismantled.</li> <li>2. Scraping the cathode and grinding</li> </ol>	Electrochemical lithiation: cycling spent cathode and pure lithium in a coin cell. Chemical lithiation: spent cathode powder was soaked in 1 M lithium iodide solution for 20 h.	The re-lithiated samples regained capacity of 150–155 mAh g <sup>-1</sup> .	The main failure mechanism of LIB is the loss of Li during cycles. Regenerated cathode showed 50 % less of cumulative energy demand than the synthesis of virgin materials.

DL-malic acid, citric acid, oxalic acid and acetic acid with the addition of H<sub>2</sub>O<sub>2</sub> as a reducing agent in all cases. As one mole of citric acid can generate three moles of H<sup>+</sup> ions, citric acid achieved the highest leaching efficiencies among all investigated organic acids with 92.53 % of lithium and 81.50 % of cobalt.

Moreover, in order to have a better understanding on different acids from an industrial perspective, rather than only leaching ability, Anwani, et al. [105] introduced more parameters for comparison, such as economical index, CO<sub>2</sub> release during process, product purity and overall efficiency as shown in Fig. 7. Both inorganic acids (H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl) and organic acids (oxalic acid, acetic acid, formic acid) were selected as the candidates. The economic analysis was based on the recycling of 10 g of cathode materials and the costs included the leaching solvent, the reagents for precipitation and the electricity bills. The CO<sub>2</sub> release data was obtained via GaBi software simulation [105], and the whole recycling processes for different acids

were programmed in the software; the product purity *P* was defined as below,

$$P = (P_{Co} * P_{Li}) * 100\%; \quad (1)$$

where the *P*<sub>Co</sub> and *P*<sub>Li</sub> represented the purities of Co product and Li product respectively:

The overall efficiency *η* was calculated via:

$$\eta = (\eta_d * \eta_{Co} * \eta_{Li}) * 100\%, \quad (2)$$

where the *η*<sub>d</sub> stood for the dissolution efficiency of cathode materials, *η*<sub>Co</sub> and *η*<sub>Li</sub> represented the extraction efficiencies for cobalt and lithium, respectively.

The analysis to the different data of the product purity *P* and the overall efficiency *η* can better reveal how an acid system works in the leaching of cathodic materials. Sulfuric acid and oxalic acid were the

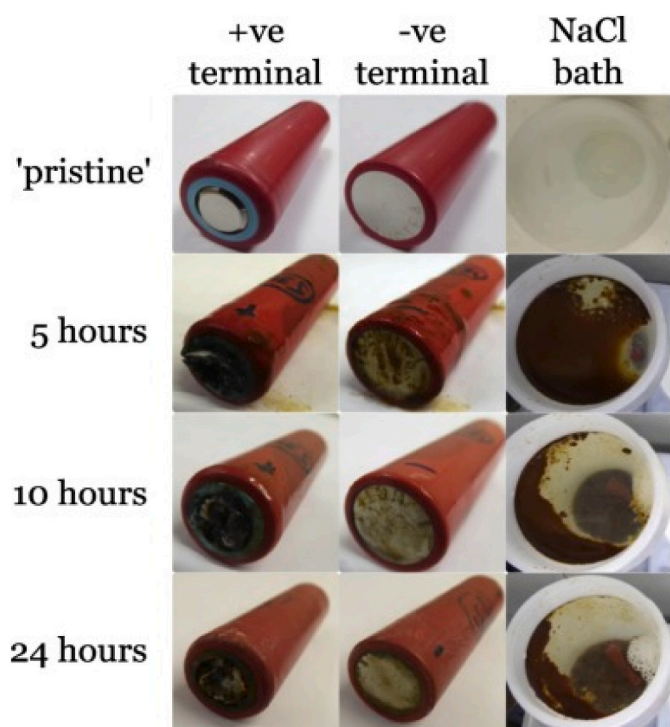


Fig. 6. The positive and negative terminals, and the NaCl solution at different times after discharging the cell in the NaCl solution. [102].

two candidates entering the final stage with an eye-catching performance in those four filters (economical index, CO<sub>2</sub> release during process, product purity and overall efficiency). Anwani, et al. [105] recommended oxalic acid as the optimum choice because the use of oxalic acid was more cost-effective than the use of sulfuric acid, which

consumed much NaOH in the extraction stage to manipulate pH value. However, if the product purity was the priority, then sulfuric acid would win with a product purity of 90.9 % than 75.52 % of oxalic acid.

Apart from acids, deep eutectic solvent (DES) was reported to be a promising leaching reagent which has a satisfying leaching efficiency, little harm to both human and environment as well as recyclability itself [93]. DES is composed of a hydrogen bond donor and a hydrogen bond acceptor, and the most common recipe is choline chloride: ethylene glycol (molar ratio 1:2). The recyclability of DES is one of the key properties that makes it advantageous over other leaching reagents. However, after leaching, electro-deposition is required to extract Co out for DES reuse [93], as the addition of the solvents for precipitating would break the eutectic state of DES [106]. This has made the subsequent extraction process more difficult than acid leaching. Besides, in some investigations [95,107], DES reuse was suggested, however, no data was presented to support this 'advantage'.

For the LCO leaching research, type and concentration of leaching reagent and reductant leaching temperature and time are the most frequently studied variables. However, the pressure in the leaching container is believed to influence the leaching process as well. It is noticed that some trials had similar leaching temperature, reagents and leaching efficiencies, but the leaching time varied a lot. The volume of container and the usage of condenser could have affected the pressure during leaching process, which explained the leaching time variation. Leaching efficiency is the most used data to reveal the performance of such a recycling process and the results are all of high level. The reason behind is that the researchers manipulated pulp density to get a satisfying result, making the comparison of different recycling approaches more difficult.

Pyrometallurgical approach, such as roasting, is another LCO recycling option. Roasting is usually conducted after the pre-treatment of the WLIBs, where the black mass is already separated from the current collector and all the organic chemicals are removed. This process can extract valuable metal elements through chemical reactions under argon atmosphere with the help of various reagents such as sodium hydrogen

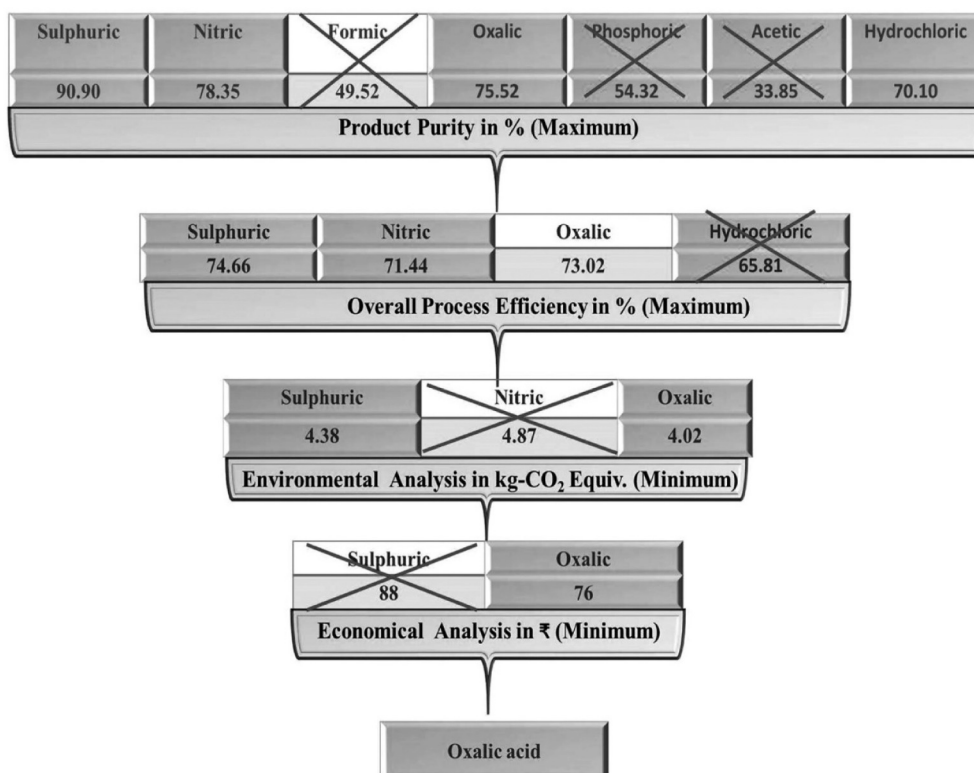


Fig. 7. Selection of environmentally benign and economically viable leaching process using sequential filters [105].



sulfate [108], carbon [109,110], ammonium sulfate [111] and calcium chloride [112] in a heating furnace. Take carbon as an example, it causes a carbothermic reduction which reduces the metal to lower valance product, such as NiO, MnO and CoO [113]. During the roasting process, the reducing agent breaks the bonds of the cathode active materials. For instance, the attracting force between reductive carbon and oxygen in LCO can break the O octahedron microstructures within  $\text{LiCoO}_2$  [110], releasing the trapped Li and Co in the “cage” and promoting the kinetics of the reaction. Consequently, with the carbon reduction, lower temperature is needed to achieve the extraction, saving vast amounts of energy [110,111]. As mentioned previously, the anodes of LIB are mostly graphite which can be used as the reducing reagent for roasting process, making this process more recyclable. However, subsequent refining, usually hydrometallurgical process, is mandatory to acquire high purity product for pyrometallurgical methods. To simplify the subsequent refining process, sodium hydrogen sulfate [108] or ammonium sulfate [111] was added during roasting to achieve water-soluble product such as  $\text{Li}_2\text{SO}_4$  or  $\text{CoSO}_4$  instead of metal oxides. However, a LCO roasting process, which requires pre-treatment as well as subsequent hydrometallurgical refining, is more complicated than the other methods, making it not as popular as hydrometallurgical or direct recycling among researchers.

Mechanical recycling is also investigated for LCO recycling. This method is relatively simple comparing with other techniques. Generally, it is a two-step method: 1. Grinding or crushing the batteries; 2. Sieving to separate different compounds. Fig. 8 illustrates the size groups of LCO after grinding, and it can be concluded that Al and Cu contamination decreases the purity of final Co product. Although Al and Cu can be removed via pre-treatment, it disobeys the simplicity of mechanical recycling strategy. Therefore, in order to make mechanical recycling more straightforward and to gain product with high purity, cryogenic grinding was investigated [114,115]. Cryogenic grinding takes advantage of the mechanical property change at low temperature (75 K–77 K) to be more selective in LCO recycling. The grinding was conducted at low temperature with the help of liquid nitrogen. The crystal transition of PVDF as well as the mechanical properties of collectors were investigated for a better understanding [115]. The differential scanning calorimetry (DSC) results illustrated that PVDF changed its crystal structure at 235 K which led to a more brittle physical property and less binding effect, thus improving the peeling-off efficiency. The impact test results reveal that the impact strength of both Al and Cu collector was enhanced as temperature dropped from 300 K to 75 K [115], leading to larger collector particles and more pure cathode powder after sieving. Nevertheless, the recovery rate and purity of product are still not satisfying enough for recycling LCO. It may be a wise choice for those cheaper cathodes, which asks for simple and economical recycling.

Direct recycling is a completely different concept of recycling, compared to previous methods. It is based on the healing of retired cathodes. The main drawback or argue is that the electrochemical performance of regenerated cathode is not as good as the pristine cathode. In order to improve the performance, alumina was utilized as a coating on the surface of the cured LCO cathode and it was reported that the

alumina coating can help to promote the electrical performance of the regenerated LCO to the level of commercial virgin product [55]. The improved stability of the  $\text{Al}_2\text{O}_3$  coated LCO cathode was due to the decrease of c-axis strain in the LCO microstructure, which was caused by the absence of a phase transition from a hexagonal to monoclinic phase [117]. However, the introduction of Al onto cathode makes future recycling more difficult and more battery cells should be tested under extreme circumstances for measuring the safety and cyclability of this alumina-coated cathode.

Unlike traditional direct recycling which takes advantage of Li salt or Li solution as the supplementary to heal spent cathodes. Wang et al. [118] applied environmentally friendly and cost-effective  $\text{LiCl-CH}_4\text{N}_2\text{O}$  DES as the Li source which is capable of healing both Li and Co defects in the spent cathodes. Besides, the DES can also be used up to 3 times to form a closed-loop recycling method. Another abnormal direct recycling was investigated by Wang et al. [119] which did not heal the cathodic material. Instead,  $(\text{NH}_4)\text{SO}_4$  was utilized as the reducing reagent to help reduce the cobalt in spent LCO cathode at low temperature roasting process. The decrease in roasting temperature is due to the decomposition reaction of  $(\text{NH}_4)\text{SO}_4$ , which generates sulfuric acid to react with LCO, thus saving more energy. However, the obtained regenerated LCO did not perform well in terms of cyclability.  $\text{MgF}_2$  was then added to improve the electrochemical performance and the result was significantly better.

## 2.2. $\text{LiMnO}_2$

As a cheaper substitute for LCO, LMO does not attract too much attention in recycling investigation. With high energy consumption and capital investment, pyro-methods are not in favor of cheap cathodes. The hydro-recycling method of LMO is also not interesting for researchers as the NMC hydro-recycling is more challenging and it can also be applied to LMO.

A ‘one-step’ direct recycling method is specially designed for recycling cheap LCO cathodes like LMO [96]. The direct recycling steps in this work is typical which immersed spent cathodes in LiOH solution and heated the sample to heal the cathodes. The highlight is that many characterizations have been done to acquire more knowledge of the process and the regenerated cathodes. The XPS spectra revealed that the relative ratio of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  can be used as a criterion to judge the lifetime of a LMO battery. The more  $\text{Mn}^{4+}$ , the more Li + has been lost during operation. The crystal structure analysis indicates that this direct recycling can compensate Li lost as well as recover the distorted lattice to pristine materials. Furthermore, cost analysis has been conducted and this approach was reported to have a considerable advantage over pyrometallurgical and hydrometallurgical methods in terms of energy consumption, cost and profit. This work is comprehensive and provides profound knowledge for direct recycling theory.

## 2.3. $\text{Li Ni}_x \text{Mn}_y \text{Co}_{1-x-y} \text{O}_2$

The recycling of NMC batteries is more complicated for researchers

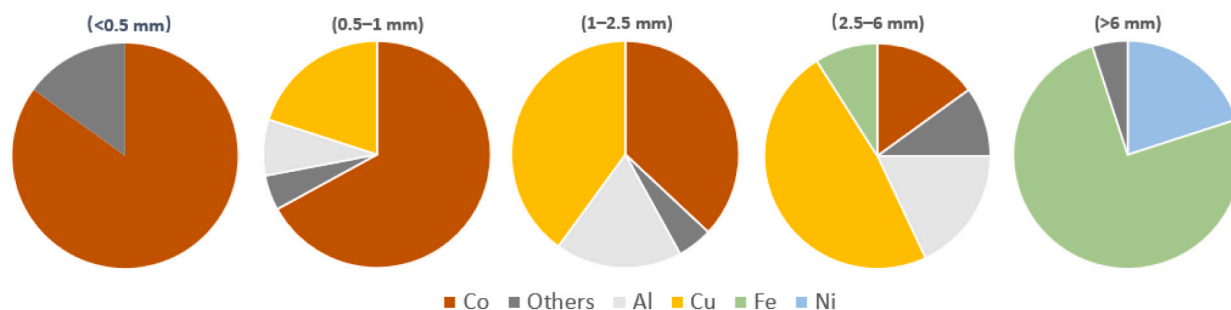


Fig. 8. The compositions of different components in five size groups of LCO battery after grinding (Data of this figure is from [116]) (Color needed for print).

to deal with due to the three transition metals which are similar in terms of chemical properties, thus being difficult to selectively recycle them. Much effort has been devoted to achieving an efficient selective recycling, which can obtain metal products with high purity.

However, for the purpose of manufacturing new NMC batteries with spent NMC batteries, the selectivity of recycling is not of great importance. In a NMC hydrometallurgical recycling approach [120], three transition metals were dissolved via DL-malic acid and then the concentration of these metals were measured by ICP-OES (Inductively coupled plasma optical emission spectroscopy). Subsequently, with the addition of  $\text{CH}_3\text{COOM}$  ( $M = \text{Ni, Co, Mn}$ ), the molar ratio of Ni, Co and Mn were controlled to 3:1:1. The transition metals were precipitated simultaneously as carbonate and were used as raw materials for  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  in the following thermal process. This method is an ideal option for battery companies to recycle their own retired product and can be further improved by a more efficient leaching as well as extracting. Moreover, spent NMC can be also utilized to produce catalysts for zinc-air batteries production with the help of acid leaching and radiative heating, which also took Ni, Mn and Co as a whole group instead of selective recovering them [121].

As for the NMC leaching, Liu et al. [122] compared the performance of four inorganic acids:  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HCl}$ . The variables were the concentration of the acids, the temperature (from 40 to 80 °C), time (from 5 to 120 min) and pulp density (10 to 50 g/L). No reductants were used in these trials. Because of its powerful reduction ability, hydrochloric acid can reduce metal ions to a lower valance without the help of reductants, thus increasing the solubility of metals and the leaching efficiencies. Under optimum conditions, the leaching efficiencies could reach as high as 100 %, 99.7 %, 99.3 % and 99.7 % for Li, Ni, Co, and Mn, respectively. As for extracting, selective adsorption for transition metals can be a more convenient choice compared to precipitation. Alginate aerogel can be taken into consideration which has been widely investigated in wastewater treatment [123–125] and it can be selective via different coatings.

Pyrometallurgical [126,127] and mechanical methods [115] can also be applied to NMC recycling, but they are not selective enough to separate Ni, Co and Mn. As these processes are quite similar to that of LCO recycling, they will not be discussed repeatedly here.

On the other hand, selective NMC recycling is particularly prevailing and aims at recovering these metals separately. Principally, the

selectivity is accomplished by hydrometallurgy, with the addition of several reagents which are designated for Ni, Co and Mn. For instance, in the work of Chen [79], after sulfuric acid leaching, Na-Cyanex 272 was first used to separate Co and Mn from Li and Ni by extracting Co and Mn into organic phase. Then the Mn is separated to organic phase by the addition of Na-D2EHPA (Na-Di-(2-ethylhexyl) phosphate) while cobalt is left in the solution. As for the Ni and Li, DMG (dimethylglyoxime) is utilized to precipitate Ni out while Li is still in the solution. Another investigation started with a solution containing  $\text{Li}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$  [128]. N,N,N',N'-tetra(n-octyl) digly-colamide (TODGA) was dissolved in 1-butyl-3-methylimidazolium bis(tri-fluoromethylsulfonyl) imide (abbreviated as [C4mim][NTf2]) and then was added to extract Mn while kept Li, Ni and Co in the solution. Then tri-hexyl tetradecyl-phosphonium chloride (abbreviated as [P66614][Cl]) is added to the solution for the extraction of Co. A DES (decanoic acid and lidocaine (2:1 M ratio)) is applied to extract Ni out, leaving Li in the solution. These approaches are extremely complicated in terms of reagents synthesis and preparation as well as processing. A relatively more straightforward process took advantage of the solubility difference of the target metals at different temperatures in a DES (choline chloride: ethylene glycol (molar ratio 1:2)) to separate metals in the leaching process [107] shown in Fig. 9. In the pre-treatment, Al collector was removed by NaOH dissolving. Then Cu collector was leached into the DES at 90 °C, while the other metals kept solid. Subsequently, Li, Co and Mn were leached by the DES at 180 °C while Ni stayed as solid. The leached Mn was extracted via the addition of D2EHPA while the leached cobalt was precipitated as cobalt oxalate afterwards. As mentioned above in LCO chapter, DES is a cost-effective and eco-friendly leaching reagent, and this selective solubility of Cu and Ni makes it even more advantageous.

Different from typical direct recycling, Shi et al. [98] applied a post-annealing process or a solid-state sintering after hydrothermal healing. It was concluded that the crystal structure of spent cathodes changed from the spinel and rock salt phase to the layered form with the help of annealing or sintering, thus improving the capacity, cycling stability as well as rate performance. Besides, the Ni content in NMC cathodes makes a difference in choosing sintering annealing atmosphere. While NMC with less Ni (NMC111) can be sintered in air to be recovered, NMC with more Ni (NMC532) requires more oxygen for achieving high layered phase purity. As Ni is responsible for the formation of rock salt

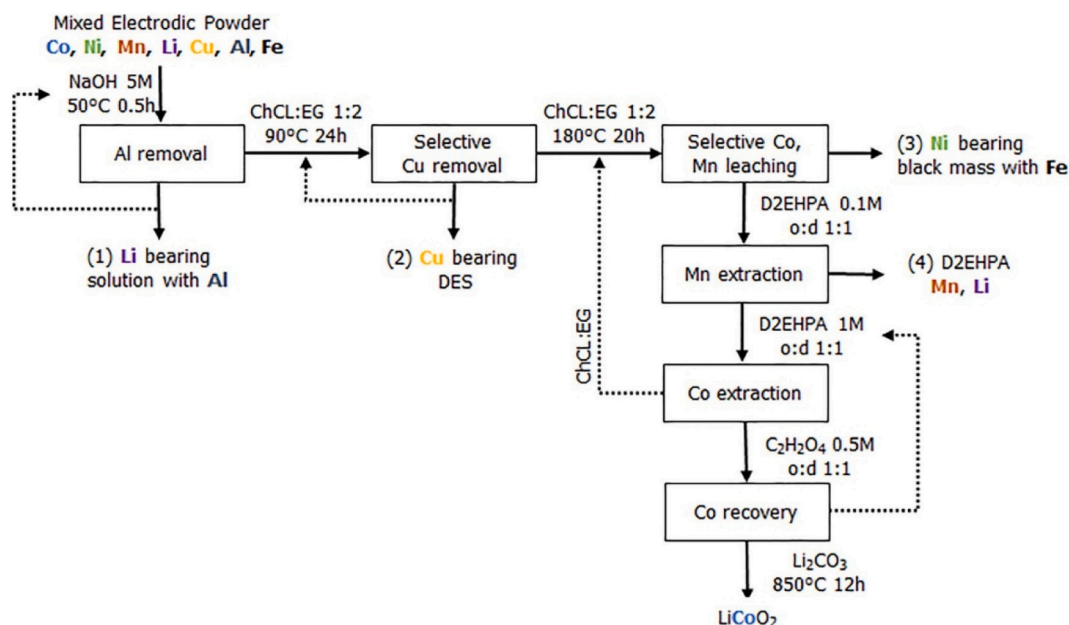


Fig. 9. Proof of concept of solvometallurgical recycling route using ChCl:EG deep eutectic solvent [107].

phase, more oxygen is necessary for converting rock salt phase to layered structure. Furthermore, the cation mixing in Ni rich NMC cathodes is another problem to solve for re-lithiation. Because of the similar sizes of  $\text{Ni}^{2+}$  and  $\text{Li}^+$ , the Li vacancies can be occupied by Ni as well which limits the re-lithiation efficiency. In this investigation [98], post-thermal treatment in oxygen atmosphere is considered to be an answer for the cation mixing. Nevertheless, as these thermal treatments consume much energy, combining the post thermal treatment with the hydrothermal healing to a one-step method could be a more efficient approach.

Another work from Qin et al. [129] sought the possibility of using a ternary molten salt as the lithium source for NMC direct recycling.  $\text{CH}_3\text{COOLi}$  was the third and key salt added to the mixture of  $\text{LiOH}$  and  $\text{LiNO}_3$  salts, which lowers the eutectic point of the salt. As for the results, the regenerated cathodes presented a capacity of  $150 \text{ mAh g}^{-1}$  at 0.5C and the capacity remained 93.7 % after 100 cycles which reaches the level of pristine materials. However, more lithium salts combination can be investigated to optimize the choice of lithium source in direct recycling. Apart from lithium salts,  $\text{Li}^+$  solution is another common choice as the lithium source for hydrothermal regeneration of spent cathodes. While water-based  $\text{Li}^+$  solutions are widely investigated, Wang et al. applied ionic liquid as both solvent and potential template or structure-directing agent in the formation [130]. The usage of ionic liquid has brought the benefit that lower temperature ( $150 \text{ }^\circ\text{C}$ – $250 \text{ }^\circ\text{C}$ ) is required for the regeneration process compared to the conventional molten salt method, thus saving energy. The XRD and electrochemical results proved this method to be practical.

The direct recycling of NMC is pretty popular nowadays. The key is to guarantee the electrochemical performance of the regenerated cathodes while seeking for environmentally friendly process. Future research goals are not only embedded in optimizing the process itself, but also lies on a more recycling friendly design of the next generation LIB.

#### 2.4. $\text{LiFePO}_4$

Compared to aforementioned cathodes, LFP has many advantages such as long cycling life, low toxicity, cheap price as well as high safety. It is widely used in electrical vehicles and other energy storage devices nowadays [131]. Although the potential and specific capacity of LFP are not as satisfying as the layer-structured LCO and NMC, much work has been done to enhance the electrochemical properties such as doping [132].

With regards to LFP recycling, inexpensive and highly efficient recycling methods are preferred as the cathodes are cheap compared to Co-based cathodes. As for hydro-leaching methods, while  $\text{H}_2\text{SO}_4$  acid leaching utilized  $\text{H}_2\text{O}_2$  [133] or  $\text{O}_2$  [134] as oxidant, alkaline leaching [135] took advantage of  $\text{Na}_2\text{S}_2\text{O}_8$  powder to oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and form  $\text{FePO}_4$  in the residue to separate Li out. These methods can achieve high purity products and be selective for Li and Fe. Organic acids [136,137] were also investigated for a greener method, however, the cost has limited its application in real LFP recycling industry.

In terms of low cost, direct recycling [99,100] and mechanical recycling [50,138] are appropriate options for LFP recovering. Unlike NMC batteries that suffer from cation mixing, LFP batteries can be directly recycled through one-step regeneration with  $\text{Li}_2\text{CO}_3$  compensator. It was reported that with regenerating temperature at around  $650 \text{ }^\circ\text{C}$ , the PVDF decomposed, and the cathode powder achieved satisfying performance. However, further temperature increase led to the decomposition of LFP, emphasizing temperature control in processing [100]. Moreover, to decrease the cost of direct recycling, a more precise target-healing method was investigated by Xu et al. [139]. The authors were able to regenerate cathodes with different degradation conditions to the level of virgin materials. The most critical factor in this research is to reduce  $\text{Fe}^{3+}$  for the benefit of efficient re-lithiation. Citric acid was chosen to be the reducing reagent and it was compared to traditional  $\text{LiOH}$  hydrothermal healing approach without reducing

reagent. The results revealed that, with the help of citric acid in  $\text{Li}^+$  solution,  $\text{Fe}^{3+}$  was reduced to  $\text{Fe}^{2+}$  which lowered the migration barrier for it to move from M1 site back to M2. In other words, the re-lithiation process was much more efficient than traditional methods without reducing reagent. It was also stated that this method can be modified to meet the needs of other cheap cathodes, such as LMO. Another work from Fan et al. [140] proposed an unusual direct recycling method with a pre-lithiated functionalized separator. They replaced the commercial separator in spent batteries with the pre-lithiated separator to compensate for the lithium loss. This approach not only saves the effort of cathode liberation, which is pretty problematic, but also takes full advantage of spent batteries where all the battery components were recovered safe and sound. Although the synthesis of the pre-lithiated separator is complicated, this method is promising in terms of its simplicity and low cost.

To avoid the energy-consuming thermal treatment, a mechanical centrifugation-based method was investigated [138]. The centrifugation chamber was first filled with water, then the self-made LFP black slurries were injected into the chamber by a pipe at a certain flow rate as shown in Fig. 10. The results revealed that at optimum conditions, almost all LFP particles were in the sediment and the centrifugation was strong enough to break the binding effect. Besides, no degradation of the electrochemical properties was reported, indicating that the centrifugation did no harm to the cathodes. This centrifugation process could be further investigated with spent LFP cathodes. Meanwhile, the water in the chamber could be replaced by Li supplemental solution to heal the cathode while being separated, thus integrating separation and regeneration as one process. A mechanochemical method was reported by K. Liu et al. [50], which took advantage of oxidation grinding to achieve Li separation. The spent cathodes were mixed with  $\text{Na}_2\text{S}_2\text{O}_8$  powder first and grinded in a ball mill. Subsequently, the grinded powder was leached into water and 99.7%wt Li was precipitated out as  $\text{Li}_3\text{PO}_4$  with the addition of  $\text{Na}_3\text{PO}_4$ . Using high purity  $\text{Li}_3\text{PO}_4$ , having no harmful by-products and being a simple processing, this method is promising in terms of Li recovering. Moreover, a brief cost-profit analysis was conducted to have an overall picture of this method from economical perspective.

### 3. Recycled cathode performance

In order to verify the feasibility of recycling methods, recycled cathodes are made into cells to test the electrochemical performance. The Table 5 briefly summarizes the electrochemical results of different recycling methods.

It can be noticed that the LCO from hydro recycling method performed relatively better than those from direct recycling. The reason behind is that hydro-recycling aims at selectively extracting different pure metal products, such as  $\text{Li}_2\text{CO}_3$  or  $\text{Co}(\text{OH})_2$ , from the spent cathodes and producing pristine active materials afterwards. In general, newly produced cathodic materials present better electrochemical properties than those of regenerated or healed cathodes. Consequently, for most hydrometallurgical investigations, more than the electrochemical properties, the purity of final products is better evidence to prove the practicability of the approach. As for pyro-methods, after thermal treatment the hydrometallurgical refining process is necessary, which also leads to high purity final products. Besides, it is still difficult to remove side-products from the obtained solids by mechanical recycling, so, these methods have not reached the stage of recycled material reuse.

In direct recycling, as cathode materials are non-destructively healed, electrochemical tests are mandatory to show the effectiveness of the method. Furthermore, direct recycling is always 'accused' of poor electrochemical performance when compared to virgin cathodic materials. However, the results reveal that after an optimization process the performance of re-lithiated materials is acceptable. Examples of the optimization are that 1) temperature and time adjustment [96,99]; 2)

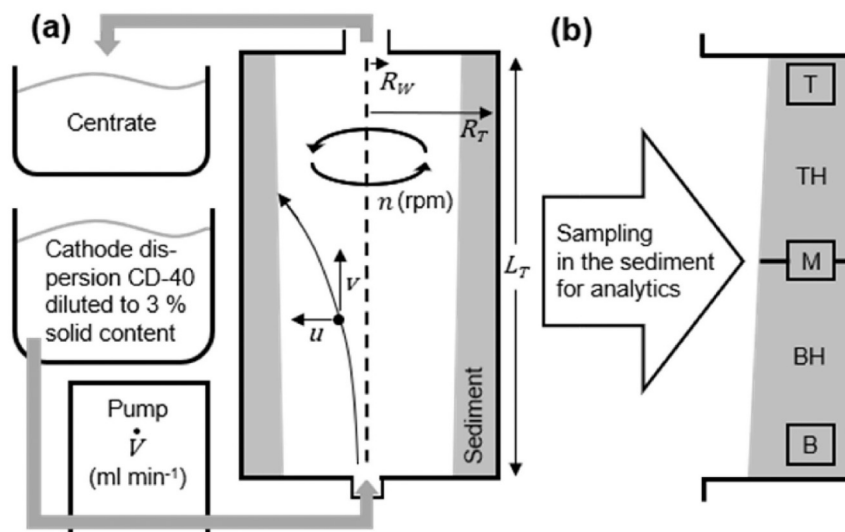


Fig. 10. Illustration of centrifugation-based process [138].

**Table 5**  
Electrochemical performance of recycled materials.

Cathode	Specific capacity (mAh g <sup>-1</sup> )	Cyclability (mAh g <sup>-1</sup> )	Recycling method	Ref.
LCO	145 (1C = 150 mA g <sup>-1</sup> )	134 (1C, 100 cycles)	Pyro	[141]
LCO	155 (1C)	145 (1C, 100 cycles)	Hydro	[80]
LCO	136.8 (20 mA g <sup>-1</sup> )	123.2 (20 mA g <sup>-1</sup> , 100 cycles)	Direct	[55]
LCO	148.2 (1C = 150 mA g <sup>-1</sup> )	135.1 (1C, 100 cycles)	Direct	[97]
LCO	154.3 (0.1C)	150.3 (0.1C, 100 cycles)	Direct	[119]
LCO	133.1 (0.1C)	119.8 (0.5C, 100 cycles)	Direct	[118]
LFP	133 (0.1C; 1C = 170 mA g <sup>-1</sup> )	128 (0.1C, 20 cycles)	Pyro	[142]
LFP	144 (0.1C; 1C = 170 mA g <sup>-1</sup> )	135 (0.1C, 100 cycles)	Direct	[99]
LFP	147.3 (0.2C; 1C = 150 mA g <sup>-1</sup> )	140.4 (0.2C, 100 cycles)	Direct	[100]
LFP	146.7 (1C; 1C = 170 mA g <sup>-1</sup> )	132 (1C, 292 cycles)	Direct	[140]
LFP	159 (0.1C; 1C = 170 mA g <sup>-1</sup> )	161 (0.5C, 100 cycles)	Direct	[139]
LMO	111 (0.5C; 1C = 148 mA g <sup>-1</sup> )	98 (0.5C, 100 cycles)	Direct	[96]
NMC311	258 (10 mA g <sup>-1</sup> )	210 (10 mA g <sup>-1</sup> , 50 cycles)	Pyro	[143]
NMC311	142.9 (1C; 1C = 180 mA g <sup>-1</sup> )	130 (1C, 50 cycles)	Hydro	[120]
NMC111	158.4 (1C; 1C = 150 mA g <sup>-1</sup> )	122.6 (1C, 100 cycles)	Direct	[98]
NMC532	160 (0.5C; 1C = 150 mA g <sup>-1</sup> )	150 (0.5C, 100 cycles)	Direct	[129]
NMC111	173.6 (0.1C)	~118 (1C, 100 cycle)	Direct	[130]

annealing after regeneration [97,98]; 3) lithium source adjustment [55]. Hydrothermal or solid sintering methods of direct recycling are quite advantageous in LIB recycling from the perspective of cost, efficiency as well as product performance. However, future investigations on the optimization of synthetic conditions (i.e., milder temperatures) as well as on the improvement of the electrochemical performance could be done.

#### 4. Emerging battery chemistries and recycling strategies

With the rocketing demand of electrical vehicles in the near future, energy storage is becoming a hot topic both in industry and academia. High energy density, long lifespan, great cycling and thermal stability and superior safety, are among the most critical parameters for a storage technology to succeed. The bottleneck is to discover a satisfying technology that has a reasonable cost, ignorable environmental impact, high electrochemical performance and outstanding recyclability. Countless efforts have been devoted to explore new systems, and solid-electrolyte batteries as well as lithium-sulfur batteries were introduced as competitive candidates.

All solid-state batteries (ASSB) refer to batteries using a solid electrolyte, such as LISICON-Li<sub>3</sub>BO<sub>3</sub> amorphous oxide [144], sulfide-based electrolyte [145] and polymer-based composite [146]. Solid electrolytes are safer as well as more stable than liquid electrolyte which is volatile at high temperature. Furthermore, Li dendrite formation can be mitigated, facilitating the utilization of high energy density Li metal anode. In terms of recycling, the electrolyte becomes an important part to recycle and regenerate. While polymer-based electrolytes can be dealt with in air, oxide-based and sulfide-based electrolytes require low humidity or inert atmosphere to keep them functional, introducing additional difficulties for the recycling process. With regards to electrodes, Li anodes can easily be leached into water and then precipitated as Li<sub>2</sub>CO<sub>3</sub> with the addition of sodium carbonate. However, the generation of flammable hydrogen during the water leaching process poses a safety concern. A hydrometallurgical method is recommended as it can deal with both the anode and the cathode electrodes simultaneously without harming the polymer electrolyte and can acquire purer Li for the re-synthesis of the anode. For the other types of solid electrolytes, humidity could affect their performance or even disable them. Controlling the atmosphere during the whole process seems to be too expensive which calls for a treatment which can heal solid electrolytes after exposing to humidity. Direct recycling is another option that can heal the cathodes from solid electrolyte batteries, which are the same as those in liquid LIBs. However, as direct recycling always focuses on cathodes, more efforts should be devoted to recycling the Li anodes as well as the solid electrolyte, making it more complicated than hydro-methods.

Another promising candidate for future energy storage is Li-S battery technology which can give gravimetric energy density values much higher than those of traditional LIBs (about 2550 Wh kg<sup>-1</sup> considering an average discharge voltage of 2.15 V and a theoretical capacity of 1167 mAh g<sup>-1</sup>). The abundance and low cost of sulfur make Li-S batteries



even more advantageous over LIBs. Nowadays, Li–S batteries are still in the laboratory stage and face various challenges, such as low coulombic efficiency, low reaction rate of the cathode, low cyclability and safety issues. Besides, recent investigation conditions are far from the industrial requirement (sulfur loading of over  $5 \text{ mg cm}^{-2}$ ) [147]. However, with unprecedented work from researchers worldwide, Li–S batteries could take a big share of portable device energy storage. As for recycling, the main target to recycle and recover is the Li anode. Due to the toxicity of sulfur by-products, such as sulfur dioxides, sulfur should be controlled during the recycling process. Hydrometallurgical methods could be an excellent option, because Li can be easily leached by water and the sulfur with carbon just floats on water once the binder is removed or decomposed. Pyrometallurgical methods are not suitable for Li–S batteries recycling, as Li is vaporized and adhere to the furnace wall which is hard to collect. Besides, post-treatment for gases emission (such as SO and SO<sub>2</sub>) is also obligatory after thermal process, which increases the cost.

As an already commercialized battery technology (**Hinabattery** in China; **Natron Energy** in USA; **Tiamat** in France; **Faradion** in UK), sodium-ion batteries (SIB) substitute Li with Na, which has similar chemical properties, and it is more abundant as well as cheaper than lithium. Moreover, to further decrease the cost, some works are focused on producing SIB with recycled materials, such as baby diapers [148]. Generally, the SIB cathodes can be categorized into 5 groups: layered oxides; polyanionic materials; conversion materials; organic materials as well as Prussian blue analogues [149]. Although the performance of SIB cathodes is not as good as that of LIB, it is still important to pursue a more sustainable approach to the exploitation of nature resources. Examples of cathodes are NaMnO<sub>2</sub>(O3), NaFeO<sub>2</sub>(O3), Na<sub>0.6</sub>MnO<sub>2</sub>(P2). Na, Mn, Fe, Ni, Zn, Ti and Co are possible elements in SIB cathodes, and the strategies of recycling SIB are similar to that of LIB. The most critical factor of SIB recycling is the cost, as most metal elements used are not very valuable. Herein, direct recycling is recommended for SIB. However, more investigations about the phase change and Na refill efficiency during the thermal treatment should be conducted. Table 6 summarizes the recycling strategies for the emerging battery chemistries above.

## 5. Future directions for recycling

### 5.1. Recycling-friendly battery

As most of the investigations on LIB recycling focus on boosting the electrochemical properties of LIB, the theoretical threshold of materials has set a limit. LIB is becoming the most prevalent energy storage unit in the near future, recycling-friendly module is calling for more attention to create a close-loop industry, which asks for recycling-oriented research instead of performance-oriented ones. Possible topics are: 1. lighter, reliable as well as easy to remove design of battery outer shell, which can reduce the total weight of battery modules as well as facilitating the dismantling of spent batteries; 2. recyclable and safer electrolyte, which reduces the potential danger during the recycling process, such as solid electrolyte or water; 3. a binder which can be easily

**Table 6**  
Recycling strategies for emerging battery chemistries.

Battery type	Recommended strategy	Key factor to be noted
ASSB	Hydrometallurgical; direct recycling	<ul style="list-style-type: none"> <li>• Solid electrolyte recycling and refuction</li> <li>• Recycling atmosphere for different solid electrolytes</li> </ul>
Li-S	Hydrometallurgical	<ul style="list-style-type: none"> <li>• Lithium anode recycling</li> <li>• Sulfur contamination</li> <li>• Lithium extraction</li> <li>• Safety concern during dismantling</li> </ul>
SIB	Direct recycling	<ul style="list-style-type: none"> <li>• Crystal structure shift in thermal treatment</li> <li>• Possible cation mixing</li> </ul>

removed, such as just heating or selectively sensitive to a cheap solvent, improving the cathode liberation efficiency. An example is the work of Li et al. [150] about water-based LIB, which applied water-soluble binder to replace toxic NMP with water during the electrode synthesis process. This research has taken the whole lifespan of LIB into account which include synthesis and direct recycling. The replacement of NMP benefits both the synthesis and direct recycling in terms of safety and cost. Besides, the electrochemical performance of the regenerated cathodes is comparable to the pristine ones.

### 5.2. Reuse of regenerated materials

The research works on hydrometallurgical, pyrometallurgical and mechanical recycling have obtained the products with high purity. However, the reuse of these regenerated materials should be further investigated, such as testing electrochemical properties of cells made from those materials. This could help to build a whole picture for the recycling process.

### 5.3. Mechano-direct recycling method

As previously mentioned in LFP centrifugation-based recycling method [138], the re-lithiation process can be integrated with the mechanical process which can achieve cathode separation and regeneration in one operation, saving much time and effort. Another opportunity could be ultrasound-aided separation with hydrothermal regeneration, while ultrasound can possibly accelerate the decomposition of PVDF binder as well as improve Li refilling into vacancies.

### 5.4. Extracting technique

In recent hydrometallurgical investigations, the extraction topic concentrates on selective extraction of Ni, Co and Mn. The selective separation benefits the recycling companies as they can sell Ni, Co and Mn as individual product. Nevertheless, for the battery companies, selective extraction is not that attractive when compared with efficient extraction, because these elements have to be mixed together anyway. Alginate-based beads are widely known for their absorbability of metal ions, and they can be selectively adsorbable with some modifications, such as coating [151–153]. The organic beads can be directly fed into furnace for the cathode synthesis after adsorption, saving much time from filtering, centrifugation. Besides, they are cheap, environmentally friendly as well as efficient.

### 5.5. Disassembling improvement

In battery recycling pre-treatment, disassembling is either done by hand or mechanical crushing. The manual dismantling is time-consuming as well as harmful for operators while the mechanical crushing mixes unwanted Al and Cu collector into cathodic materials. For the purpose of being more efficient, more efforts are required in this process. Possible solutions can be mechanochemically disassembling, which dissolves PVDF binder and liberates cathodic powders at the same time.

### 5.6. Close-loop hydrometallurgical recycling method

Leaching reagent, reducing reagent and precipitating reagent are commonly utilized in hydrometallurgical methods. For the purpose of achieving a greener, cheaper method, the reuse and recovery of these reagents should be taken into consideration. As reported in some researches [93,107], deep eutectic solvent can be recycled which seems to be promising for creating a close-loop leaching process. However, the recyclability of DES is not supported by detailed data till now, and more work should be done in finding a recyclable leaching reagent. As for reducing reagent, graphite anodes are often ignored due to its low price.

However, carbon anodes can be the reductant in carbothermal reduction process, reducing metal ions to lower valence state which is beneficial for subsequent leaching. With regards to precipitating reagent, NaOH is now widely utilized for Ni, Mn and Co precipitation. Recyclable precipitating reagent and close-loop metal extraction method still demand more investigations.

### 5.7. Cost-benefit analysis

In order to accelerate the industrialization of applicable techniques, economic data is required for a profound understanding of certain recycling approaches. Due to the huge difference between lab-scale investigation and mass production, the cost-benefit analysis should be based on an industrial background, calling for more professional knowledge of economics as well as computer modelling.

### 5.8. Lithium recovering in pyrometallurgical methods

In most traditional pyrometallurgical methods, lithium vaporizes and is attached to the surface of furnace or tube, which is tough to collect [154]. However, lithium is becoming increasingly critical in future electrolyte and anodes. A pyrometallurgical method which can recover lithium from cathode, electrolyte as well as anode would become much more advantageous. Possible solution can be the post-treatment of gas emitted with the help of air pumping. However, this has to be done before the lithium vapor solidifies, demanding extra heating for gases in the tube.

## 6. Conclusions

Present work emphasizes the significance of recycling spent LIB which will dominate the energy storage market in the near future. Different methods for recycling typical cathodes and the electrochemical performance of these recycled materials are introduced briefly. It can be concluded that the recycled materials behaved reasonably satisfying in terms of their specific capacity and cyclability, indicating that the recycling approaches in published papers are practical to some extent. However, as battery chemistries upgrade from time to time, recycling strategies for emerging batteries, such as all solid-state batteries, Li–S batteries as well as sodium ion batteries, are needed to build up and have been discussed in this work. Furthermore, the outlook for future investigations is included to provide potential opportunities in battery recycling.

### CRedit authorship contribution statement

**Yifeng Wang:** Conceptualization, Methodology, Writing – original draft, Visualization. **Eider Goikolea:** Writing – review & editing, Supervision, Resources. **Idoia Ruiz de Larramendi:** Writing – review & editing, Resources. **Senentxu Lanceros-Méndez:** Project administration, Funding acquisition, Writing – review & editing. **Qi Zhang:** Writing – review & editing, Supervision, Funding acquisition.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

No data was used for the research described in the article.

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