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Green Industrial Processes—Review

A Mini-Review on Metal Recycling from Spent Lithium Ion Batteries

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ABSTRACT

The rapid growth of lithium ion batteries (LIBs) for portable electronic devices and electric vehicles has resulted in an increased number of spent LIBs. Spent LIBs contain not only dangerous heavy metals but also toxic chemicals that pose a serious threat to ecosystems and human health. Therefore, a great deal of attention has been paid to the development of an efficient process to recycle spent LIBs for both economic aspects and environmental protection. In this paper, we review the state-of-the-art processes for metal recycling from spent LIBs, introduce the structure of a LIB, and summarize all available technologies that are used in different recovery processes. It is notable that metal extraction and pretreatment play important roles in the whole recovery process, based on one or more of the principles of pyrometallurgy, hydrometallurgy, biometallurgy, and so forth. By further comparing different recycling methods, existing challenges are identified and suggestions for improving the recycling effectiveness can be proposed.

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1. Introduction

Since the 1990s, lithium ion batteries (LIBs) have been widely used in portable electronic devices and electric vehicles [1–3] because of their high energy density, long storage life, small volume, light weight, low self-discharge efficiency, non-memory effect, wide range of application temperatures, and advantages in environmentally compatible operations [3–6]. However, a large number of spent LIBs have been produced in recent years due to the accelerated updating of consumer electronics and the continued promotion of LIBs in electric vehicles. According to statistics, the lifetime of LIBs in digital products is only one to three years, and the lifetime of LIBs in power vehicles is five to eight years [7,8]. Based on these statistics, China will produce 2.5 billion of spent LIBs with a mass of about 500 000 t by 2020 [9]. A LIB is generally composed of cathode materials, anode materials, an electrolyte, a separator, and so on. Some of the materials used in LIBs, such as heavy metals and toxic electrolytes, pose a special threat to ecosystems and human health. It has been reported that 4000 t of spent LIBs contain 1100 t of heavy metals as well as more than 200 t of toxic electrolyte [10]. If the spent LIB is disposed of by

landfilling, this may lead to the infiltration of toxic heavy metals into underground waterbodies, resulting in serious environmental pollution. Similarly, if the spent LIB is burned as a general type of solid waste, it will produce a considerable amount of poisonous gases, such as hydrogen fluoride (HF) gas, thereby polluting the atmosphere. Therefore, harmless treatment for spent LIBs is very necessary. In addition, spent LIBs have a high economic value because they contain a significant amount of valuable metals, some with an even higher grade than the metal grade in natural ores [11]. Spent LIBs usually contain 5%–20% cobalt (Co), 5%–10% nickel (Ni), 5%–7% lithium (Li), 5%–10% other metals (copper (Cu), aluminum (Al), iron (Fe), etc.), 15% organic compounds, and 7% plastic [10], although their compositions differ depending on the manufacturers. Valuable metals such as lithium, nickel, cobalt, and manganese (Mn) from spent LIBs bring significant economic benefits if they can be recycled.

Spent LIBs are a new kind of waste that are different from other kinds of solid waste. On the one hand, the purpose of recycling spent LIBs is to reduce or eliminate potential environment impacts; on the other hand, such recycling also realizes the valuable metal recycling of resources, thus promoting the sustainable development of the LIB industry and industrial upgrading. Although a great deal of research has been carried out all over the world on the recycling of LIBs, the technology and process for recycling LIBs remain

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at the laboratory level because of the complex structure of the spent LIBs. The most commonly used technology for the industrial recycling of spent LIBs is pyrometallurgical processes [12]. Using these processes, nickel, cobalt, and copper can be recovered effectively, while lithium and aluminum are lost in slag [13]. However, pretreatment of spent LIBs is unnecessary in such processes, and their higher energy consumption, high equipment investment, and environmental pollution hinder their application. Therefore, many hydrometallurgical processes have been developed by various companies, such as the processes developed by Accurec, Toxco Inc. (now Retriev Technologies Inc.), and so on [12,13]. In these companies, spent LIBs are recycled through the following steps: pretreatment, leaching, solvent extraction, and precipitation. The advantages of hydrometallurgical processes are low energy consumption and the ability to recycle lithium and aluminum. However, the drawbacks of these processes are their long route. This paper reviews the main methods and processes of spent LIB recycling, analyzes their main problems, and provides a reference for the future development of spent LIB recovery technology.

2. Structure of the LIB

A LIB is usually made of a cathode, an anode, electrolyte, a separator, and so on [5,10,14,15]. The cathode materials of LIBs are mainly lithium intercalation oxides, such as LiNiO_2 , LiMn_2O_4 , LiCoO_2 , LiFePO_4 , $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$, and so forth [16–19]. Because of the advantages of low cost, large discharge capacity, good cyclic performance, and stable structure, the $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ cathode material has become the most promising cathode material for LIBs and has been applied in the field of electric vehicles. The electrolyte of a LIB usually includes solvents and solutes, where the solutes used are usually LiClO_4 , LiPF_6 , LiBF_4 , and so forth [20]. One of the most common solutes used in LIBs is LiPF_6 . Organic solvents that are used include dimethyl sulfoxide (DMSO), propylene carbonate (PC), and diethyl carbonate (DEC) [21], and the solvent solutions used are usually mixtures of one or more of the reagents listed above. The separator prevents short circuiting due to direct contact between the anode and the cathode. LIB separators are usually a single layer or multi-layer of polyethylene (PE) or polypropylene (PP) [22].

LIBs have been considered to be greener and cleaner energy storage devices than other batteries because of their higher voltage, high energy density, low self-discharge efficiency, and lower harmfulness to the environment. However, LIBs still pose a threat to the environment and to human health because of the hazardous materials they contain. As shown in Table 1, LIBs contain heavy metals from the cathode materials as well as hazardous organic materials from the electrolyte, separator, and binder. Therefore, it is necessary to harmlessly recycle spent LIBs in order to recover their major components.

3. State of the art for spent LIB recycling

A spent LIB contains not only highly valuable metals such as Li, Ni, and Co [5,9,10,23], but also Fe, Al, phosphorus (P), and other elements with low recovery values. Driven by economic interests,

the recovery of spent LIBs mainly focuses on recycling highly valuable metals such as Co, Li, and Ni from cathode materials; the recovery of anode materials and electrolyte is rarely reported. A summary of current metal-recycling processes is shown in Fig. 1. State-of-the-art processes for metal recycling from spent LIBs can be divided into three types of processes: namely, pretreatment processes, metal-extraction processes, and product preparation processes. It is notable that metal-extraction processes play an important role in the entire recovery process and involve one or both of the pyrometallurgical method and the hydrometallurgical method.

3.1. Pretreatment process

In order to prevent short circuiting or spontaneous combustion, spent LIBs are discharged first [11,24]. A common method of discharging is to immerse the spent LIBs in a salt solution. Next, the spent LIBs are treated by manual dismantling or mechanical separation. Manual dismantling is usually used to separate the cathode, anode, and other components, as follows: The plastic shell of the battery is removed first; then liquid nitrogen is used to inactivate harmful substances. The battery is then fixed on a lathe. The end of the battery shell is removed by a saw; the battery is then opened longitudinally and the outer shell is removed. Finally, the cathode, anode, and separator are separated and then dried in an oven for 24 h at 60 °C [9,11]. The obtained cathode and anode are further separated for the metal-extraction process. The cathode material is generally adhered to aluminum foil by the binder (polyvinylidene fluoride (PVDF) or polytetrafluoroethylene (PTFE)), making it difficult to separate the cathode material from the foil. To properly separate the cathode material from the foil, a solvent dissolution method [15,25–27], sodium hydroxide (NaOH) dissolution method [28–31], ultrasonic-assisted separation [24,32,33], thermal treatment method [16,34,35], and mechanical method [36–38] have been tested.

3.1.1. Solvent dissolution method

A solvent dissolution method [15,25–27] using organic solvent weakens the adhesion of the binder of cathode scraps to remove the cathode materials from the aluminum foil. Therefore, the key to the solvent dissolution method is to select the optimum organic solvent to dissolve the binder. The organic solvent N-methyl pyrrolidone (NMP) is usually chosen to dissolve PVDF binder. Con-testabile et al. [8] developed a laboratory process for recycling LIBs in which the anode and cathode that were obtained after removing the shell were heated with an NMP solution below 100 °C. This method allowed LiCoO_2 and graphite to be separated from the collector effectively, while Al and Cu were still in metal form. However, the separation of LiCoO_2 is affected by the type of binder and by the rolling method of the electrodes. In order to achieve separation of the cathode materials from the aluminum foil, Zhou et al. [39] chose dimethylformamide (DMF) to dissolve PVDF. They showed that the solubility of PVDF in DMF at 60 °C is 176 $\text{g}\cdot\text{L}^{-1}$. However, these reported organic solvents are not suitable to separate a PTFE-based cathode. To solve the challenge for PTFE-based LIBs, Zhang et al. [40] proposed a novel process to separate the

Table 1
Environmental hazards of LIBs.

Component	Materials	Hazardous
Cathode	LiNiO_2 , LiMn_2O_4 , LiCoO_2 , LiFePO_4 , $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$	Heavy metals such as Ni and Co pose a threat to the environment and to human health
Electrolyte	LiClO_4 , LiPF_6 , LiBF_4 , DMSO, PC, and DEC	Corrosive, produces hazardous gas such as HF, chlorine (Cl_2), carbon dioxide (CO_2), and carbon monoxide (CO) when burned
Binder	Polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE)	Produces HF when heated

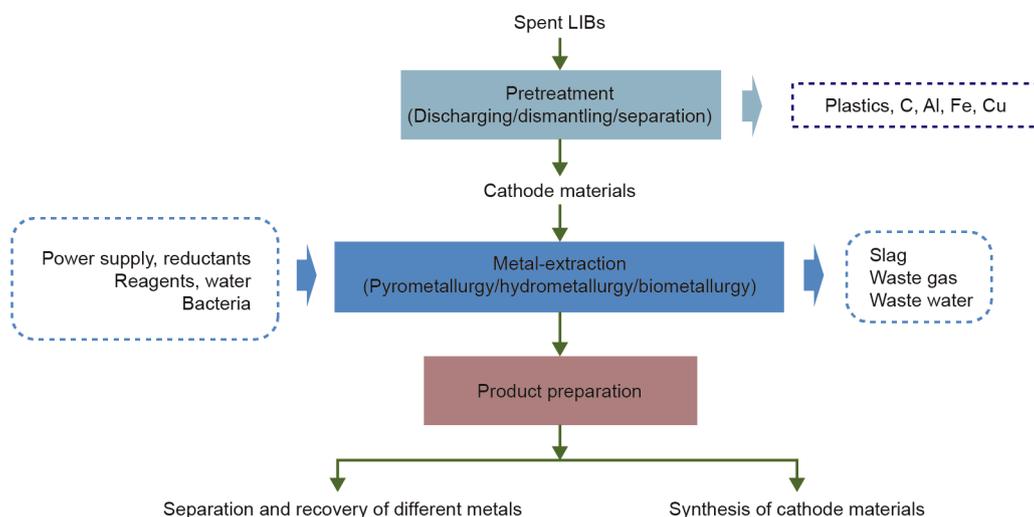


Fig. 1. General schematic of the methods and processes for recycling spent LIBs.

cathode material from the aluminum foil using trifluoroacetate (TFA). The cathode material was completely separated from the aluminum foil when the volume fraction of the acetic acid was 15 vol%, the liquid-to-solid ratio (L/S ratio) was $8 \text{ mL}\cdot\text{g}^{-1}$, the temperature was 40°C , and the reaction time was 180 min. This solvent dissolution method offers great efficiency in separating the cathode material from the aluminum foil. However, the methods used in the literature mainly deal with cathodes with a PVDF binder; research seldom focuses on dealing with PTFE-based cathodes. In addition, the solvents used in the separation process are very expensive and have a certain degree of toxicity, thus posing a threat to the environment and human health.

3.1.2. NaOH dissolution method

In many proposed recycling processes, the cathode materials are separated from the aluminum foil by leaching the cathode with a NaOH solution, which works to separate the materials because of the amphoteric property of aluminum [27–31]. In their process to recover the cathode material, Nan et al. [31] used NaOH solution to realize the separation of cathode material from aluminum foil. Using a NaOH solution with a 10 wt% concentration, $100 \text{ g}\cdot\text{L}^{-1}$ solid-to-liquid ratio (S/L ratio), 5 h reaction time, at room temperature, about 98% of the aluminum foil was dissolved. When a NaOH solution is used to dissolve the aluminum foil of the cathode, two substances are dissolved: the protective layer covering the surface of the collector and the aluminum [29].



This method has the advantages of simple operation and high separation efficiency. However, the recovery of Al is difficult due to the ionic form of Al. In addition, the alkali wastewater (i.e., NaOH solution) is very environmentally harmful.

3.1.3. Ultrasonic-assisted separation

It is difficult to remove cathode material from aluminum foil during the recycling of spent LIBs because of the strong adhesive force of the PVDF binder. Ultrasonic treatment is considered to be an effective method for stripping cathode material from aluminum foil because of its cavitation effect [24,32,33]. When studying the effects of agitation and ultrasonic treatment on the separation of cathode materials, Li et al. [33] discovered that most of the cathode materials continued to adhere to the surface of the

collectors when mechanical agitation alone was used. When ultrasonic cleaning alone was used, only parts of the cathode materials were separated. However, when both methods were used simultaneously, almost all of the cathode materials could be stripped from the collectors. This may be because the cavitation effect of ultrasonic cleaning can generate greater pressure to destroy insoluble materials and disperse them in water. The rinsing effect of mechanical agitation further promotes the separation of cathode materials from the collector. He et al. [32] attributed the mechanism by which cathode materials were separated from aluminum foil by ultrasonic cleaning to the dissolution of the binder and to the cavitation effect produced by the ultrasound. Based on this mechanism, the stripping efficiency of the cathode material reached 99% with NMP as the cleaning solution at 70°C , 240 W ultrasonic power, and 90 min ultrasonic processing time. Cathode material that was separated from the aluminum foil by ultrasonic cleaning exhibited a low degree of agglomeration, which facilitated subsequent leaching processes.

3.1.4. Thermal treatment method

The thermal treatment method [16,28,34,35] utilizes high-temperature binder decomposition to reduce the bonding force between particles of cathode material; the cathode materials can then be easily separated by sieving and so on. It is reported that PVDF binder generally decomposes above 350°C , while other components (e.g., acetylene black, conductive carbon, etc.) generally decompose above 600°C [34]. Sun and Qiu [35] proposed a novel method to separate cathode material by means of vacuum pyrolysis. Through the process of pyrolysis, the electrolyte and binder were evaporated or decomposed, which reduced the adhesion of the cathode material and collector. When the pyrolysis temperature was lower than 450°C , the cathode materials did not peel away from the collectors. When the temperature was between 500 and 600°C , the separation efficiency increased with an increase in the temperature. However, the aluminum foil became fragile at temperatures above 600°C , making it difficult to separate the cathode material from the collector. Yang et al. [16] proposed a reducing thermal treatment process to achieve the separation of the cathode materials from the Al collectors. It was shown that controlling the reduction reaction temperature allows the cathode materials to be clearly separated from the current collectors. In addition, this process changes the molecular structures of the active cathode materials, which facilitates the leaching of metals in the leaching steps. The advantages of thermal treatment are

its simple operation and high throughput. However, its disadvantage is that poisonous gas is generated during the thermal treatment of the binder and additives.

3.1.5. Mechanical methods

Mechanical methods are generally recognized to be an effective pretreatment to deal with spent LIBs; these methods include sieving, crushing, magnetic separation, and so on. In order to provide basic information related to mechanical methods, Zhang et al. [37] performed chemical and process mineralogical characterizations of spent LIBs by combining several analytical techniques. It was found that spent LIBs manifested excellent selective crushing properties. The crushing products of spent LIBs consist of three parts: an Al-enriched fraction (> 2 mm), a Cu- and Al-enriched fraction (0.25–2 mm), and a Co- and graphite-enriched fraction (< 0.25 mm). The mineral phase and the chemical state analysis revealed that the cathode materials obtained from the < 0.25 mm fraction retained their original crystalline structure and chemical state in LIBs. However, the surface of these powders was coated with a layer of hydrocarbons, leading to difficulty in flotation operations. Shin et al. [41] proposed a combined process to recover metals from spent LIBs that used mechanical separation for the collection of cathode materials, followed by a hydrometallurgical process for metal recovery. Enriched particles of LiCoO₂ were obtained through a series of mechanical treatments such as crushing, sieving, and magnetic separation; next, LiCoO₂ and small pieces of aluminum foil were separated by finely grinding the LiCoO₂-enriched particles. The efficiency of the targeted metals recovery can be improved using mechanical separation processed before the metal-leaching process. The main disadvantage of mechanical methods is that the components of spent LIBs cannot be completely separated from each other; in addition, the decomposition of LiPF₆, DEC, and PC during mechanical processes poses a threat to the environment.

Although many pretreatment methods have been developed by researchers, challenges still exist regarding pretreatment of spent LIBs. The advantages and disadvantages of different pretreatment methods are summarized in Table 2.

3.2. Metal-extraction process

The metal-extraction process is a significant part of the whole recovery process. The metal-extraction process focuses on changing the solid metals in spent LIBs into their alloy form or solution state, which facilitates the subsequent separation and recovery of metal components. The main approaches adopted during the extraction process include pyrometallurgy, hydrometallurgy, biometallurgy, and so forth. Of these approaches, hydrometallurgy has become a promising process due to its desirable recovery rate and high purity of the product.

3.2.1. Pyrometallurgy

A typical pyrometallurgical process for recycling valuable metals from spent LIBs is high-temperature smelting reduction; after

this process, valuable metals are reduced and then recovered in the form of alloys [42]. For example, a combination of pyrometallurgical and hydrometallurgical processes was developed to recycle spent batteries by Umicore process [12]. Spent LIBs are put directly into a smelting furnace without pretreatment. The plastics, organic solvents, and graphite in the batteries provide heat during combustion, while the metal components are reduced and converted to alloys. The obtained alloys are further purified via sulfuric acid (H₂SO₄) leaching and solvent extraction to obtain cobalt oxides and nickel hydroxide (Ni(OH)₂). Although this process does not require pretreatment, it results in the loss of Li. With the aim of reducing the loss of Li in the recovery process, researchers have proposed a novel process that combines pyrometallurgy and hydrometallurgy to recycle valuable metals from spent LIBs. Georgi-Maschler et al. [43] used a reduction smelting method to recover valuable metals from spent LIBs. These valuable metals, including Fe, Co, Ni, and Mn, were converted to alloys. However, Li entered into the slag or dust during the process. With further leaching using H₂SO₄, purified Li was obtained. In addition, Träger et al. [44] proposed a process involving vacuum evaporation and selective carrier gas evaporation at high temperatures to evaporate Li from spent LIBs. However, the temperature applied during the process was higher than 1400 °C, which inevitably led to high energy consumption. Li et al. [1] roasted LiCoO₂ and graphite at 1000 °C for 30 min under nitrogen protection. The roasting products were lithium carbonate (Li₂CO₃), carbon (C), and Co; the roasting products were then dissolved in water and separated by magnetic separation. The concentration of the lithium-rich solution was only 337.4 mg·L⁻¹, making it difficult to recover Li. Based on previous studies, Hu et al. [45] proposed a novel method to recover spent LIBs by low-temperature roasting under an argon atmosphere, followed by the recovery of Li₂CO₃ from the roasting product by means of water leaching. The results showed that the roasting products were Li₂CO₃, Ni, Co, and manganese(II) oxide (MnO) when the cathode was reduced at 650 °C for 3 h with 19% carbon dosage. The roasting products were then dissolved in water and fed with CO₂; this resulted in the conversion of insoluble Li₂CO₃ into LiHCO₃. The Li₂CO₃ was then recovered by evaporation crystallization. The concentration of Li in the leaching solution reached 4.36 g·L⁻¹ when the S/L ratio was adjusted to 100 g·L⁻¹ the CO₂ flow rate was confined to 20 mL·min⁻¹, and the leaching time was maintained for 2 h.

Although recycling valuable metals from spent LIBs via pyrometallurgy is simple, it is not environmentally friendly due to its high energy consumption and secondary pollution [4,42,46,47]. In addition, the loss of Li during the recycling process is a significant problem that needs to be solved.

3.2.2. Hydrometallurgy

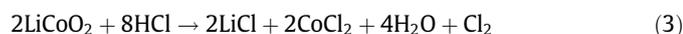
Recycling metals from spent LIBs using the hydrometallurgical method involves leaching, which dissolves the metallic fraction and recycled metal solutions for subsequent separation and recovery. Typical leaching agents used in the leaching process are inorganic acids, organic acids, and ammonia-ammonium salt systems.

Table 2
Advantages and disadvantages of different pretreatment methods.

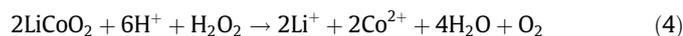
Technology	Advantages	Disadvantages
Solvent dissolution	High separation efficiency	High cost of solvent, environmental hazards
NaOH dissolution	Simple operation, high separation efficiency	Difficulty in aluminum recovery, alkali wastewater emission
Ultrasonic-assisted separation	Simple operation, almost no exhaust emission	Noise pollution, high device investment
Thermal treatment	Simple operation, high throughput	High energy consumption, high device investment, poisonous gas emission
Mechanical methods	Simple and convenient operation	Poisonous gas emission, cannot separate all kind of components in spent LIBs completely

The inorganic acids hydrochloric acid (HCl) [14,48–50], H₂SO₄ [11,28,29,31,51], nitric acid (HNO₃) [52], and phosphoric acid (H₃PO₄) [53,54] are usually used as leaching agents to leach metals from spent LIBs. With the help of reducing agents such as hydrogen peroxide (H₂O₂) [11,28,29,51,52,55], sodium bisulfite [56], or glucose [57], Co or Mn with a high-valent state in the solid phase is reduced to easily soluble Co²⁺ or Mn²⁺. The main factors affecting the leaching process include the temperature, reaction time, concentration of leaching agents, S/L ratio, and concentration of reducing agents.

Joulié et al. [49] investigated the leaching of lithium nickel cobalt aluminum oxide (NCA) cathodes in H₂SO₄, HNO₃, and HCl, respectively. The results indicate that the nature of the acid has a significant effect on the leaching rate of the metals, with HCl providing the best leaching efficiency. The optimum conditions for leaching are: 4 mol·L⁻¹ HCl, 90 °C, 18 h, and 50 g·L⁻¹ S/L ratio. Almost 100% of the valuable metals in the cathode material could be dissolved under experimental conditions. Leaching Co³⁺ from the NCA cathode in the absence of reducing agents is generally difficult due to the conversion of Co³⁺ to Co²⁺. Consequently, when H₂SO₄, HNO₃, or HCl is chosen as the leaching agent without the addition of other reducing agents, HCl provides a higher leaching efficiency because of its chlorine ions, which promote the dissolution. When HCl is used as the leaching agent and LiCoO₂ is used as the raw material, the process mainly occurs as follows [5]:

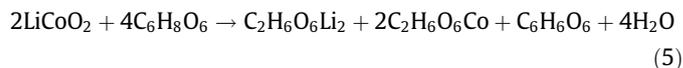


According to Eq. (3), chlorine (Cl₂) is generated during the leaching process, which may result in serious environmental problems. Thus, some researchers use HNO₃ or H₂SO₄ instead of HCl to leach LiCoO₂. For example, Lee and Rhee [52] treated LiCoO₂ cathode with 1 mol·L⁻¹ HNO₃ and H₂O₂ at 75 °C. It was revealed that the leaching efficiencies of Li and Co were only 75% and 40%, respectively, in the absence of H₂O₂. However, the leaching rates of Co and Li exceeded 99% when the content of H₂O₂ was 1.7% (v/v), mainly because insoluble Co³⁺ was reduced into soluble Co²⁺ in the presence of H₂O₂. Chen et al. [28] proposed a hydrometallurgical approach for recycling cobalt oxalate (CoC₂O₄) from spent LIBs; this approach consists of alkali leaching, acid leaching, solvent extraction, and chemical precipitation. H₂SO₄ was applied as the leaching agent and H₂O₂ was applied as the reducing agent. The results indicated that the leaching rates of Co and Li were 95% and 96% under the following conditions: 85 °C, 100 g·L⁻¹ S/L ratio, 120 min, 4 mol·L⁻¹ H₂SO₄, and 10% H₂O₂ (v/v). The pH of the solution was adjusted to remove ionic impurities from the leachate. Co was then extracted with the extractant P507, followed by precipitation with ammonium oxalate ((NH₄)₂C₂O₄) to obtain cobalt oxalate (CoC₂O₄), which resulted in a purity higher than 99%. The leaching reactions may be represented as follows:

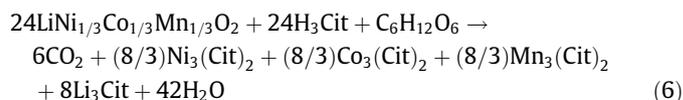


It is relatively easy to achieve high metal-leaching efficiencies using inorganic acids. However, inorganic acids will produce acidic wastewater, Cl₂, SO₂, NO_x, and other harmful gases, which will cause environmental pollutions [25]. Thus, environmentally friendly organic acids have been used as the leaching agents for metal recovery from spent LIBs; these organic acids include ascorbic acid [24,58–60], citric acid [25,46,60–62], oxalic acid [63,64], formic acid [65], acetic acid [46,66], succinic acid [67], tartaric acid [68], and so forth. Li et al. [24] developed a combined process consisting of ultrasonic cleaning, roasting, and organic acid leaching to recycle valuable metals (Co and Li) from spent LIBs. Ascorbic acid was chosen as the leaching agent as well as the reducing agent in order to increase the leaching rate of Co. Using 1.25 mol·L⁻¹ ascorbic acid and a 25 g·L⁻¹ S/L ratio, the leaching rates of Li and

Co reached 98.5% and 94.8%, respectively. When LiCoO₂ is leached under these conditions, it first dissolves to produce soluble C₆H₆O₆Li₂; the insoluble Co³⁺ in LiCoO₂ is converted to the easily soluble Co²⁺ by the ascorbic acid, and the C₆H₈O₆ is oxidized to C₆H₆O₆. The reaction for leaching can be simply expressed as follows:



Chen et al. [61] developed an economically effective approach for valuable metals recycling from spent LIBs that combined reduction leaching with selective precipitation. Citric acid was selected as the leaching agent, and *D*-glucose was used as the reducing agent to dissolve the spent cathode material. About 99% of the Li, 91% of the Ni, 92% of the Co, and 94% of the Mn were dissolved under the following conditions: 1.5 mol·L⁻¹ citric acid concentration, 20 g·L⁻¹ S/L ratio, 0.5 g·g⁻¹ reducing agent content, 80 °C temperature, and 120 min reaction time. The selective precipitation method was then used to separate and recycle the valuable metals. It was also found that the residue leachate after precipitation could be reused as a leaching agent, which revealed a similar leaching performance when compared with fresh leaching agent. The atomic utilization efficiency was as high as 98% for the whole recycling process.



Zhang et al. [69] used biodegradable trichloroacetic acid (TCA) as the leaching agent and H₂O₂ as the reducing agent to selectively leach LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂. Under optimum conditions (3.0 mol·L⁻¹ TCA concentration, 50 g·L⁻¹ S/L ratio, 4 vol% H₂O₂, 60 °C temperature, 30 min), the leaching efficiencies of Co, Ni, Mn, and Li were 91.8%, 93.0%, 89.8%, and 99.7%, respectively, whereas the leaching efficiency of Al was only 7.0%. In addition, the leaching efficiency of Al could be further controlled depending on the use of the leachate.

At present, the cathode material used for leaching is obtained from LIBs by manual dismantling or in the form of cathode scraps from LIB production processes, which manifests higher purity. Industrial materials recovered from spent LIBs are generally more complex than the cathode scraps from production processes, and the cathodes that are obtained after pretreatment usually contain complex metal components. Leaching the cathode material using acid does not manifest ideal selectivity; the leachate usually contains many ionic impurities, which increases the burden of subsequent separation and purification. Therefore, ammonia-ammonium sulfate ((NH₄)₂SO₄) is applied as the leaching agent and sodium sulfite (Na₂SO₃) is chosen as the reducing agent in order to selectively leach valuable metals such as Li, Co, and Ni from LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ [42]. Optimum conditions were explored, and it was found that in the presence of 4 mol·L⁻¹ ammonia, 1.5 mol·L⁻¹ ammonium sulfate, 0.5 mol·L⁻¹ sodium sulfite, 500 r·min⁻¹ stirring rate, and 10 g·L⁻¹ S/L ratio, the leaching efficiencies of Li, Ni, Co, and Al were 95.3%, 89.8%, 80.7%, and 4.3%, respectively. The total selectivity of Li, Ni, and Co was more than 98.6% during the leaching process. It was also found that Mn from LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ was leached into the solution during the leaching process and then precipitated from the solution in the form of (NH₄)₂Mn(SO₃)₂·H₂O.

3.2.3. Biometallurgy

Due to their higher efficiency, low cost, and lower equipment requirement, biometallurgical processes are considered to be one of the most promising alternatives to traditional

hydrometallurgical processes. In biometallurgical processes, inorganic and organic acids produced by microbial activities promote the leaching of metals from spent LIBs [9]. Mishra et al. [70] introduced the Fe- and sulfur (S)-oxidizing bacterium, *Acidithiobacillus ferrooxidans*, for the leaching of Co and Li from spent LIBs. It was found that the leaching rate of Co was faster than that of Li, but the dissolution of Co and Li was still low under optimized conditions. Xin et al. [71] investigated the bioleaching mechanisms of spent LIBs using a mixed culture of sulfur-oxidizing and iron-oxidizing bacteria with different energy sources. It was found that Li release was due to acid dissolution and was independent of the type of energy source; however, the leaching mechanism for Co differed according to the type of energy source. In the S system, acid dissolution acted as the mechanism for the leaching of Co. In the FeS₂ or FeS₂ + S system, the dissolution of Co was affected by the combined action of acid dissolution and Fe²⁺-catalyzed reduction. Xin et al. [72] explored the bioleaching of LiFePO₄, LiMn₂O₄, and LiNi_xCo_yMn_{1-x-y}O₂ for the first time with an S/L ratio of 10 g·L⁻¹. The maximum extraction efficiency of Li was found in the sulfur-*Acidithiobacillus thiooxidans* system, indicating that the leaching mechanism of Li was affected by the release of H₂SO₄ from microorganisms. However, the leaching of Ni, Co, and Mn was controlled by Fe²⁺ reduction and acid dissolution.

Compared with pyrometallurgical processes and hydrometallurgical processes, the drawbacks of biometallurgical processes include their slow kinetics and low pulp density. In order to improve the metal dissolution rate in the bioleaching process, Zeng et al. [73] proposed a copper-catalyzed leaching process to recover Co and Li from spent LIBs; they applied Cu²⁺ as the catalyst and *Acidithiobacillus ferrooxidans* as the bacteria. It was shown that the leaching efficiency of Co was 99% when the concentration of Cu²⁺ was 0.75 g·L⁻¹ and the leaching time was 6 d. However, the leaching efficiency of Co was only 43.1% without Cu²⁺ for 10 d. Niu et al. [74] investigated the effect of pulp density on bioleaching, and found that the leaching efficiency decreased from 52% to 10% for Co and from 80% to 37% for Li when the pulp density increased from 1% to 4%. Even though the maximum leaching efficiency of Co and Li could be obtained through process controls such as increasing the dose of mixed energy substrate or increasing the bioleaching temperature, the metal dissolution rate was still low. Biometallurgical processes have the advantages of being cost-effective, with easy operation and mild reaction conditions; however, their disadvantages are that the bacteria used for leaching is difficult to cultivate, the leaching time is long, and the leaching efficiency is low.

3.2.4. Other methods

In general, pyrometallurgy and hydrometallurgy are the two main approaches applied for recycling valuable metals from spent LIBs. However, the energy consumption and metal-loss rate of pyrometallurgy is very high. In the recycling process of hydrometallurgy, the consumption of chemical reagents is huge. Therefore, pyrometallurgy and hydrometallurgy are not environmentally friendly. In recent years, researchers have begun to explore new methods aimed at recycling valuable metals from spent LIBs.

Mechanochemical methods have already been used to recycle valuable metals from spent LIBs [3,75,76]. During the milling process, the structure and physicochemical properties of the reactants are changed due to the mechanical energy, which facilitates the progress of chemical reactions. Saeki et al. [76] proposed a novel process for recycling Li and Co from spent LIBs via co-grinding LiCoO₂ with polyvinyl chloride (PVC) in a planetary ball mill. During this process, Li and Co chlorides were produced; the grinding products were then leached with water to extract Li and Co. It was found that the leaching rates of Li and Co were improved by grinding, and that the leaching rates of Co and Li were 90% and nearly 100% after 30 h of grinding, respectively. In addition, 90% of the chlorine in PVC was converted to inorganic chlorides. The following reaction occurs during grinding:



Wang et al. [47] proposed a combined process that involves co-grinding PVC, Fe, and LiCoO₂, and then leaching with water to recover metals from spent LIBs. The conversion rates of Li, Co, and Cl were 100%, 8.1%, and 96.4%, respectively, under the following conditions: a LiCoO₂/PVC/Fe ratio of 1:1:2, a ball-to-powder ratio of 50:1, and a total grinding time of 12 h; 91.9% of the Co remained in residue for the preparation of CoFe_xO_y. These scholars also investigated co-grinding LiCoO₂ with various additives by mechanochemical methods and extracting Li and Co by water leaching [3]. It was found that ethylenediaminetetraacetic acid (EDTA) was the most suitable additive. Moreover, the recovery rate of Co and Li reached 98% and 99%, respectively, under the conditions of a 1:4 mass ratio of LiCoO₂ to EDTA, 4 h milling time, 600 r·min⁻¹ rotary speed, and 80:1 ball-to-powder mass. The results of the mechanism study showed that the lone pair electrons offered by two nitrogen atoms and four hydroxyl oxygen atoms of EDTA could be inserted into the empty orbit of Co and Li via a solid–solid reaction. Afterward, stable water-soluble metal chelates formed, such as Li-EDTA and Co-EDTA. The advantages of a mechanochemical reaction are its simple process, lower energy consumption, lower use of chemical reagents, and lower degree of environmental pollution. However, its long processing time, low processing capacity, and large investment in equipment limit its development.

3.2.5. Comparison of methods for metal extraction

Table 3 summarizes the main methods used in the metal-extraction processes described above, including the advantages, disadvantages, and environmental impacts. Pyrometallurgical methods with relatively simple operation and large processing capacity, have been applied in industry for spent LIB recycling. However, these processes are limited by their high cost, high energy consumption, and high metal loss. In addition, pyrometallurgical methods release harmful gases through the decomposition of the toxic electrolyte and organic materials. Therefore, a waste gas treatment device should be equipped during practical application. Biometallurgical processes use the acids

Table 3
Comparison of methods for metal-extraction processes.

Process	Advantages	Disadvantages	Environmental hazards
Pyrometallurgy	Great capacity, simple operation	High temperature, high energy consumption, low metal recovery rate	Waste gas, dust
Hydrometallurgy	Low energy consumption, high metal recovery rate, high product purity	Long recovery process, high chemical reagents consumption	Wastewater
Biometallurgy	Low energy consumption, mild operating conditions, high metal recovery rate	Long reaction period, bacteria are difficult to cultivate	Wastewater

produced from microbial metabolism to dissolve the cathode material of spent LIBs in order to obtain the leachate. Although these processes have the advantages of low energy consumption and low cost, the bacteria are difficult to cultivate and easily polluted. Because of their advantages of high metal recovery and high product purity, hydrometallurgical processes are seen as a promising way to recover spent LIBs. However, the recovery process requires the consumption of a great deal of chemical reagents. The purity of the recovered product is affected by impurities of the chemical reagents, the recovery process, and the process parameters. In addition, the separation and recycling of metal components have the disadvantages of complex processes, low recovery of metal components, high processing costs, and serious environmental pollution. Compared with the technologies shown in Table 3, mechanochemistry usually introduced during hydrometallurgical processing, has the advantages of lowering the chemical reagent consumption and milder reaction conditions. However, its high energy consumption and large equipment investment limit the industrial application.

3.3. Product preparation process

During the product preparation process, products can be obtained by different methods. Metal salts can be recovered if the valuable metals are separated and then respectively recovered by solvent extraction, chemical precipitation, and so on. The precursor for cathode material can be directly prepared by adjusting the composition of the solution.

3.3.1. Recovery of metals from leachate

The leachate obtained after acid leaching usually contains many metal ions. A combination of solvent extraction [10,31,77–80], chemical precipitation [5,50,81,82], and crystallization [29] is usually used to separate and recover the metals in the leachate. For example, in order to recover the Co in sulfuric leachate, Ferreira et al. [29] studied a method of evaporating crystallization to recover CoSO_4 . When the evaporation of the solution was 90%, there was about 70% Co crystallization in the solution, and the purity of metal was at its highest (19%). It was also found that the evaporation rate of the solution has a positive effect on the crystallization rate of Co. When the evaporation rate of the solution increases, the crystallization rate of Co increases. However, the content of the impurities Al and Li in the solid phase increased correspondingly. As a result, 85% of the evaporation rate was considered to be the most suitable condition, yielding a content of Al and Li that was less than 0.4% and 0.6%, respectively. Huang et al. [83] adopted a combined process composed of leaching, flotation, and precipitation to recover Li, Mn, and Fe from mixed cathode materials (mixed LiFePO_4 and LiMn_2O_4). First, the Li, Fe, and Mn in the cathode materials were leached by HCl, using H_2O_2 as reductant. Next, the Fe^{3+} in the leachate was floated selectively and recovered in the form of FeCl_3 . Finally, $\text{Mn}^{2+}/\text{Mn}^{3+}$ and Li^+ were successively precipitated using saturated KMnO_4 solution and hot saturated Na_3PO_4 solution, respectively. Mn and Li were recovered in the forms of $\text{MnO}_2/\text{Mn}_2\text{O}_3$ and Li_3PO_4 . About 80% of the Li, 85% of the Fe, and 81% of the Mn was recoverable under optimized conditions; the corresponding purity of the Li_3PO_4 , FeCl_3 , and $\text{MnO}_2/\text{Mn}_2\text{O}_3$ compounds was 99.32%, 97.91%, and 8.73%, respectively. A combined process of solvent extraction and chemical precipitation was used by Chen et al. [84] to recover Cu, Mn, Co, Ni, and Li from spent LIB leachate. After the impurities were removed, Mextral 5640H was first used as an extractant to extract and separate Cu^{2+} ; next, KMnO_4 solution was used to precipitate Mn^{2+} . About 99.2% of the Mn^{2+} in the solution was precipitated in the form of MnO_2 and Mn_2O_3 . Co^{2+} was then extracted with Mextral 272P. Finally, Ni^{2+} and Li^+ were sequentially precipitated

and recovered in the forms of $\text{Ni}(\text{OH})_2$ and Li_3PO_4 , using NaOH and saturated Na_3PO_4 solutions, respectively. The following recovery efficiency was achieved under optimum conditions: 100% for Cu, 99.2% for Mn, 97.8% for Co, 99.1% for Ni, and 95.8% for Li.

Due to the complexity of the spent LIBs, the solution that is obtained after leaching usually contains a variety of metal ions. Although a combination of chemical precipitation and solvent extraction can achieve the separation and recovery of metal components from the leaching solution, a large amount of chemical reagents is consumed in the recovery process, and the purity of the product is affected by the impurities and by the recovery process.

3.3.2. Preparation of cathode material

Since the transition metal ions in the solution, such as Co, Ni, and Mn, are similar in nature, it is difficult to separate them. To avoid complicated separation steps, a precursor material is directly prepared by adjusting the composition of the leaching solution; the cathode material is then further regenerated by co-precipitation [15,85,86] and sol-gel [6,25].

The leachate of spent LIBs usually contains various metals such as Cu, Li, Co, Ni, and Mn. To reduce complex steps and the costs of separating Ni, Co, and Mn from the leachate, Sa et al. [85] evaluated the feasibility of synthesizing the precursor $\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}(\text{OH})_2$ from leachate that was obtained from mixed LIBs. The $\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}(\text{OH})_2$ precursor was synthesized by co-precipitation with strictly controlled reaction parameters. The magnification capacities and cycle performances of the final products were tested in order to assess the electrochemical performances. It was shown that the first discharge capacity of the cathode material that was re-synthesized from mixed spent LIBs at the rate of 0.1 C was $158 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$, and the first discharge capacity in the cycle-life test at the rate of 0.5 C was $139 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$. After 100 and 200 charging and discharging cycles, the discharge capacity retention rates were still higher than 80% and 65%, respectively. Yang et al. [87] developed a high value-added process to regenerate $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$, and $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ cathode materials from spent LIBs using co-precipitation. It was revealed that regenerated cathode materials manifested a clear lamellar structure, which retained the spherical morphology of their corresponding hydroxide precursors with a particle diameter in the range of 9–12 μm . Electrochemical tests demonstrated that the regenerated cathode material manifested excellent electrochemical properties. The first discharge capacity of the regenerated $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$, and $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ were 197.7, 174.3, and $168.3 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$, respectively. The discharge capacities of all the materials decreased as the discharge current density increased. After 50 cycles of charging and discharging (at the rate of 1 C), the capacity retention rates of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$, and $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ were 86.3%, 95%, and 96%, respectively. In general, the regenerated $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$, and $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ exhibited comparable performance to that of materials that were prepared using mixed solutions of pure Ni, Co, and Mn. Co-precipitation is the most commonly used method for synthesizing ternary cathode materials. The advantage of this method is that the equipment required is simple, which benefits industrial production. However, there are many influence factors for precipitation, which probably lead to impurities.

The sol-gel method is another commonly used method for synthesizing electrode materials. This method comprises the following steps: ① dispersing the raw material in a solvent; ② adding an appropriate amount of complexing agent to cause the hydrolysis and polymerization to form a sol; ③ generating a sol with a certain

spatial structure gel; and finally, ④ obtaining the product via heat treatment. Yao et al. [25] regenerated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ materials from spent LIBs by means of the sol–gel method. In this process, citric acid was applied both as the leaching agent and as the complexing agent. First, the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material was leached with citric acid; next, the ratio of Li, Mn, Ni, and Co in the citric acid leachate was adjusted to 3.05:1:1:1 using LiNO_3 , $\text{Mn}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, and $\text{Ni}(\text{NO}_3)_2$. The pH of the solution was then altered to 8 with an appropriate amount of aqueous ammonia. Finally, the new LIB cathode material $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was regenerated by means of sol–gel. The regenerated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ manifested high crystallinity, fairly good lamellar structure, and acceptable electrochemical cycling performances. The discharge capacity of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was up to $147 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ by sol–gel, and the discharge capacity retention rate was 93% after 50 charge–discharge cycles. In addition, they studied the application of *D,L*-malic acid as a complexing agent, followed by the sol–gel method to obtain the cathode material $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [6]. By adjusting the metal ion ratio and the pH value of the leaching solution, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was regenerated by the sol–gel method without the use of an additional chelating agent. Electrochemical tests demonstrated that the first charging and discharging capacities of the regenerated materials were 152.9 and $147.2 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ (2.75–4.25 V, 0.2 C), respectively, and that the capacity retention rate was still 95.06% (2.75–4.25 V, 0.5 C) after 100 charge–discharge cycles. Therefore, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ that was prepared from spent LIBs manifested fairly good electrochemical performances. The sol–gel method has the advantages of low operation temperature, short reaction time, and atomic-level mixing of each component. However, its reproducibility is poor, and it is mainly used in the laboratory.

4. Conclusions and perspectives

In recent years, the recycling of spent LIBs has become a growing community concern. With the boom in portable devices and electric vehicles, an increasing number of spent LIBs are being generated. Hence, recycling these spent LIBs is imperative. At present, the main recycling process for spent LIBs includes a pretreatment process, metal-extraction process, and product preparation process. The metal-extraction process is very important to the entire recovery process, and the main methods used for this process are pyrometallurgy, hydrometallurgy, and biometallurgy. However, there are several environmental issues regarding wastewater, residue, and exhaust gas that require further treatment. The problems and prospects of spent LIB recycling processes are as follows:

(1) One purpose of the pretreatment process is to reduce the volume of spent LIBs and environmental pollution during recycling. The other purpose is to achieve the enrichment of valuable metal components. In the pretreatment stage, the question of how to safely, efficiently, and automatically dismantle the spent LIB becomes significant, hindering the development of industrial recycling of the spent LIB. In addition, the pretreatment process produces many pollutants such as HF, PF_5 , and other harmful gases, which result in secondary pollution to the environment.

(2) Current recovery processes focus on the recovery of high-value metal components; this is especially true for the recovery of negative carbon materials and electrolytes. Therefore, it is necessary to further study the systematically recycling and reuse of all components of spent LIBs.

(3) The metal-extraction process is very important to the whole recovery process, and the main methods applied for metal extraction are pyrometallurgy and hydrometallurgy. However, these methods have several environmental issues that require further discussion—such as wastewater, residue, and exhaust gas—which

pose a threat to the environment and human health. Therefore, reducing or avoiding secondary pollution is a major concern for recycling.

(4) The recovery process is complicated because of the complicated metal components of spent LIBs. The metal components in the solution that is obtained after the metal-extraction process is complicated, and the separation and recovery of the metal components require a combination of chemical precipitation and solvent extraction. The performance of the materials and the cost of recycling also need to be considered in the direct synthesis of cathode materials.

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Compliance with ethics guidelines

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