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Recycling of lithium-ion batteries: Recent advances and perspectives

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Abstract: With the ever-growing need for lithium-ion batteries, particularly from the electric transportation industry, a large amount of lithium-ion batteries is bound to retire in the near future, thereby leading to serious disposal problems and detrimental impacts on environment and energy conservation. Currently, commercial lithium-ion batteries are composed of transition metal oxides or phosphates, aluminum, copper, graphite, organic electrolytes with harmful lithium salts, polymer separators, and plastic or metallic cases. The lack of proper disposal of spent lithium-ion batteries probably results in grave consequences, such as environmental pollution and waste of resources. Thus, recycling of spent lithium-ion batteries starts to receive attentions in recent years. However, owing to the pursuit of lithium-ion batteries with higher energy density, higher safety and more affordable price, the materials used in lithium-ion batteries are of a wide diversity and ever-evolving, consequently bringing

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difficulties to the recycling of spent lithium-ion batteries. To address this issue, both technological innovations and the participation of governments are required. This article provides a review of recent advances in recycling technologies of spent lithium-ion batteries, including the development of recycling processes, the products obtained from recycling, and the effects of recycling on environmental burdens. In addition, the remaining challenges and future perspectives are also highlighted.

Keywords: Recycling; Recovery; Spent lithium-ion batteries; Perspectives

1. Introduction

Owing to the high energy density, long lifespan and low self-discharge, lithium-ion batteries (LIBs) are higher portable than other commercial energy storage devices and have become the most leading power source for consumer electronics (CEs) since they were successfully commercialized by SONY in 1990s[1-5]. Nowadays, with the rapid advances in microprocessor technology and constant offers of upgrades, the period of product updating for CEs has been largely shortened, resulting in rising production of LIBs, as well as rapid generation of spent LIBs from waste CEs[6]. In the past several years, with the development of new electrode materials possessing higher energy density and power output, the application targets of LIBs have spread into the electric vehicles (EVs)[7-10]. In the meanwhile, with the maturity of high energy-density LIBs and policy orientations, the EV market is growing rapidly. Fig. 1 shows the development of EVs in the world[11]. It can be seen that both the global EV stock and EV registrations have increased fast since 2012, particularly in China and US. Considering that the EV market is just beginning to boom, and the lifetime of EV batteries is designed to be longer than that of the ones used in CEs, we may not face serious disposal problems of spent LIBs from EVs in a few years[8, 12]. However, we should foresee the influences of numerous retired LIBs from EVs on resource conservation and environmental protection in the near future, and be aware what actions should be taken now to deal with the spent LIBs.

It can be predicted that the lack of proper disposal and post-treatment of spent LIBs will result in grave consequences, such as environmental pollution and waste of

resources. Generally, a LIB is composed of a cathode, an anode, a separator, electrolyte, an outer case and sealing parts. Commercial LIBs are currently using various types of Li-containing oxides and phosphides as cathode materials, such as $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$, $LiNi_{1-x-y}Co_xMn_yO_2$ (NCM), etc. It is shown from a survey in 2012 that more than half of the cathode material market was still occupied by $LiCoO_2$ and $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$, which contain hazardous heavy metal, i.e., cobalt[13]. In addition, organic electrolytes also contain harmful substances such as flammable organic solvents and fluorine-containing lithium salts[14]. Thus, directly dumping LIBs in the trash will cause serious environmental pollution. Moreover, LIBs contain high-value metals, such as Li, Co, Ni, Cu, Al, etc. Among them, Co and Li are rare and relatively more expensive than other metals, and their contents in LIBs are 5-15 wt. % and 2-7 wt. %, respectively, which are higher than those in natural ores[15, 16].

Based on the above-mentioned point of view, recycling of spent LIBs is highly desirable and the corresponding recycling technologies and regulations should be development for establishing a complete recycling system for spent LIBs. In fact, there is already well-operated lead-acid battery recycling system, which may provide experience and guidance. For example, in the United States, ~99% of lead-acid batteries are recycled, even more than any other common daily wastes (e.g. tires, paper, aluminum cans, glass, etc.)[12]. However, it is worth mentioning that lead-acid batteries and LIBs are quite different in terms of the chemical composition of their components. For the former, ~60% of the battery mass is lead, which can be easily

separated from other components after disassembling the battery[12]. For the latter, by contrast, the diversity of the materials used in LIBs makes the recycling process more complicated. As a comparison, the materials used in the components of lead-acid batteries and LIBs are listed in Table 1. Moreover, the shapes and sizes of a lithium-ion cell vary greatly, and the amount of individual cells in battery packs or modules may vary from tens to thousands (e.g. the battery module in Tesla electric car) depending on the applications, causing big problems for the recycling. The diversity of the materials and the variety of the shapes and sizes leave the recycling system for LIBs far behind that for lead-acid batteries. In spite of this, opportunities always coexist with challenges; hence recycling of spent LIBs is attracting ever-increasing attentions and many studies related to this topic have been reported[12]. This article provides a review of recent advances in recycling technologies of spent LIBs, including the development of recycling processes, the products obtained from recycling, and the effects of recycling on environmental burdens. In addition, remaining challenges and perspectives are highlighted as well.

2. Approaches for recycling lithium-ion batteries

A complete recycling process for LIBs generally needs two typical processes: physical processes and chemical processes due to the complicated assembly of LIBs or battery packs, as well as the diversity of electrode materials. It is noteworthy that spent LIBs still have residual energy, which may lead to fire and explosion during recycling[17, 18]. For this reason, spent LIBs usually need to be discharged before entering recycling process. Physical processes include pretreatments, such as

dismantling, crushing, screening, magnetic separation, washing, thermal pretreatment, etc.[15], and some processes which enable direct recovery of electrode materials from spent LIBs without chemical treatment[19]. Chemical processes can be classified into pyrometallurgical processes and hydrometallurgical processes, in which leaching, separation, extraction, and chemical/electrochemical precipitation are usually involved[20]. Some typical recycling processes including pretreatments and hydrometallurgical processes for recycling spent LIBs are illustrated by Fig. 2.

2.1 Pretreatment

Generally, pretreatments are aimed to separate components and materials in spent LIBs according to different physical properties such as shape, density, conductivity, magnetic property, etc.[15]. With the help of pretreatments, the components, materials and metallic scraps with similar physical properties can be separated and enriched, resulting in improved recovery rate and reduction of energy consumption of the following pyrometallurgical or hydrometallurgical processes.

Some studies have demonstrated the advantages of pretreatments in recycling processes for spent LIBs. For example, Shin et al.[21] proposed a two-step crushing and sieving process before recovery of cobalt and lithium by hydrometallurgical method. Their pretreatment was considered to be effective for enhancing the leaching efficiency of the hydrometallurgical process and applicable in recycling industry. Lee et al.[22] employed thermal pretreatment and shredding to peel off and collect $LiCoO_2$ from spent LIBs. For further improving the energy-efficiency of pretreatment, Li et al.[23] combined crushing and ultrasonic washing as pretreatment process in

LIBs recycling. In their work, the effects of the crusher screen aperture, as well as the temperature and duration of ultrasonic washing were investigated. A 12 mm aperture screen was confirmed to have the best selectivity for enriching Co-containing scraps, and 15-min ultrasonic washing with agitation at room temperature was recommended for separating $LiCoO_2$ and crushed current collector (Al foil). The Li's method is superior in energy efficiency to those reported by Shin et al. and Lee et al., because the ultrasonic washing consumes much less energy than an extra crushing step or thermal treatment.

2.2 Pyrometallurgical process

Pyrometallurgical process has been employed by commercial recycling plants for the recovery of cobalt[24]. For example, the Umicore Group developed a pyrometallurgical process in which spent LIBs are treated like natural ores[25]. In this process, the only pretreatment stage is a simple dismantlement of big battery packs to individual cells. Then, the battery cells are fed into a shaft furnace with three temperature zones, called pre-heating zone, plastics pyrolizing zone and smelting and reducing zone. In the pre-heating zone, spent LIBs are heated at a temperature lower than 300 ^{o}C in order to release the electrolyte vapor without explosion. The plastics pyrolizing zone is operated at ~700 ^{o}C, aiming to incinerate the plastic components of the spent LIBs to maintain the temperature and reduce the energy consumption of the smelting step. In the last zone, the materials are smelt and an alloy with copper, cobalt, nickel, and iron forms, together with the formation of a slag containing lithium, aluminum, silicon, calcium and a part of iron. Obviously, this process can only

recover copper, cobalt, nickel and a part of iron from spent LIBs. It is worth mentioning that the economic efficiency of this process strongly depends on the cobalt price, as well as the cobalt content in batteries. It has been widely-recognized that cobalt is being gradually replaced in the automotive LIBs, and the cathode materials for LIBs are ever-evolving[26, 27]. For example, the cathode material for the batteries adopted by GM Volt is $LiMn_2O_4$, and the cathode material for A123 batteries is $LiFePO_4$. What is worth mentioning is that the industrialized pyrometallurgical process cannot recover lithium, which is expected to be scarcer as the production of EVs increases[28, 29]. Hence, such traditional pyrometallurgical process may face the risk of being profitless in the future.

For simultaneously recovering cobalt and lithium from spent LIBs, Georgi-Maschler et al.[30] developed a selective pyrometallurgical treatment using electric arc furnace, which could transform the material fractions of spent LIBs into a cobalt alloy and lithium-containing concentrates. Lithium in the latter could be recovered as Li_2CO_3 through a hydrometallurgical step. In addition, other material fractions such as iron-nickel fraction, aluminum fraction and copper fraction could be obtained for further treatments. The recycling process can be illustrated by Fig. 3. It is noteworthy that before the pyrometallurgical step there are four physical processes (including pretreatment), by which the dismantled components and materials fractions can be collected and enriched separately, even for the electrolyte. That may enhance the effectiveness of the whole recycling. However, the estimated economic efficiency of the process also significantly depends on the cobalt price.

Pyrometallurgical process has some disadvantages such as materials loss, high energy consumption and hazardous gas (e.g dioxins, furans, etc.) release[31-33]. Therefore, alternative recycling processes with higher recovery rate, lower energy consumption and less environment hazards are needed to deal with a huge number of spent LIBs in the future.

2.3 Hydrometallurgical process

Hydrometallurgical process is the most major approach for recycling spent LIBs since more than half of the recycling processes are hydrometallurgical process[17]. It includes leaching (e.g. acid leaching, bioleaching, etc.) and recovery steps (e.g. solvent extraction, chemical precipitation, electrochemical deposition, etc.) (see Fig. 2). Hydrometallurgical process is a powerful method for recovering metals from spent LIBs. For example, over 99% of cobalt and lithium could be leached through the process reported by Zhang et al.[34]. Over 98% of copper and 97% of cobalt was recovered by Nan's hydrometallurgical method[35]. Mousavi et al.[36] developed an environmentally friendly bioleaching method, in which the metals in spent LIBs could be leached by organic acids produced by *Aspergillus niger*. In their work, 100% of copper, 100% of lithium, 77% of manganese, 75% of aluminum, 64% of cobalt and 54% of nickel could be recovered.

Acid leaching of cathode materials can be implemented by using inorganic leaching agents such as HCl[23, 34, 37-39], H_2SO_4[40-44], HNO_3[45, 46], H_3PO_4[47, 48] and some organic leaching agents such as citric acid[49, 50] and oxalate acid[51, 52]. Compared with pyrometallurgical process, acid leaching is able to achieve higher

recovery efficiency due to the high solubility of cathode materials in acidic solutions. For example, the reaction of $LiCoO_2$ cathode material in hydrochloride acid is described by Equation (1).

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

In the HCl leaching process, Co(III) in the $LiCoO_2$ powder can be reduced to Co(II) which is readily soluble in aqueous phase[45]. Thus, HCl solution is a high-efficient leaching agent for extraction of cobalt from spent LIBs. However, a big problem of HCl leaching method is the release of strongly corrosive and harmful Cl_2, which needs further treatment(s). To address this issue, H_2SO_4 leaching was proposed by researchers. In the meanwhile, reduction agent H_2O_2 was needed in this process for reducing Co(III) to Co(II)[44] according to Equation (2).

$$2LiCoO_2 + 3H_2SO_4 + H_2O_2 \rightarrow 2CoSO_4 + O_2 + Li_2SO_4 + 4H_2O \quad (2)$$

Other than strong inorganic acids, some mild organic acids have attracted many attentions in recent years. Oxalic acid can enable short-cut recovery of cobalt and lithium from waste $LiCoO_2$ cathode materials because leaching and precipitation occur simultaneously (formation of CoC_2O_4) in the leaching step[51]. In this case, cobalt can be directly separated from lithium without further treatment such as chemical precipitation or solvent extraction. Moreover, no additional reduction agent is required since the oxalic acid solution is reductive.

H_3PO_4, a mild inorganic acid, was also demonstrated to be able to leach and separate cobalt and lithium simultaneously[48]. In the H_3PO_4 leaching process, cobalt can be directly recovered as $Co_3(PO_4)_2$ precipitation, leaving lithium in the leach

liquor.

For acid leaching processes, the leaching efficiency can be significantly influenced by several operational parameters, such as temperature, acid concentration (or H^+ concentration), leaching time, ratio of solid to liquid, and additives. In order to balance leaching efficiency and economy, the optimization of leaching conditions is necessary. For example, Li et al.[23] found that the leaching rate of cobalt and lithium from waste $LiCoO_2$ cathode material was maximized after 2 h leaching in a 4M HCl solution at 80 ºC. Under that condition, 97% of lithium and 99% of cobalt were dissolved, as shown in Fig. 4. In addition, some optimal operation conditions for the leaching of materials fraction of spent LIBs by different acidic leaching agent are summarized and listed in Table 2.

Bioleaching is another type of hydrometallurgical process, which utilizes metabolites excreted by microorganisms to dissolve waste electrode materials and extract valuable metals[53-55]. Some bacteria and fungi are capable of bioleaching metals from spent LIBs. Mishra et al.[55] employed chemolithotrophic and acidophilic bacteria *Acidithiobacillus ferrooxidans* to treat waste $LiCoO_2$ cathode material. In this process, the bacteria utilized elemental sulfur and ferrous ion to produce sulfuric acids and ferric ion in the leaching medium, which could dissolve the waste $LiCoO_2$ cathode material. The *Aspergillus niger* used in Mousavi et al.'s work[36] is a haploid filamentous fungus found in mesophilic environments such as decaying vegetation and soil. This fungus can produce organic acids, including gluconic acid, citric acid, oxalic acid and malic acid, in sucrose medium[56]. Then the

excreted one or more organic acids provide H^+ and organic ligands for the extraction of lithium and cobalt from waste cathode materials.

Because of the use of living biomass, bioleaching process is more difficult to control[48]. For instance, Xin et al.[57] compared the bioleaching behavior of *Alicyclobacillus* sp. at different pulp density, and found that the leaching efficiency was considerably influenced by the pulp density, as shown in Fig. 5a-d. As can be seen, the leaching efficiency decreased from 52% to 10% for cobalt and from 80% to 37% for lithium with the increase of pulp density from 1% to 4%. Similar result was also observed in Mousavi et al.'s work[36] in which they studied the effect of pulp density on the metal recovery for the *Aspergillus niger* bioleaching process, as shown in Fig. 5e. This phenomenon could be explained by the sensitivity of the microorganisms to the toxic electrolyte in spent LIBs[57], because higher pulp density would bring more amount of toxic organic electrolyte which contained $LiPF_6$, $LiClO_4$ and $LiBF_4$.

At the last stage of hydrometallurgical process, separation and recovery of metals should be implemented by the means of solvent extraction, chemical precipitation, and electrochemical deposition. Solvent extraction is a liquid-liquid extraction process for separating metals in leach liquor by extractants. Several extractants have been used to recover Li, Co, Mn, Cu, etc. from spent LIBs, such as bis-(2,4,4-tri-methyl-pentyl) phosphinic acid (Cyanex 272)[43, 58-60], di-(2-ethylhexyl) phosphoric acid (D2EHPA)[34, 61], Acorga M5640[60, 62, 63], trioctylamine (TOA)[63], 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester

(PC-88A)[64, 65], etc. Chen et al.[61] used Co loaded D2EHPA (Co-D2EHPA) to extract Mn from Mn, Co, and Li-containing leach liquor. Over 99% Mn was extracted under the conditions as following: extraction time-5 min, equilibrium pH-3.5, concentration of Co-D2EHPA-15 vol. %, and O:A ratio of 1:1. Solvent extraction has some advantages such as low energy consumption, good separation effect and easy operational conditions. However, the extractants are expensive so will increase the treatment cost in recycling industry.

For the chemical precipitation method, precipitation agents are employed to precipitate valuable metals in the leach liquor. For example, Contestabile et al.[66] used bubbling CO_2 gas to convert dissolved lithium into lithium carbonate precipitation. Zhang et al.[34] adopted a saturated sodium carbonate solution to precipitate lithium carbonate. In Zhang's work, the precipitation process was performed at close to 100 ºC, since the solubility of lithium carbonate in an aqueous solution is inversely proportional to temperature. After precipitation, about 80% of the lithium could be recovered. Chemical precipitation has the advantages of low cost and low energy consumption, but its applications may be discouraged by the difficulties in terms of the separation and recycling of metals from complicated solutions.

Electrochemical deposition is an effective way to recover metals from leach liquor in the forms of pure metal or metal hydroxide. Freitas et al.[67] recovered cobalt from spent LIBs by electrodeposition. In their process, pure cobalt was formed on the surface of the electrode, and at pH 5.4, the largest charge efficiency of 96.9% was achieved. Lupi et al.[68] recovered nickel from waste $LiCo_xNi_{1-x}O_2$ cathode using

galvanostatic and potentiostatic electrowinning. When at a current density of 250 A m^{-2}, 50 °C, pH value of 3~3.2, and with an electrolyte having about 50 g/l Ni and 20 g/l H_3BO_3 composition, nickel could be deposited with a current efficiency and a specific energy consumption of about 87% and 2.96 kWh kg^{-1}, respectively, leaving less than 100 ppm of nickel in the mother liquor. Myoung et al.[69] applied an electrochemical deposition to recover cobalt from waste $LiCoO_2$ cathodes. In their work, cobalt was recovered in the form of $Co(OH)_2$. Since hydroxide ions can be formed near the electrode via the electro-reduction of dissolved oxygen and nitrate ions, leading to an increase in the local surface pH of the titanium substrate, under appropriate pH conditions, cobalt hydroxide could be precipitated on the substrate. With the help of electrochemical deposition, high-purity metals and high recovery rate can be achieved; however, the energy consumption during this process is significant.

2.4 Direct physical recycling process

Direct physical recycling process is to recover components from spent LIBs without processes involving complicated chemical treatments. A typical direct physical recycling process can be illustrated by Fig. 6a, a flow chart of direct recycling of spent LIBs with $LiMn_2O_4$ as cathode material[24]. In this process, spent LIBs are firstly discharged and disassembled to cell level. Subsequently, the cells are treated with supercritical CO_2, which can extract the electrolyte. Then, CO_2 can be separated from the electrolyte after the temperature and pressure are reduced, and the electrolyte can be reused again in battery manufacture. The cells, which are devoid of electrolyte, are dismantled and crushed. After that, the cell components are separated

by physical techniques; subsequently the cathode materials are collected and reused in new batteries, probably with relithiation.

Chen et al.[70] firstly developed a direct recycling process and a small scale model line to recycle $LiFePO_4$ from soft package spent LIBs. In their process, discharged spent LIBs were dismantled, disassembled, crushed and washed in a seal box without recovering electrolyte, as seen in Fig. 6b. The recovered $LiFePO_4$ material without any treatment had low tap density and poor electrochemical performance due to the residue of poly(vinylidene fluoride) (PVDF) binder and the decomposition of the material after numerous charge-discharge cycles. After heat-treatment, the recovered cathode material exhibited improved tap density and electrochemical properties. Especially when treated at 650 ^{o}C, the cathode material displayed almost the same discharge capacity and energy density as the fresh one at high discharge current densities.

Rothermel et al.[19] compared three direct physical recycling processes for recovering graphite anode material from spent LIBs. The first method was based on a thermal treatment of graphite without electrolyte recovery. The second one is to extract electrolyte using subcritical CO_2, followed by heat treatment. The third one also included electrolyte extraction and heat treatment in addition to the use of supercritical CO_2 as extractant. The experimental results indicated that the electrolyte extraction using subcritical CO_2 was the best recycling method. With this approach, the recovered graphite outperformed the commercial synthetic graphite TIMREX SLP50, and the electrolyte was recovered by 90%. It is worth mentioning that the

conductive salt ($LiPF_6$) can also be recovered along with the electrolyte solvents as long as some functional additives (e.g. acetonitrile/propylene carbonate in 3:1) are added in the extrantant CO_2[71].

Song et al.[72] regenerated $LiFePO_4$ material from spent LIBs through sintering the recovered material with fresh powder after physically direct recycling process. In this process, the spent LIBs were firstly dismantled to separate the cathode and anode plate. For separating $LiFePO_4$ material and Al foil, the cathode was soaked in dimethylacetamide (DMAC) at 30 ºC for 30 min with a solid/liquid ratio of 1:20 g ml^{-1}. Then the recovered spent material was regenerated by sintering with fresh $LiFePO_4$. The electrochemical performances of the batteries made from the regenerated $LiFePO_4$ can meet the basic requirements for reuse.

The direct physical recycling process has the advantages of short recycling route, low energy consumption, environmental friendliness and high recovery rate. However, it is not clear whether the recovered materials will match the long-term performance of fresh ones.

In summary, all of the above-discussed recycling processes aim at recycling resources from spent LIBs. However, the recycling processes reach different stages of development due to their different technical difficulties and economic benefits. For example, the pyrometallurgical process has been commercialized due to its easy operation and high efficiency for recovering cobalt, which is the most valuable metal in spent LIBs. With the development of battery technology, cobalt content in electrode materials is decreasing, whereas the use of nickel and manganese is increasing. In

addition, the reserves of lithium resources have turned out to be an issue of prime importance since the consumption of lithium for batteries increased fast in the last few years due to the rapid expansion of the EVs market. Therefore, recycling technologies should be moved away from cobalt recovery to the comprehensive utilization of spent LIBs. Moreover, appropriate disposal or recovery of some materials which may harm the environment, such as electrolyte, should also be taken into account when developing recycling process for spent LIBs.

3. Products from recycling spent LIBs

At the last stage of a battery recycling process, the metal values from spent LIBs are transferred into other substances, such as alloys, slags, solutions and precipitates. For example, after a pyrometallurgical process, the lithium, aluminum and some iron will go into the slag, which can be used as a beneficial aggregate in concrete; an alloy with copper, cobalt, nickel and some iron will be further separated and refined into pure metals for reuse. As for hydrometallurgical process, a solution containing various ions is obtained after leaching step, which can be processed into different valuable products, such as metals, chemicals, new electrode materials, and other functional materials.

3.1 Metals and chemicals

Generally, pure metals are obtained through electrochemical deposition from leach liquor. For example, Freitas et al.[67] employed the electrochemical method to obtain pure cobalt from spent cellular phone batteries. Lupi et al.[68] obtained pure nickel from spent $LiCo_xNi_{1-x}O_2$ material by electrowinning. Prabaharan et al.[73] used

an electrochemical leaching process followed by an electrowinning to produce cobalt, copper and electrolytic manganese dioxide (EMD) with the purities of 99.2%, 99.5% and 96%, respectively. Bertuol et al.[74] recovered cobalt with the purity of 99.5% using electrowinning from the leach liquor of waste $LiCoO_2$. The recovered metals can be further processed into alloys or chemical raw materials.

For obtaining chemical raw materials from spent LIBs, a wise shortcut is to direct produce high-purity and high value-added chemicals using leach liquor. To date, more researches are focused on the direct synthesis of various compounds rather than pure metals, such as $CoC_2O_4 \cdot 2H_2O$[35, 42, 52, 64], $Co(OH)_2$[38, 39], $Co_2O_3 \cdot 2H_2O$[31, 37], $CoCO_3$[75], $Co_2(PO_4)_2$[48], $CoSO_4 \cdot 7H_2O$[76], $Ni(OH)_2$[37, 39], $NiCl_2$[31], $NiSO_4 \cdot 6H_2O$[76], Li_2CO_3[31, 35, 38, 39, 42, 75-78], Li_3PO_4[79], $CuSO_4$[35], MnO_2[39, 79], $MnSO_4 \cdot H_2O$[76], $FeCl_3$[79], Ni-Co-Mn hydroxide[77], etc. Most of the produced chemicals have high purity which can be used as raw materials for the manufacture of new materials without further purification. Table 3 summarizes some reported metals and chemicals obtained from recycling of spent LIBs, and the corresponding purities are given as well.

3.2 Electrode materials

As discussed above, the metals such as lithium, cobalt, nickel, manganese, iron, etc. in the cathode materials of spent LIBs can be recovered with high purity through recycling processes. In recent years, many transition metal oxides also have been considered as potential anode materials for LIBs[80-82]. Hence, the metal values recovered from spent LIBs can be an important source of raw materials for

synthesizing new electrode materials.

Lee et al.[22] synthesized $LiCoO_2$ cathode material using leach liquor of spent $LiCoO_2$. The molar ratio of Li and Co in the leach liquor was firstly adjusted to 1.1:1 by adding fresh $LiNO_3$ solution. Then, the modified leach liquor was directly made into $LiCoO_2$ through a sol-gel method. The regenerated $LiCoO_2$ delivered charge and discharge capacities of 165 and 154 mAh g^{-1}. After 30 cycles, the capacity retention was more than 90% (Fig. 7a and b).

Yang et al.[83] regenerate $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ from spent commercial LIBs. In their work, both the precursors Li_2CO_3 and $Ni_{1/3}Co_{1/3}Mn_{1/3}(OH)_2$ with high purity were obtained from the leach liquor. The regenerated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ had spherical morphology without any impurities, which exhibited good electrochemical performance. The discharge capacities of the regenerated material at 0.5 C, 1 C, 2 C and 5 C current densities were 150, 145, 130, and 100 mAh g^{-1}, respectively, as shown in Fig. 7c. Moreover, the capacity retentions after 100 cycles at 0.5 C, 1 C and 2 C current densities were 94%, 92.8% and 88%, respectively. Those properties are comparable to the materials synthesized with pure precursors.

Bian et al.[84] synthesized $LiFePO_4$/C hierarchical microflowers using $FePO_4 \cdot 2H_2O$ microflowers precursor, which was synthesized by using the leach liquor of spent $LiFePO_4$ material. The rate capability and long-term cycling performance of the re-synthesized $LiFePO_4$/C are shown in Fig. 7d and e. As can be seen that the re-synthesized $LiFePO_4$/C delivered a very high specific capacity of 159.3 mAh g^{-1} at 0.1 C current density and 86.3 mAh g^{-1} at 20 C current density, respectively. It still

had a specific capacity of 105 mAh g^{-1} with a capacity retention of 95.4% after 500 cycles at 5 C current density. In addition, the electrochemical performance of the re-synthesized sample was compared with the spent one. The result showed that the former had significantly enhanced specific capacity and cycling stability than the latter.

Senćanski et al.[85] synthesized a $LiCo_{0.415}Mn_{0.435}Ni_{0.15}O_2$ cathode material from spent LIBs. The re-synthesized material was obtained through a co-precipitation-thermal treatment route after acid leaching step. The material was tested in aqueous Li-ion and Na-ion batteries. The results are displayed in Fig. 7f and g, from which we can see that a high sodium storage capacity of 93 mAh g^{-1} at a current density of 100 mA g^{-1} could be achieved. In addition, an initial lithium intercalation capacity of ~64 mAh g^{-1} was delivered in potentiodynamical test at very high scan rate of 20 mV s^{-1}.

Hu et al.[86] synthesized nano-Co_3O_4 anode material using cobalt oxalate, which was recovered from spent LIBs through chemical precipitation. The nano-Co_3O_4 showed discharged specific capacity of 760.9 mAh g^{-1} at the current density of 125 mA g^{-1}, and the specific capacity of 442.3 mAh g^{-1} after 20 cycles at a current density of 250 mA g^{-1} was delivered, as shown in Fig. 7h and i.

3.3 Other functional materials

The leach liquor obtained from hydrometallurgical recycling processes, as well as its derivatives can be made into some compounds possessing special functionalities, such as magnetic materials (e.g. NiCo ferrite[87-90], CuCo ferrite[91]),

electrocatalytic materials (e.g. spinel $MnCo_2O_4$[92]), photocatalytic materials (e.g. $Co_3O_4/LiCoO_2$[93]) and other functional materials (e.g. MnO_2/graphene adsorbent[94]). Some of the materials are discussed as follows.

Yao et al.[87] synthesized nano-crystalline cobalt ferrite powders with a spinel structure from leach liquor of spent LIBs *via* a sol-gel-hydrothermal process. The obtained material showed the morphology of hedgehog-like microsphere with particle size of ~5 μm (Fig. 8a). The maximum magnetostriction coefficient was -158.5 ppm and the maximum train derivative coefficient was -1.69×10^{-9} $A^{-1}m$ when the material was obtained at 240 ºC for 12 h under hydrothermal treatment (Fig. 8b and c).

Natarajan et al.[92] synthesized spherical spinel $MnCo_2O_4$ (Fig. 8d) using leach liquor of spent LIBs. The obtained material was demonstrated to be effective in catalyzing the oxygen evolution reaction (OER) in 1 M KOH solution and required over-potentials of 358 and 400 mV to generate current densities of 5 and 10 mA cm^{-2}, respectively, with a low catalyst loading of 0.001025 g cm^{-2}. Moreover, the $MnCo_2O_4$ showed better performance than recovered $LiCoO_2$, recovered Li_xMnO_{x+1}, commercial Co_3O_4 (c-Co_3O_4) and commercial MnO_2 (c-MnO_2), and comparable activity to commercial RuO_2 (c-RuO_2), with very little difference in overpotential (~50 mV) at current densities of 5 and 10 mA cm^{-2} (Fig. 8e).

Santana et al.[93] synthesized a $Co_3O_4/LiCoO_2$ mixture using leach liquor of spent $LiCoO_2$ cathode material. The $Co_3O_4/LiCoO_2$ was composed of agglomerated particles with porous morphology (Fig. 8f). Its photocatalytic properties were tested in the discoloration of methylene blue dye. The discoloration efficiency of the material

was 90% after 10 h and 100% after 24 h (Fig. 8g).

Zhao et al.[94] prepared MnO_2-modified artificial graphite (MnO_2-AG, Fig. 8h) sorbents from spent LIBs for wastewater treatment. In their work, the graphite coated copper foils were used as the raw material. The recovered graphite powder underwent a thermal treatment, followed by being immersed in $KMnO_4$ solution for the loading of MnO_2 particles. The MnO_2-AG showed excellent removal capacity toward Pb(II), Cd(II), and Ag(I), whose removal rates were 99.9%, 79.7%, and 99.8%, respectively (Fig. 8i).

In summary, some progresses in recycling technologies have been achieved. Owing to that, metals, chemicals or regenerated functional materials can be obtained. However, most of the recycling processes aiming at recovery of such high value-added products require expensive reagents and complicated treatment steps. In addition, mixing the LIBs that contain different materials may add extra difficulties to the recycling processes, as well as introduce impurities to the re-generated products, because the separation steps will be rather more complicated. Some impurities of the re-generated products (e.g. electrode materials) from the recycling process could lead to inferior performance. For example, Fe could lead to fast self-discharge since the free Fe ions or metal in the electrolyte will be oxidized on the surface of the cathode and deposit on the anode during the storage in the charged state. That the reason why re-generated materials may not be comparable to fresh ones, even though they significantly outperform the spent ones. Hence, for facilitating the recovery of high value-added products, spent LIBs should be identified and sorted before recycling, so

that different types of waste materials will not be mixed together.

4. Effect of recycling spent LIBs on environmental burdens

Generally, EVs are considered as “zero emission” vehicles compared with those equipped with internal-combustion engines. However, although EVs have no gas emission in operation, many factors related with LIBs, which are the power sources of EVs, indeed have significant impact on environment. With the market expansion of EVs, LIBs manufacture and the upstream industries have increased substantially, consequently creating environmental burdens, such as resources consumption, energy generation and wastes emission (including gaseous, liquid and solid wastes). Similarly, the LIBs recycling, which can be seen as the downstream step of LIBs manufacture, also has non-negligible environmental impacts. To date, most of the studies related to LIBs recycling are focused on the recycling processes and resources recoveries, and the effects of recycling on environment are less concerned. In order to arouse more attentions to focus on this field, this review discuss the environmental pollution, resources conservation, energy consumption and wastes emission associated with the recycling of spent LIBs.

As discussed above, recycling spent LIBs reduces the environmental pollution and the waste of resources, since they contain heavy metals (e.g. Cu, Co, Ni and Mn) and toxic organic electrolytes. Hence, if environmental protection is taken into account, these harmful substances should be recovered firstly. Considering that the conservation of mineral resources is another way to environmental protection, an ideal recycling process should be capable of recovering all materials of LIBs with low

energy consumption and zero environmental pollution. However, more recovered substances usually come with longer and more sophisticated recycling processes, together with more energy input and wastes emission. Therefore, what also should be paid attention to is the environmental burdens imposed by the recycling processes themselves, including the energy demand and wastes emission.

The energy requirement for recovery of metals depends on the specific recycling process employed, as well as the forms of the final products. To date, commercial recycling industries (e.g. Umicore) employ the pyrometallurgical process to recover Co and Ni from spent LIBs. In other words, the crushed LIBs are treated like natural ores. Li will go into the slag which also can be further treated like lithium ores. Taking the commercial pyrometallurgical process as an example, the energy requirement for metallurgical recovery of Co, Ni and Li could be estimated based on the industry data of traditional pyrometallurgical process. However, the contents of Co and Li in LIBs are higher than those found in natural ores or even concentrated ores[16]. The contents of these elements in the spent LIBs should also be considered when estimating the energy requirement for metallurgical recovery of them.

Dunn et al.[24] comprehensively estimated the possible benefits of automotive LIBs recycling in terms of the reduction of energy consumption and greenhouse gas emission. In their work, these environmental burdens of the material production, assembly and recycling (as-called “cradle-to-gate” route) of automotive LIBs with $LiMn_2O_4$ as cathode material were analyzed. Based on their estimation, the direct physical process was considered to be the most energy-saving method, as it could

directly recover cathode materials without or only with minor relithiation. The hydrometallurgical and intermediate physical processes also showed beneficial impacts on total energy consumption of battery manufacture when cathode material, aluminum and copper were cycled. This work could be a good reference for the calculation of energy demand in the recycling processes.

Another important thing to note is that the energy associated with the production of required reagents and the processing of the wastes should not be neglected when estimating the total energy consumption of a recycling process. To date, hydrometallurgical recycling has been considered as an energy-saving route as compared to pyrometallurgical method[48, 95, 96]. To our best knowledge, however, there is no published work to systematically compare the total energy consumption between hydrometallurgical and pyrometallurgical approaches. In practice, the energy associated with the production of acid and auxiliary reagents, the acid recovery and the treatment of acid sludge has considerable impact on the energy-efficiency of the whole hydrometallurgical process. Therefore, more efforts are still needed to figure out the specific energy demand for recycling.

Lastly, it is meaningful to estimate the amount of wastes produced in the recycling. Theoretically, the amount can be calculated through chemical engineering calculation based on the leaching reactions. In addition, chemical treatments are needed to render the waste acceptable for landfill. For example, a large amount of acid and some other auxiliary reagents are needed in hydrometallurgical process. After the chemical recovery, a large volume of waste acid sludge will be generated.

The acid must be recycled or neutralized and the heavy metals and harmful organic substances in the sludge must be removed before landfill. That is the reason why hydrometallurgical process is hardly adopted by commercial recycling plants. Therefore, it is reasonable to conclude that estimating the amount of wastes emissions is essential to evaluating the environmental burdens and economic efficiency for a recycling process.

In summary, the effects of spent LIBs recycling on environmental burdens depend on the recycling approaches. It will be advisable to analyze the environmental burdens while designing a recycling process. Moreover, the recovery or disposal of electrolyte (including solvent and $LiPF_6$) and binder, as well as the anode materials, should also be concerned in the future, although they were not major contributors to battery cradle-to-gate impacts. In addition, battery designs aiming to easy disassembly and separation of battery materials, as well as the standardization of materials are recommended, since those may facilitate the recycling of spent LIBs and energy conservation.

5. Conclusion and perspectives

The substantial increase in the EVs production results in numerous spent LIBs in the near future. The appropriate recycling of them is noteworthy, since they contain various valuable metals and harmful substances. Many recycling processes aiming at recovering the metal values from spent LIBs have been developed, and some of them have been industrialized. An ideal recycling process should be capable of recovering all components of spent LIBs with low energy consumption and no environmental

pollution. To date, there are research achievements developed on the technologies which are able to satisfy such requirements. However, almost all of them require complicated processing steps or expensive reagents due to the diversity of materials in LIBs. Therefore, many efforts are still needed for the development of more powerful recycling technologies.

In addition, there are other challenges which the LIBs recycling industry must face. Firstly, unlike lead-acid batteries, the technology and chemistry of LIBs are ever-evolving, leaving the recycling technologies behind. For example, the pyrometallurgical process may have no economic efficiency if the cathodes are fabricated with cobalt-free materials. Secondly, with the development of LIBs recycling industry, the issue of cross-contamination of battery type in recycling stream may emerge. For example, LIBs and lead-acid batteries may be designed to be geometrically equivalent for interchangeable use in some instances, such as on mini-sized electric vehicles or electric bicycles. That may lead to the inclusion of LIBs in the input stream of lead smelters, resulting in fires, explosions and contamination. Thirdly, there is no perfect laws, regulations, and standards system regarding LIBs recycling, which can standardize the recycling, and assure safe collection, transport and handling of spent LIBs during the recycling processes.

Finally, in order to speed up the establishment of efficient recycling system for spent LIBs, further effort may concentrate on, but not be limited to the following. (1) Identifying and sorting spent LIBs to be recycled in different ways. (2) User-friendly labeling or marking LIBs at the manufacture and recycling, which could help routing

and supervising the recycling. (3) Designing LIBs with recycling in mind, and avoiding irreversible or complex assembling. (4) Accelerating legislation to standardize the recycling processes.

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Figure captions

Fig. 1 The development of EVs in the world. (a) Global EV stock; (b) global EV registrations. Ref. [11].

Fig. 2 Flowchart of typical processes for recycling spent LIBs

Fig. 3 Flowchart of recycling process proposed by Georgi-Maschler et al. Ref. [30], reproduced with permission from Elsevier

Fig. 4 Effect of (a) temperature (c_{H+} = 4 M, t = 2.5 h), (b) H^+ concentration (T = 80 ºC, t = 2.5 h), and (c) leaching time (c_{H+} = 4 M, T = 80 ºC) on the HCl leaching efficiency of cobalt and lithium from $LiCoO_2$. Ref. [23], reproduced with permission from Elsevier.

Fig. 5 Time-courses for (a) Li extraction efficiency, (b) Co extraction efficiency, (c) Li dissolution concentration and (d) Co dissolution concentration during bioleaching of spent LIBs under different pulp densities (squares 1%, circles 2%, and triangles 4%). Ref. [57], reproduced with permission from Elsevier; (e) metal recovery under different pulp densities in the *Aspergillus niger* bioleaching process. Ref. [36], reproduced with permission from Elsevier.

Fig. 6 (a) Flowchart of direct physical recycling of spent LIBs with $LiMn_2O_4$ as cathode material. Ref. [24], reproduced with permission from American Chemical Society; (b) flowchart of direct physical recycling of soft package spent $LiFePO_4$ battery. Ref. [70], reproduced with permission from Royal Society of Chemistry.

Fig. 7 (a, b) charge-discharge plots and cycling performance of the $LiCoO_2$ powder reported in Ref. [22], reproduced with permission from Elsevier; (c) rate capability of

the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ material reported in Ref. [83], reproduced with permission from Elsevier; (d, e) rate capabilities and cycling performances of the re-synthesized and spent $LiFePO_4$ samples reported in Ref. [84], reproduced with permission from Elsevier; (f, g) charge-discharge curves and potentiodynamical cycling performance of the re-synthesized $LiCo_{0.415}Mn_{0.435}Ni_{0.15}O_2$ cathode reported in Ref. [85], reproduced with permission from Elsevier; (h, i) charge-discharge plots and cycling performance of Co_3O_4 anode material reported in Ref. [86], reproduced with permission from Elsevier.

Fig. 8 (a) Scanning electron microscopy (SEM) images of the $CoFe_2O_4$ synthesized by hydrothermal process (H-$CoFe_2O_4$), together with the (b, c) strain derivative curves and magnetostriction curves of H- $CoFe_2O_4$ and sintered $CoFe_2O_4$ (S- $CoFe_2O_4$) reported in Ref. [87], reproduced with permission from Elsevier; (d, e) SEM image of the spinel $MnCo_2O_4$ and current density-overpotential plots of the samples in the comparative study reported in Ref. [92], reproduced with permission from Royal Society of Chemistry; (f) SEM image of the $Co_3O_4/LiCoO_2$, and (g) discoloration rate of methylene blue dye for absorption peak at 664 nm and 613 nm, reported in Ref. [93], reproduced with permission from Elsevier; (h) schematic diagram of MnO_2-AG, and (i) comparison of removal rates of Pb(II), Cd(II) and Ag(I) between MnO_2-AG and AG, reported in Ref. [94], reproduced with permission from American Chemical Society.

Table captions

Table 1 The materials used in the components of lead-acid batteries and LIBs.

Table 2 Summary of optimal operation conditions for the leaching of materials fraction of spent LIBs by different acidic leaching agent.

Table 3 Summary of metals and chemicals obtained from recycling of spent LIBs.

Fig. 1 The development of EVs in the world. (a) Global EV stock; (b) global EV registrations. Ref. [11].

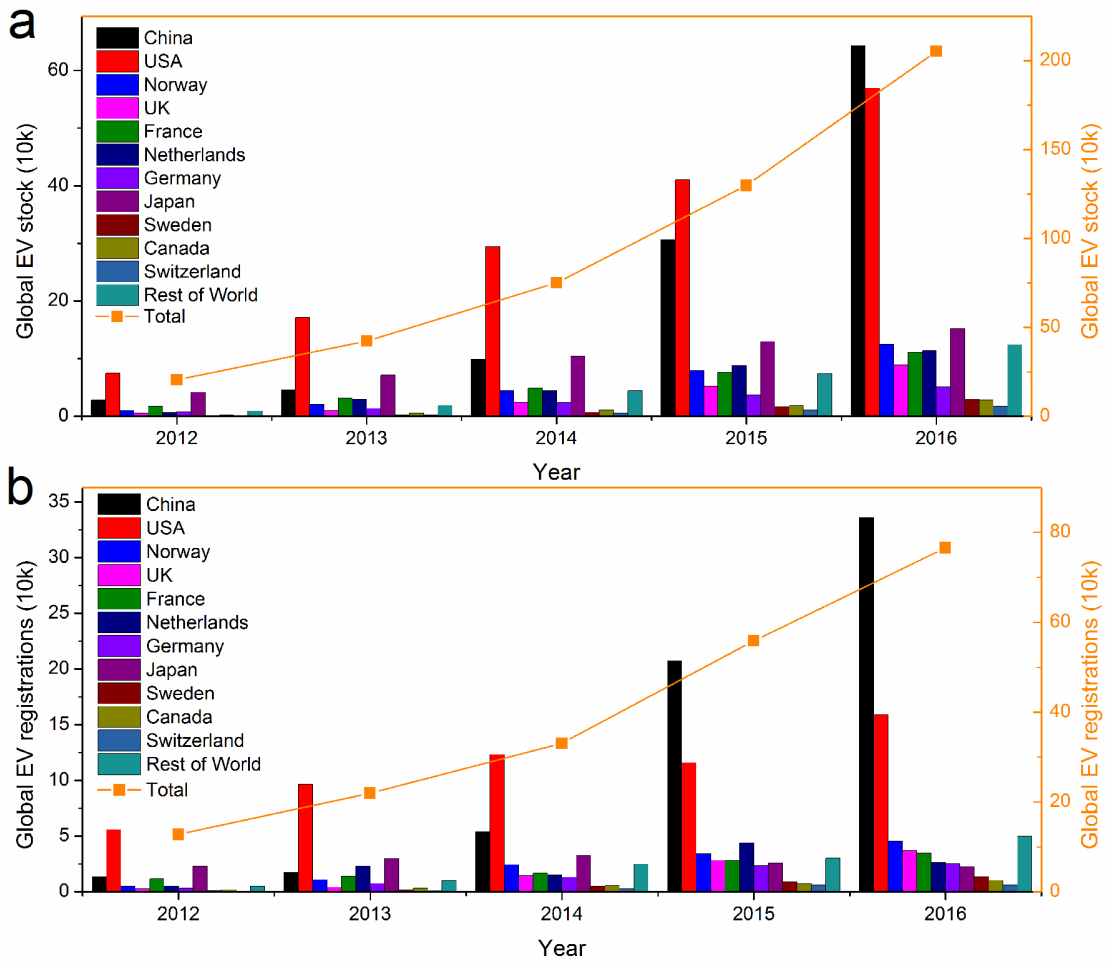

Fig. 2 Flowchart of typical processes for recycling spent LIBs

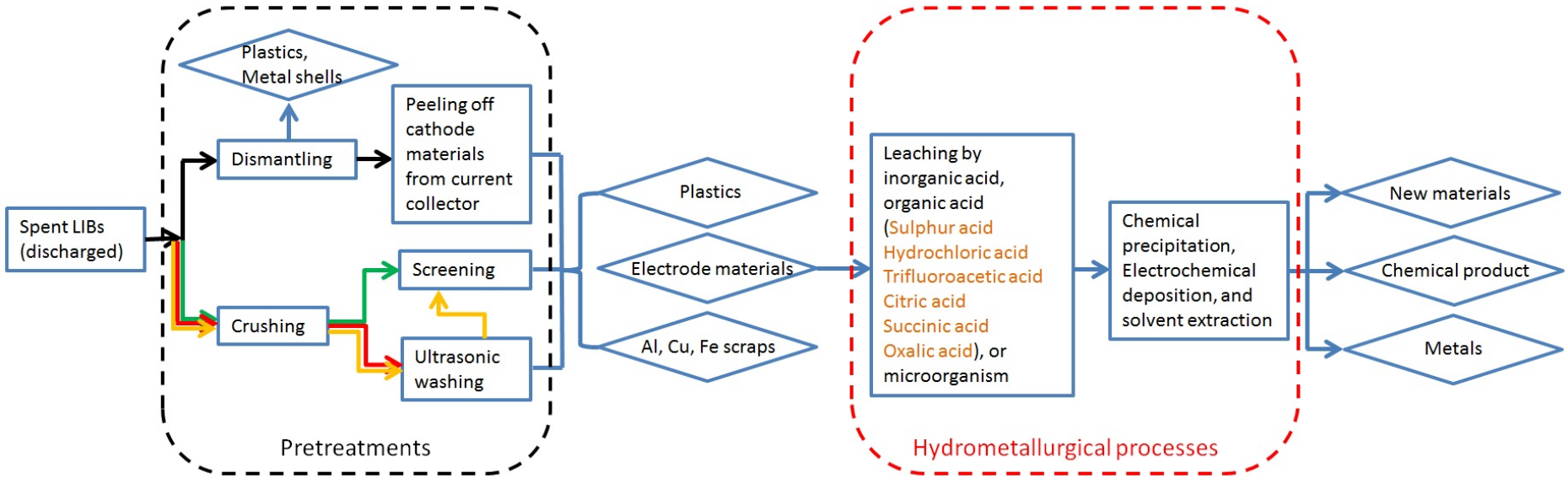

Fig. 3 Flowchart of recycling process proposed by Georgi-Maschler et al. Ref. [30], reproduced with permission from Elsevier.

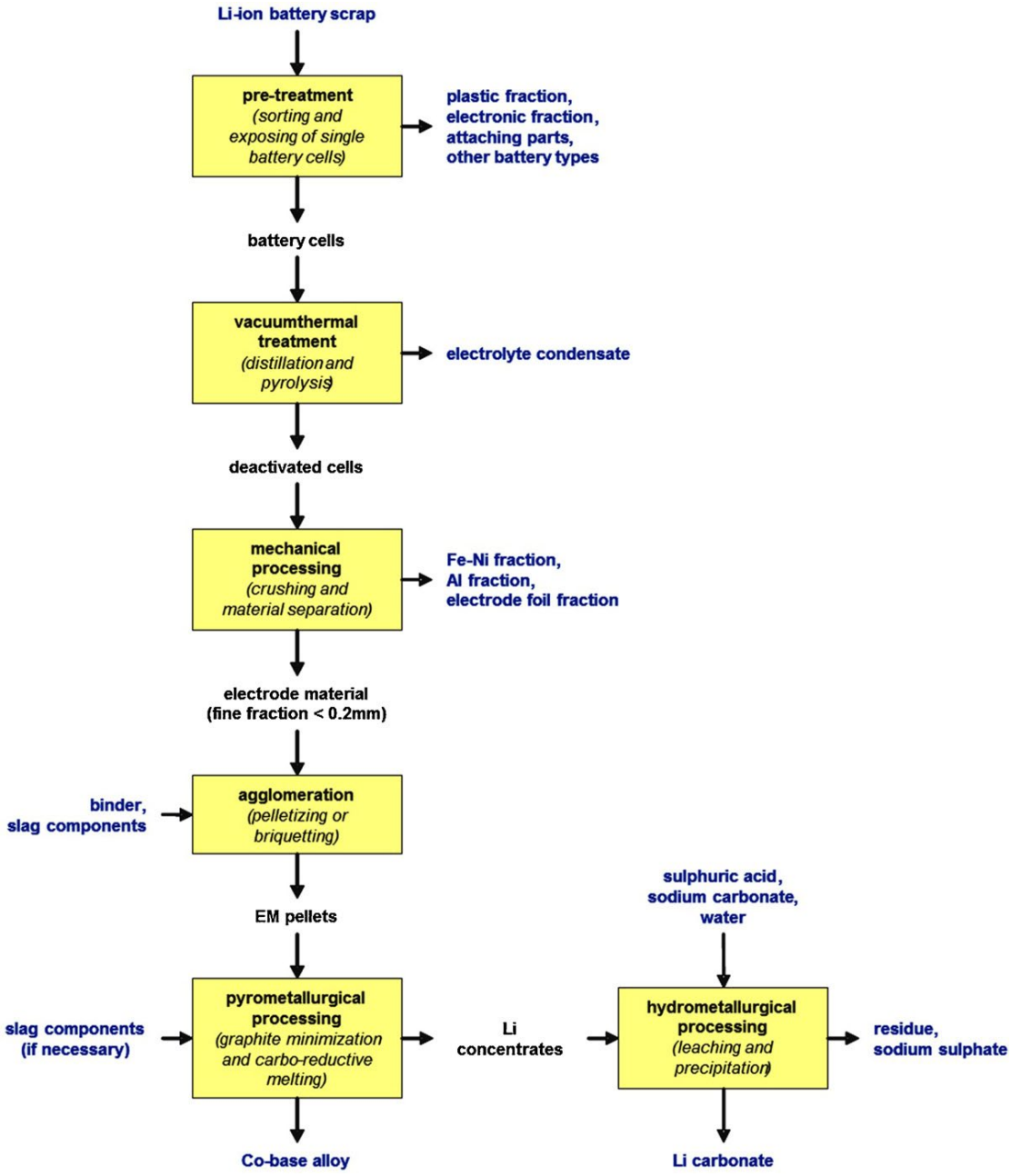

Fig. 4 Effect of (a) temperature (c_{H+} = 4 M, t = 2.5 h), (b) H^+ concentration (T = 80 ºC, t = 2.5 h), and (c) leaching time (c_{H+} = 4 M, T = 80 ºC) on the HCl leaching efficiency of cobalt and lithium from $LiCoO_2$. Ref. [23], reproduced with permission from Elsevier.

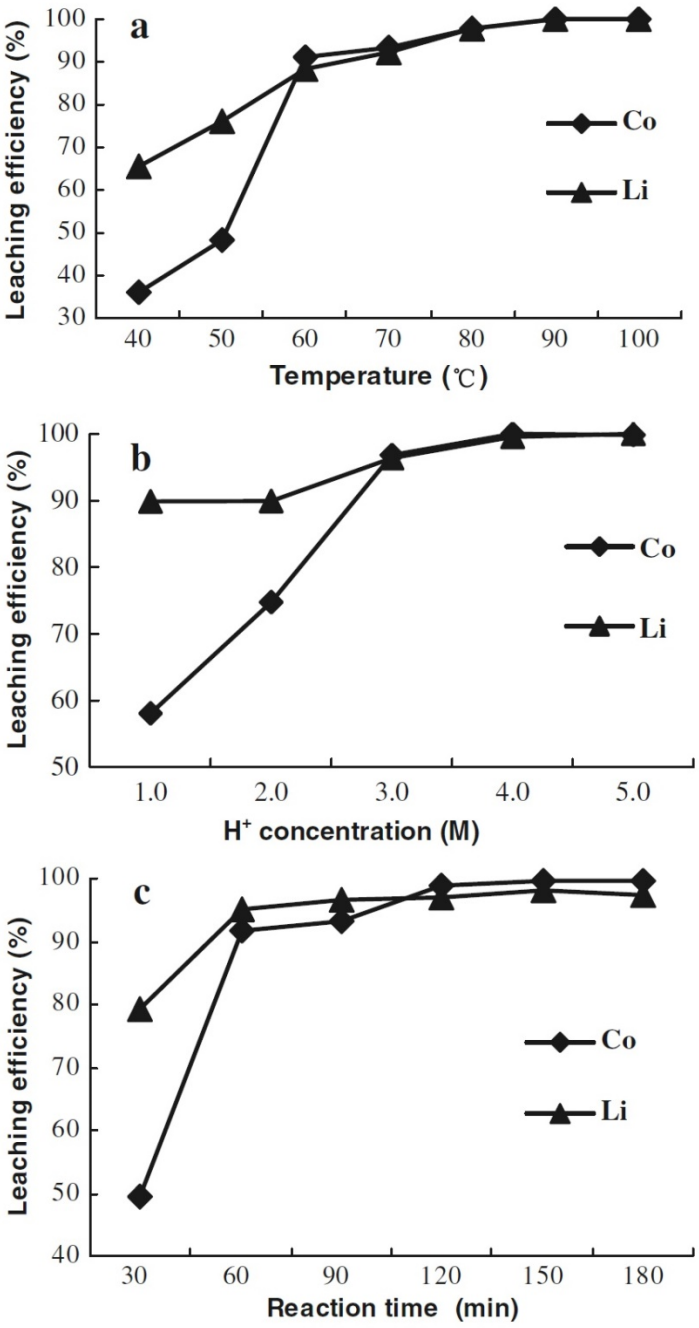

Fig. 5 Time-courses for (a) Li extraction efficiency, (b) Co extraction efficiency, (c) Li dissolution concentration and (d) Co dissolution concentration during bioleaching of spent LIBs under different pulp densities (squares 1%, circles 2%, and triangles 4%). Ref. [57], reproduced with permission from Elsevier; (e) metal recovery under different pulp densities in the *Aspergillus niger* bioleaching process. Ref. [36], reproduced with permission from Elsevier.

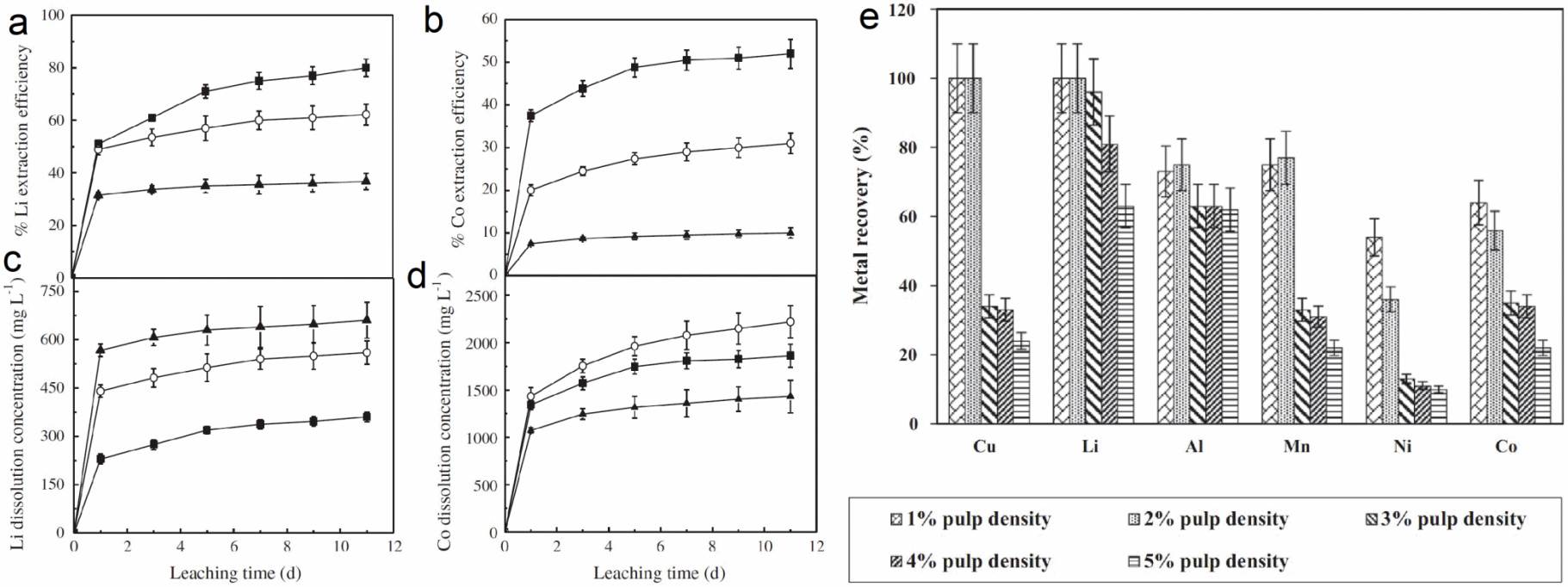

Fig. 6 (a) Flowchart of direct physical recycling of spent LIBs with $LiMn_2O_4$ as cathode material. Ref. [24], reproduced with permission from American Chemical Society; (b) flowchart of direct physical recycling of soft package spent $LiFePO_4$ battery. Ref. [70], reproduced with permission from Royal Society of Chemistry.

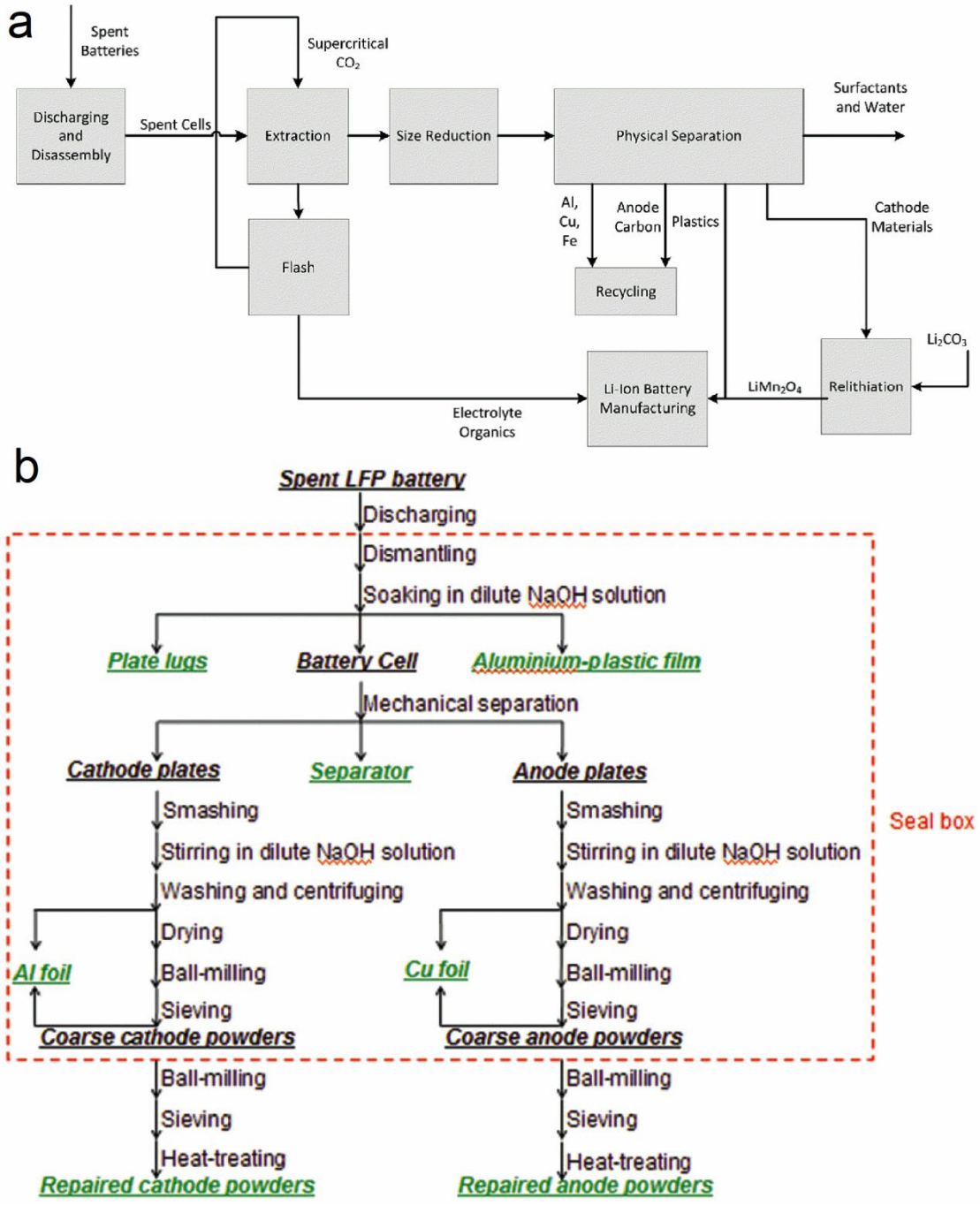

Fig. 7 (a, b) charge-discharge plots and cycling performance of the $LiCoO_2$ powder reported in Ref. [22], reproduced with permission from Elsevier; (c) rate capability of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ material reported in Ref. [83], reproduced with permission from Elsevier; (d, e) rate capabilities and cycling performances of the re-synthesized and spent $LiFePO_4$ samples reported in Ref. [84], reproduced with permission from Elsevier; (f, g) charge-discharge curves and potentiodynamical cycling performance of the re-synthesized $LiCo_{0.415}Mn_{0.435}Ni_{0.15}O_2$ cathode reported in Ref. [85], reproduced with permission from Elsevier; (h, i) charge-discharge plots and cycling performance of Co_3O_4 anode material reported in Ref. [86], reproduced with permission from Elsevier.

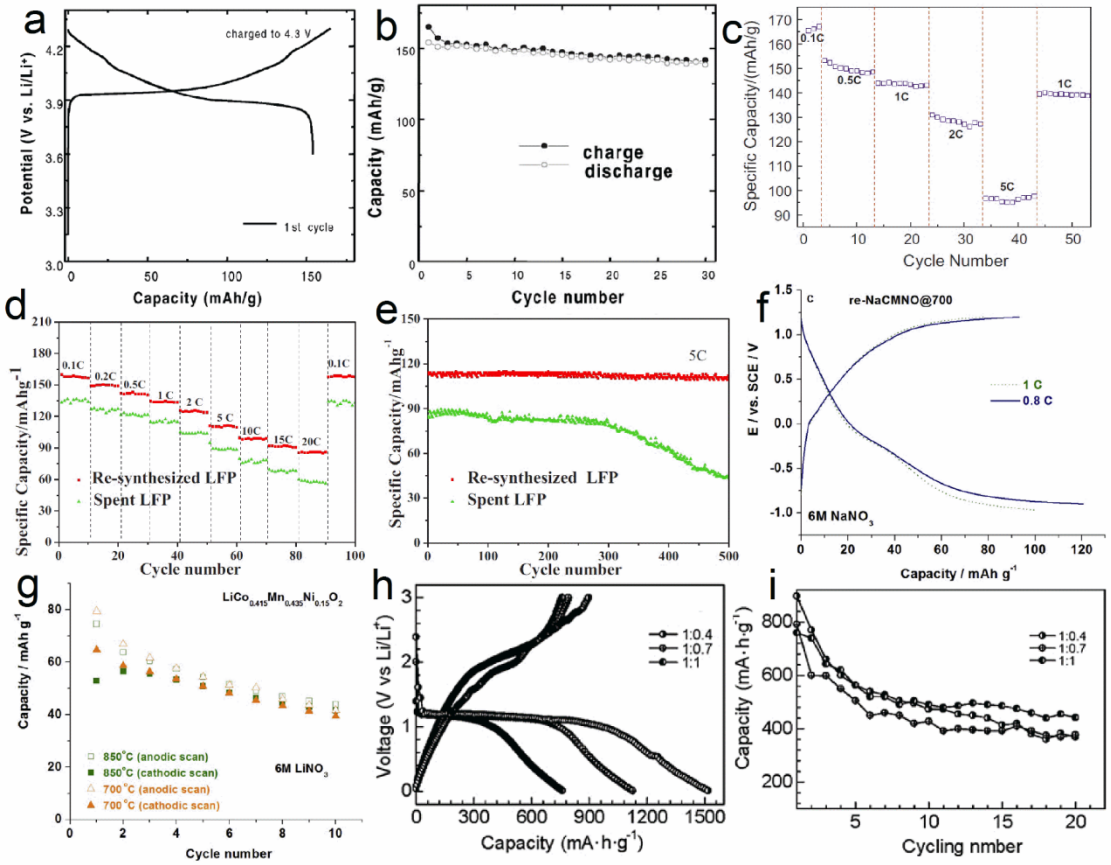

Fig. 8 (a) Scanning electron microscopy (SEM) images of the $CoFe_2O_4$ synthesized by hydrothermal process (H-$CoFe_2O_4$), together with the (b, c) strain derivative curves and magnetostriction curves of H- $CoFe_2O_4$ and sintered $CoFe_2O_4$ (S- $CoFe_2O_4$) reported in Ref. [87], reproduced with permission from Elsevier; (d, e) SEM image of the spinel $MnCo_2O_4$ and current density-overpotential plots of the samples in the comparative study reported in Ref. [92], reproduced with permission from Royal Society of Chemistry; (f) SEM image of the Co_3O_4/$LiCoO_2$, and (g) discoloration rate of methylene blue dye for absorption peak at 664 nm and 613 nm, reported in Ref. [93], reproduced with permission from Elsevier; (h) schematic diagram of MnO_2-AG, and (i) comparison of removal rates of Pb(II), Cd(II) and Ag(I) between MnO_2-AG and AG, reported in Ref. [94], reproduced with permission from American Chemical Society.

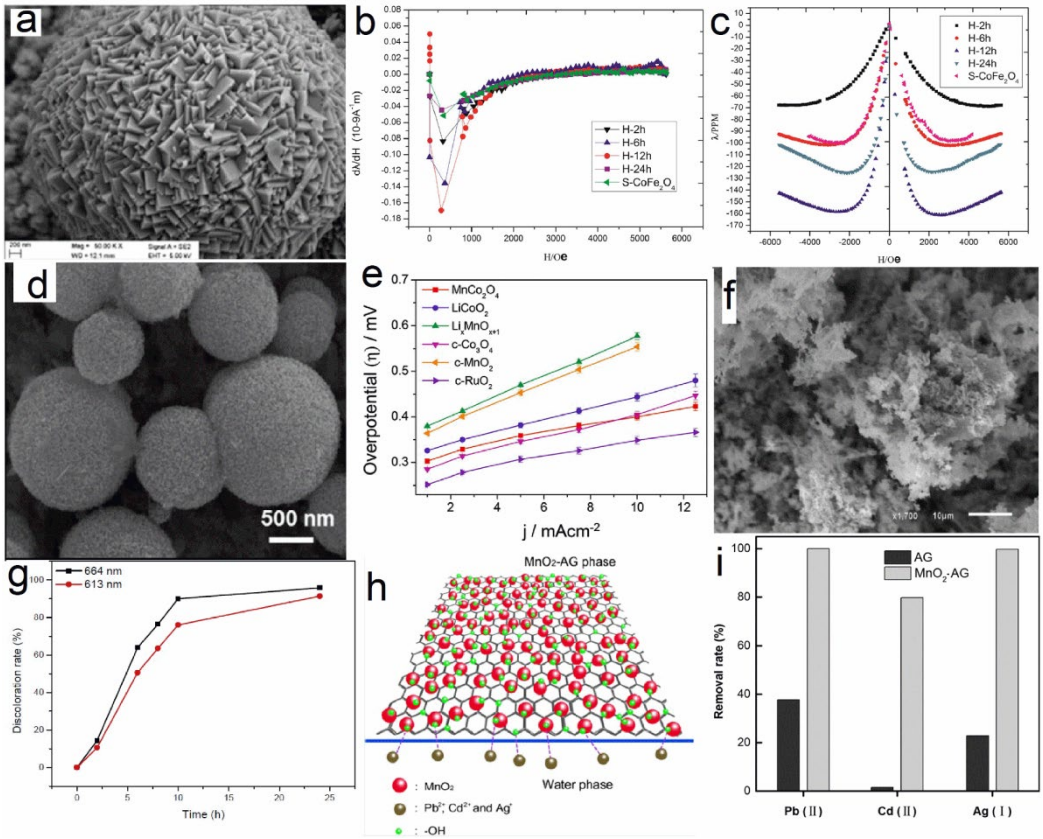

Table 1 The materials used in the components of lead-acid batteries and LIBs.

Component	Lead-acid batteries	LIBs
Cathode/current collector	PbO_2/Pb	$LiMO_2$ (M=Co, Ni, Mn), $LiFePO_4$/Al
Anode/current collector	Pb/Pb	Graphite/Cu
Electrolyte	H_2SO_4	$LiPF_6$ + organic solvent (EC, DMC, EMC, DEC, etc)
Separator	PE or PVC w/silica	PE/PP
Case	PP	Al-plastic film, Al, SS

EC = ethylene carbonate; DMC = dimethyl carbonate; EMC = ethyl methyl carbonate; DEC = diethyl carbonate;

PE = polyethylene; PVC = polyvinyl chloride; PP = polypropylene; SS = stainless steel

Table 2 Summary of optimal operation conditions for the leaching of materials fraction of spent LIBs by different acidic leaching agent.

Materials	Leaching agent	Leaching condition	Reduction agent	Solid/liquid ratio	Leaching rate	References
$LiCoO_2$	4 M HCl	80 ºC + 2 h	N/A	N/A	Li 97%, Co 99%	[23]
$LiCoO_2$	4 M HCl	80 ºC + 1h	N/A	10% (w/v)	Li >99%, Co >99%	[34]
$LiCoO_2$ + $LiMn_2O_4$ + $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$	4 M HCl	80 ºC + 1h	N/A	5% (w/v)	Ni, Co, Mn, Li >99%	[39]
$LiCoO_2$	3 M HCl	80 ºC + 1h	3.5% H_2O_2 (v/v)	5% (w/v)	Li, Co 89%	[38]
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	4 M HCl	90 ºC + 18 h	N/A	5% (w/v)	Li, Ni, Co, Al 100%	[37]
$LiCoO_2$	2 M H_2SO_4	75 ºC + 1 h	5% H_2O_2 (v/v)	10% (w/v)	Li 99.1%, Co 70.0%	[41]
Mixed cathode materials containing Li, Co, Ni, Mn	1 M H_2SO_4	95 ºC + 4 h	N/A	5% (w/v)	Li 93.1%, Co 66.2%, Ni 96.3%, Mn 50.2%	[40]
$LiCoO_2$	2M H_2SO_4	75 ºC + 0.5 h	5% H_2O_2 (v/v)	10% (w/v)	Li 94%, Co 93%	[44]
$LiCoO_2$	2M H_2SO_4	60 ºC + 1 h	6% H_2O_2 (v/v)	10% (w/v)	Co 99%	[43]

$LiCoO_2$	2M H_2SO_4	60 ºC + 2 h	2% H_2O_2 (v/v)	3.3% (w/v)	Li 87.5%, Co 96.3%	[42]
$LiCoO_2$	1 M HNO_3	75 ºC + 0.5 h	1.7% H_2O_2 (v/v)	1~2% (w/v)	Li, Co >95%	[45]
Mixed cathode materials containing Li, Mn	2 M HNO_3	80 ºC + 2 h	N/A	N/A	Li, ~100%	[46]
$LiCoO_2$	0.7 M H_3PO_4	40 ºC + 1 h	4% H_2O_2 (v/v)	5% (w/v)	Li, Co >99%	[48]
$LiCoO_2$	2% (v/v) H_3PO_4	90 ºC + 1 h	2% H_2O_2 (v/v)	0.8% (w/v)	Li, Co ~99%	[47]
$LiCoO_2$	Citric acid (100 mM) + ascorbic acid (20 mM)	80 ºC + 6 h	ascorbic acid in the acidic solution	0.2% (w/v)	Li, Co ~100%	[50]
$LiCoO_2$	1 M oxalic acid	80 ºC + 2 h	N/A	5% (w/v)	Li, Co ~98%	[52]
$LiCoO_2$	1 M oxalic acid	95 ºC + 2.5 h	N/A	1.5% (w/v)	Li 98%, Co 97%	[51]
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	1.5 M Citric acid	80 ºC + 2 h	D-glucose	2% (w/v)	Li 99%, Co 92%, Ni 91%, Mn 94%	[49]

Table 3 Summary of metals and chemicals obtained from recycling of spent LIBs.

Spent LIBs or materials	Obtained products	Purity	Recycling process	References
$LiCoO_2$	Co	~100%	Electrodeposition after leaching	[67]
$LiCo_xNi_{1-x}O_2$	Ni	~100%	Electrodeposition after leaching and solvent extraction	[68]
Mixed spent LIBs	Co	99.2%	Electrodeposition after electrochemical leaching	[73]
	Cu	99.5%		
	MnO_2	96%		
$LiCoO_2$	Co	99.5%	Electrodeposition after leaching and supercritical fluid extraction	[74]
Mixture of $LiCoO_2$, $LiMn_2O_4$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	Li_2CO_3	96.97%	Chemical precipitation after leaching and separation (solvent extraction)	[39]
	MnO_2 with manganese hydroxide	98.23%		
	$Co(OH)_2$	96.94%		

	$Ni(OH)_2$	97.43%		
Spent LIBs from mobile phones	$CoC_2O_4 \cdot 2H_2O$	>99%	Chemical precipitation after leaching and solvent extraction	[64]
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	$Co_2O_3 \cdot 2H_2O$	90.25%	Chemical precipitation after leaching	[37]
	$Ni(OH)_2$	96.36%		
LIBs wastes from an industrial pre-treatment plant	$CoCO_3$	Commercial standard	Chemical precipitation after leaching and solvent extraction	[75]
	Li_2CO_3	>98%		
Mixture of $LiCoO_2$, $LiMn_2O_4$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	$NiCl_2$	97.81%	Chemical precipitation after leaching and solvent extraction	[31]
	$CoC_2O_4 \cdot 2H_2O$	97.47%		
	Li_2CO_3	99.18%		
Mixture of $LiFePO_4$ and $LiMn_2O_4$	$FeCl_3$	97.91%	Ion flotation and chemical precipitation after leaching	[79]
	MnO_2/Mn_2O_3	98.73%		
	Li_3PO_4	99.32%		

$LiCoO_2$	$Co_3(PO_4)_2$	97.1%	Chemical precipitation during leaching process	[48]
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	Li_2CO_3	99.9%	Chemical precipitation after leaching	[77]
	Ni-Co-Mn hydroxide	N/A		
Spent LIBs from local recycling center	Li_2CO_3	Almost pure	Reduction roasting, leaching, solvent extraction and evaporation	[76]
	$CoSO_4 \cdot 7H_2O$			
	$NiSO_4 \cdot 6H_2O$			
	$MnSO_4 \cdot H_2O$			
Mixture of $LiCoO_2$, $LiMn_2O_4$ and $LiNi_xCo_yMn_zO_2$	Li_2CO_3	99.7%	Vacuum pyrolysis	[78]