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Review

State-of-the-art lithium-ion battery recycling technologies

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ABSTRACT

Lithium (Li) is primarily found in mineral resources, brines, and seawater. Extraction of Li from mineral ore deposits is expensive and energy-intensive. Li-ion batteries (LIBs) are certainly one of the important alternatives to lessen the dependence on fossil fuel resources. The global demand for LIBs for portable electrical and electronic equipment (EEE) and EVs have increased significantly, and the amount of spent LIBs (S-LIBs) is rising logarithmically. S-LIBs contain both hazardous heavy metals and toxic organic chemicals that create a serious threat to human health and the ecosystem. The current position requires the recycling of S-LIBs indispensable for the protection of the environment and the recycling of scarce raw materials from economic aspects. In this manuscript, recent developments and state-of-the-art technologies for LIB recycling were focused on and reviewed comprehensively. Pretreatment methods (such as discharging, dismantling, cathode active material (CAM) removal, binder elimination methods, classification, and separation) for S-LIBs are introduced, and all available and novel technologies that are used in different physical and chemical recovery processes are summarized and compared. The pretreatment process in LIB recycling can both improve the recovery rate of the valuable components and significantly lessen the subsequent energy consumption. Notably, pretreatment, metal extraction, and product preparation stages play vital roles in all LIB recovery processes, based on pyrometallurgy, hydrometallurgy, biometallurgy, direct recycling, and mechanical treatment and water leaching. The main goal of this review is to address the novel S-LIB materials' current recycling research status and innovations for integrated, eco-friendly, economic, low carbon, and clean energy technologies. In the end, different industrial recycling processes are compared, existing challenges are identified and suggestions and perspectives for future LIBs recycling applications are highlighted.
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1. Lithium (Li) "white gold"

Li is a soft and silvery-white element. It is highly reactive and flammable in its pure form. Li is present on Earth's crust in brines and minerals. It has several uses, but its abundance in nature is only 18 ppm by weight. Li is relatively low in abundance throughout the cosmos. Li is a scarce alkaline metal and has an atomic number of 3. Li is the lightest solid alkaline earth element with a density of 0.543 g/cm^3. Li is an electropositive metal that has the highest reactivity and high heat and electricity conductance. Li cannot be found as an element in nature, it can be found as Li^+(aq), LiOH(s), Li(s), LiH(s), $LiSO_4^-$(s), Li_2O(s), and Li_2O_2(s) forms.

According to Yang et al. (2018), there are about 230,000 Mt of Li dissolved in the seawater and it is present in the Earth's crust at between 20 and 70 ppm by weight, mainly in igneous granite rocks. New clays like hectorite resources are rare. This creates a significant problem for scientists to develop novel approaches for efficient extraction processes from existing sources. Ambrose and Kendall (2020) estimate the total global Li resource as 55–99 Mt. According to the USGS, Bolivia has 21 Mt, Argentina 19.3 Mt, Chile 9.6 Mt, USA 7.9 Mt, and Australia 6.4 Mt Li, resources globally. The major Li-bearing minerals are spodumene ($LiAlSi_2O_6$; 4%–7% Li), petalite ($LiAlSi_4O_{10}$; 2%–4% Li), lepidolite ($K[Li,Al]_3[Al,Si]_4O_{10}[OH,F]_2$); 3%–4% Li), zinnwaldite ($K[Li,Al,Fe]_3[Al,Si]_4O_{10}[OH,F]_2$), amblygonite ($[Li,Na]Al[OH,F]PO_4$; 8%–9% Li), montebrasite ($LiAl[PO_4][OH]$), eucryptite ($LiAlSiO_4$; 5.51% Li), triphylite ($Li[Fe,Mn]PO_4$), jadarite ($LiNaSiB_3O_7[OH]$) and hectorite ($Na_{0.3}[Mg,Li]_3[Si_4O_{10}][F,OH]_2 \cdot nH_2O$) containing <1%–9.7% Li_2O. Table 1 shows the summary of the major primary Li resource classification and Li extraction methods. Mineral deposits have 34% and brine deposits have 66% of total Li reserves excluding seawater. Solid mineral deposits can be found in igneous (25%–35%) and sedimentary (8%–13%) rocks and require expensive methods for Li extraction with

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Table 1
Major primary lithium resource classification and lithium extraction methods in 2019 (compiled from Can et al., 2021; Celebi, 2019; and Reich et al., 2022).

Mineral Ore Deposits (34%)		Brines (66%)		Seawater Reserve
(12.8–30.7 Mt)		(21.3–65.3 Mt)		(230 Bt)
Magmatic rocks (25%–35%) Pegmatites Greisens Alkaline granites *Spodumene ($LiAl(SiO_3)_2$) *Lepidolite	Sedimentary rocks (8%–13%) Volcano sedimentary rocks Clay hosted Li deposits (B/Li-rich clays) *Hectorite (0.5%–0.7% Li)	Brine water (52%–66%) Salt lakes Petroleum reservoirs (oil fields) Saline Geothermal brines (Cons: 0.1–68 mg/L Li)	Mine waste water Boron process wastewater in the tailing pond	Seawater
Solid rocks Expensive/Energy Intensive	(2%–5.5% Li) Environmental problems	Liquid solution Cheap (30%–50% than mined ores)	(0.02%–5% Li) Easy production Ext. 87%	0.1–0.2 ppm Li
Crushing, grinding, sieving, gravity, flotation, and magnetic separation Calcination Acid/alkaline treatment with H_2SO_4/HCl (50–250 °C) or lime or gypsum (750–1000 °C) roasting	Hydro-/pyro-metallurgy/ Pressure leach/Bioleaching (bacteria)	Evaporation Direct precipitation Sedimentation Electrodialysis Inorganic absorbent (Li-metal oxides, Ti-oxides, Al-hydroxides, Fe-oxy-hydroxides, $Li(Fe)PO_4$, Clay minerals)	Membrane processes Solvent extraction (SX) Bioabsorbent Sorption and ion exchange (IX)	SX, IX, liquid-liquid extraction, membrane separation

significant environmental problems. Aqueous brines are cheap for Li extraction.

Table 2 shows the world mine production and reserves between 2016 and 2020 according to the USGS data (https://www.usgs.gov/). In 2019 and 2022, more than 880,000 tonnes of Li were produced. Table 3 shows Li minerals and brine world production by country or region (https://www.usgs.gov/media/files/lithium-2019-tables-only-release).

2. Li lithology and production from nature resources

Li has excellent heat and electrical conductivity because of its high reactivity. Pure/free metallic Li is never found in nature due to its reactivity, but it is found as a compound such as Li-salts. They can be found in ore deposits, brines, clay, seawater, geothermal brines, and water. Although Li is used extensively, its reserves and production are unevenly distributed across the globe. South American nations, such as Argentina, Chile, and Bolivia, own more than 70% of the world's Li deposits in the Li triangle region (Fig. 1). Australia has 43.5% of the global production and followed by Chile with 32.8% of global production. Argentina and China are significant Li exporters in the world (Bae & Kim, 2021). Presently, Li is mainly extracted from two natural sources: ores and salt lakes. For brines, the Li grade and Mg/Li ratio (0.22–21.5) are important factors that affect production cost and time. Li extraction from evaporative salt lake brines is not efficient or adaptable that has an Mg/Li ratio greater than 6 (https://www.chemistryviews.org/details/ezine/11138711/Selective_Extraction_of_Lithium_from_Salt_Lake_Brines/). The brine contains 0.02%–5% Li^+, along with other cations ($Na^+$and K^+), and anions (Cl^- and SO_4^{2-}).

From the primary resources, Li is commercially extracted from hard rock spodumene minerals in igneous rocks and conventional LiCl salts are found in brine pools and seawater. A huge amount of Li is extracted from liquid brine reservoirs that are located beneath salt flats, known as salars, most of which are located in southwestern South America and China. Other Li-rich brine resources include oil fields and geothermal brines. Li brine deposits are accumulations of saline groundwater, geothermal water, and seawater that are enriched in dissolved Li (200–1500 ppm). The methods of Li extraction and processing vary depending on the source material. Li brine recovery is typically a simple but time-consuming process. In addition, the recycling of LIBs is the major secondary source of Li. Australia is the largest producer of Li from spodumene and Chile is the largest producer of Li from brine. Chile, Bolivia, and Argentina in South America comprise the "lithium triangle", named for the region's vast Li resources. Li production in China, which is the world's largest consumer of Li, was 7500 tonnes in 2019 (https://newenergy.slb.com/new-energy-sectors/sustainable-battery-grade-lithium).

Table 2
World mine production and reserves between 2016 and 2020 according to the USGS.

Country	Mine production (t)				
	2016	2017	2019	2020[a]	Reserves
Argentina	5800	5500	6300	—	2,000,000
Australia	14,000	18,700	45,000	40,000	64,700,000
Chile	14,300	14,100	19,300	18,000	9,200,000
China	10,800	14,000	2300	3000	3,200,000
Brazil	200	200	2400	1900	95,000
Portugal	400	400	900	900	60,000
Canada	—	—	200	—	530,000
Zimbabwe	1000	1000	1200	1200	220,000
World total (round)	—	—	886,000	882,000	21,000,000

[a] e: estimated.

3. Lithium usage

Since there is no free Li on the Earth, Li compounds are important components in many industrial applications and are used in LIBs, ceramics, glass, cement, special Li–Al alloys, lubricants, air conditioners, polymers, chemicals, and nuclear power plant industry as well as a psycho-medical pharmacy (Meng et al., 2021). In 2019, global total Li usage distribution is 65% in batteries, 18% in ceramic & glass, 5% in grease, 3% in casting, 3% in polymers, and 6% in others. Li is preferred as the battery material among all metals because of the lightest, highest electrochemical potential, and highest energy density. LiOH is used for LIBs, Al and steel production, and lubricants. Li_2CO_3 is used for LIBs, glass and ceramics production, Al and steel production, and drag production. LiOH is the weakest hydroxide and is mainly consumed in the production of cathode materials for LIBs such as $LiCoO_2$ and $LiFePO_4$. LiCl is used for LIBs, Li–Al alloys, and air conditioners. Adding Li to the ceramic masse enhances the glass melt rate and diminishes pulp viscosity and melting temperature. In addition, the high thermal expansion coefficient of Li makes ceramics resilient to heat shocks and improves mechanical strength. High-temperature Li grease is

Table 3
Lithium minerals and brine world production (t), by country or locality between 2015 and 2019.

Country	Lithium mineral	Brine world production (t)				
		2015	2016	2017	2018	2019
Australia	$LiAl(SiO_3)_2$	439,514	522,181	1,706,618	1,965,944	1,616,764
Chile	Li_2CO_3	50,418	70,831	73,563	87,029	99,300
	LiCl	2069	1775	2535	3826	3000
	LiOH	3888	5576	5280	6468	10,000
Brazil	concentrate	5781	8804	10,547	41,000	85,000
Zimbabwe	$LiAlSi_4O_{10}$, $(K[Li,Al]_3[Al,Si]_4O_{10}[OH,F]_2)$	50,000	50,000	40,000	80,000	80,000
Portugal	$K[Li, Al]_3[Al,Si]_4O_{10}[OH,F]_2$	17,120	25,758	52,741	76,818	77,000
China	LCE	20,470	25,400	37,300	37,800	57,500
Canada	$LiAl(SiO_3)_2$	—	—	—	114,000	9000
Namibia	$K[Li, Al]_3[Al,Si]_4O_{10}[OH,F]_2$	—	—	—	30,000	—
USA	Li_2CO_3	W	W	W	W	W

W: Withheld to avoid disclosing company proprietary data.

useful in concentrating oil and Li additives are utilized in casting to increase fluidity. Organic Li materials are used as strong bases in polymers to form C–C bonds.

4. Growing and robust Li market across borders

Strong demand growth is expected from electric vehicle (EV) sales and battery capacity growth. Li pricing is increasing as demand is expected to outstrip supply. LiOH shortages will significantly grow with time. Fig. 1(a) shows LiOH versus Li_2CO_3 demands in Mt LCE. In 2022, LiOH and Li_2CO_3 demand is less than 0.4 Mt. Fig. 1(b) shows the global Li supply and demand forecast between 2015 and 2030 for different sectors. Li-battery demand will significantly increase by 2030. There will be serious Li shortages in the 2030s. Fig. 1(c) presents Li mega factory growth rate between 2014 and 2030. There is 151 operating battery factory by the end of 2021 and 225 battery factories planned for 2030. 225 mega factories (4.2 TWh) operating at 100% capacity will need more than 3 Mt/y Li in 2030.

The Li market needs 10 to 18 times more Li production by 2030. Li was added to the critical raw materials list in the EU for the first time in 2020. LIBs represent one of the 21st Century's largest growth areas. Fig. 2 shows LIBs placed on the global market between 2018 and 2028. The demand for Li, graphite, Ni, and Co will significantly increase until 2028.

Because EVs greatly depend on LIBs, strategic Li supply security for large automotive manufacturers has become a major priority for countries, high-tech enterprises, and LIB producers. Strategic alliances and joint ventures continue were established to ensure a reliable, sustainable, and diversified supply of Li for LIB suppliers and EV manufacturers.

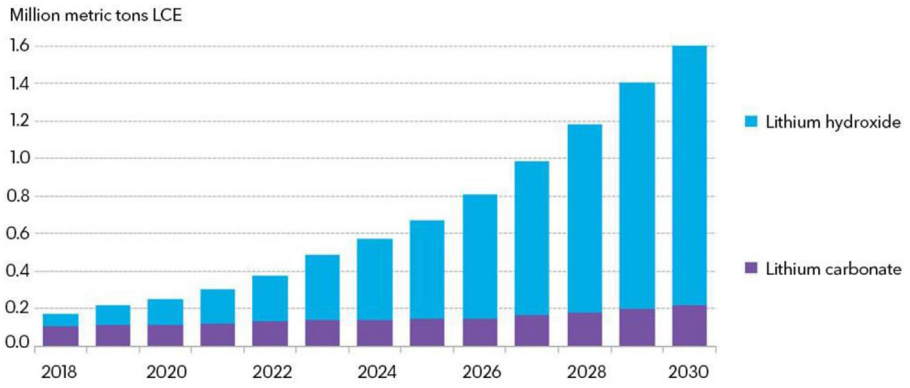
LIB market outlook growth potential is large because of emerging and growing technologies. Electricity will become the primary norm for the automotive industry. Increased growth of mobile electronics and new additions such as wearables and IoT enhances Li consumption exponentially, with about 10 million EVs being sold in 2017 globally (Lie et al., 2020). The LIBs market is expected to reach $221 billion by 2024 (Hu et al., 2017; Lie et al., 2020). The significant increase in the demand and usage of LIBs will also cause a huge generation of S-LIBs. Lie et al. (2020) and Harper et al. (2019) estimated that 250,000 tonnes of S-LIBs were generated by the end-of-life (EoL) EV LIBs that were sold in 2017 alone. In 2040, about 340,000 t/y LIBs from EVs will be available for recycling. Due to the high accumulation of S-LIBs in the waste streams, it is very important to recycle them in an eco-friendly process. The relatively short life span of LIBs leaves a huge amount of LIBs for disposal. These S-LIBs are composed of cathode and anode active materials, organic solvents, separators, shells, electrolytes, etc., which contain Co, Li, Ni, Mn, Cu, Al, and other valuable heavy metals. If these components are not handled properly, they easily leak into the environment and pose a huge threat to the ecosystem and human health (Dorella & Mansur, 2007). Moreover, S-LIBs also have a certain economic value. Specifically, Co and Li are strategic scarce resources, their content in S-LIBs is generally significantly higher than that in ores, and their recovery through effective technology will produce huge economic benefits (Mishra et al., 2008; Zeng et al., 2012). Thus, it is very important to do more research and development on recovering valuable metals from S-LIBs.

5. Lithium-ion batteries (LIBs)

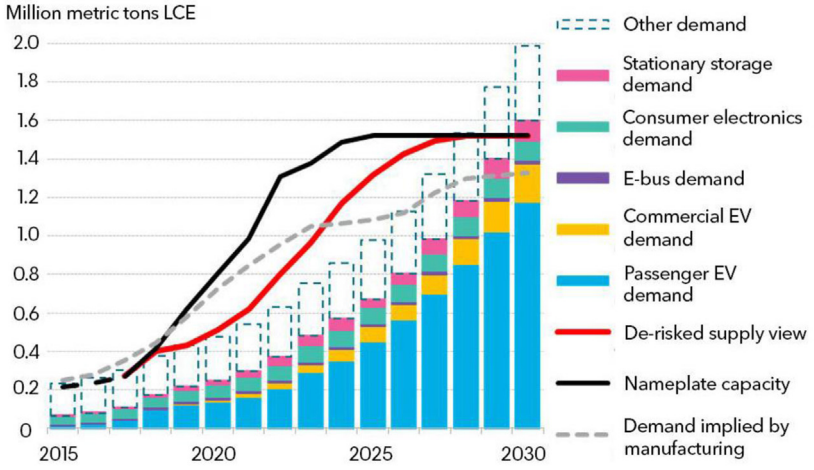
At the present time, the high consumption rates of fossil fuel resources and the need to decrease their environmental impacts drive consumers for developing to use sustainable and renewable energy resources such as better batteries, solar cells, wind turbines, and fuel cells. LIBs are one of the important alternatives to lessen the dependence on fossil fuel resources. LIBs structure, advantages and disadvantages, waste sources, recycling technologies, and environmental problems are covered in detail here.

With the rapid development of high technology, mobile/personal electronic and electrical equipment (EEE) and EVs have penetrated every corner of our lives. LIBs have become a portable power source dominant in mobile phones, laptops, PCs, cameras, video cameras, hand-held equipment, and other advanced-life appliances (Dorella & Mansur, 2007; Mishra et al., 2008; Paulino et al., 2008) because of their good performance compared with nickel-metal hydride (NiMH) or nickel-cadmium (NiCd) batteries, for example, lighter, smaller, high working voltage, high energy density, long storage life, low self-discharge, and have no memory effect (Dorella and Mansur, 2007; Mishra et al., 2008). Thus the demand and production of S-LIBs are increasing exponentially, and a large amount of production brings a lot of hazardous waste. The enormous growth in the use of LIBs has generated a great amount of S-LIBs for disposal that will cause serious environmental impacts due to the toxic heavy metals and organic electrolytes. After the end-of-life (EoL), this S-LIB acts both as a potential secondary source for the recovery of critical metals and simultaneously possess a threat to the environment. So they need to be recycled properly to gain economic benefits.

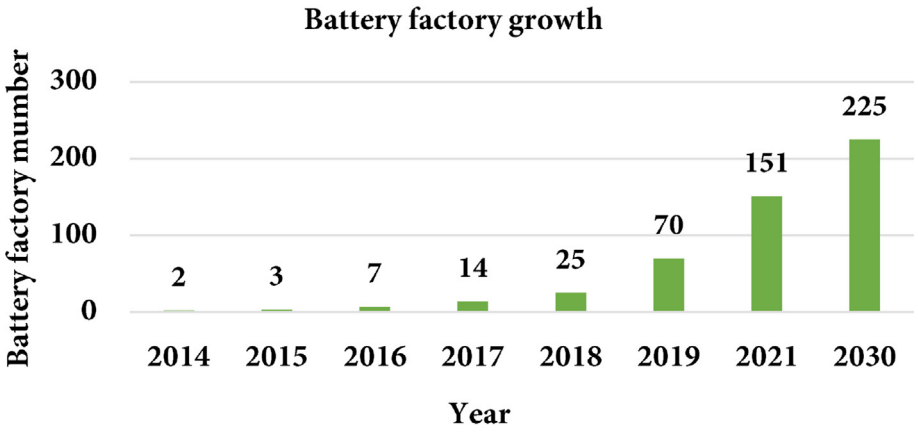
LIBs are not homogeneous and contain multi-metallic compounds that are rich in Li, Co, Ni, Cu, Al, and Mn. One of the cathode active material (CAM) of S-LIBs is lithium cobalt oxide (LCO) ($LiCoO_2$) which presents the principle and most important constituent for batteries. The chemical composition of LIBs largely changes depending on their application areas. S-LIBs are a kind of



(a)



(b)



(c)

Fig. 1. (a) LiOH versus Li_2CO_3 demands in Mt LCE between 2018 and 2030 (https://about.bnef.com/blog/will-the-real-lithium-demand-please-stand-up-challenging-the-1mt-by-2025-orthodoxy/). (b) Global Li supply and demand forecast between 2015 and 2030 for different sectors (https://about.bnef.com/blog/will-the-real-lithium-demand-please-stand-up-challenging-the-1mt-by-2025-orthodoxy/). (c) Li mega factory growth between 2014 and 2030 (https://about.bnef.com/blog/will-the-real-lithium-demand-please-stand-up-challenging-the-1mt-by-2025-orthodoxy/)

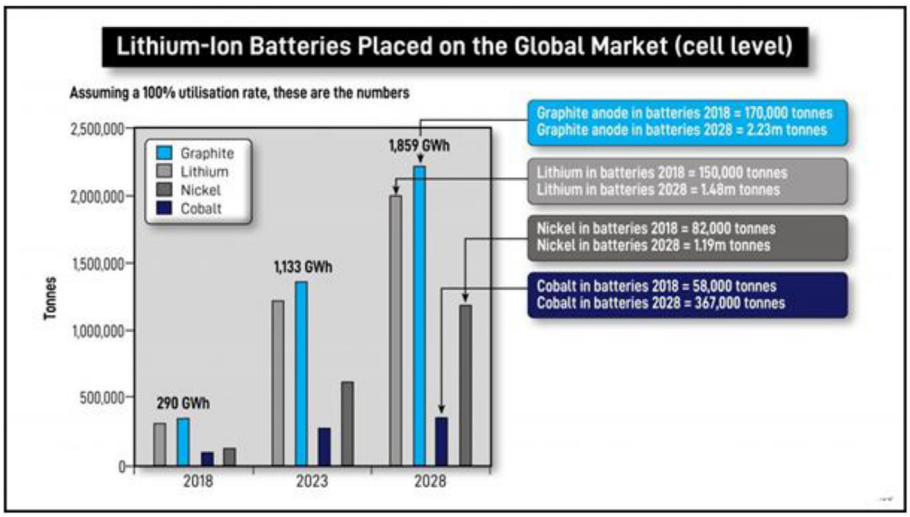


Fig. 2. LIB is placed on the global market until 2028 (https://www.neometals.com.au/products-and-markets/battery-recycling/).

hazardous waste EEE. If they are handled improperly, they will cause serious harm to human health and the ecosystem (Xin et al., 2009). However, there are also a number of valuable critical metals in the waste LIBs, such as Co (5–20 wt %), Li (5–7 wt. %), Ni, Cu, and Mn. (Contestabile et al., 1999, 2001). Therefore, recycling LIBs can bring huge economic benefits (Lee & Rhee, 2003). Then S-LIBs recycling is necessary both for environmental conservation and valuable metal recovery. Improper disposal of LIBs creates environmental hazards. Landfilling can generate toxic metal leachates and incineration creates toxic gases to the environment (Fig. 3).

6. Charging and discharging LIBs

Fig. 4 shows the charge and discharge details of LIBs. While charging LIBs, Li ions go from the cathode to the anode through the porous separator. Electrons flow from the cathode to the anode. During discharging, Li ions in the anode go back to the cathode and electrons flow from the anode to the cathode.

7. Waste LIBs

Since the 1990s, LIBs have been extensively used in portable small EEEs (>80%), large EVs, and energy storage devices (>20%) because of their small volume, lightweight, high energy voltage and density, long cycle life, low self-discharge efficiency, non-memory effect, wide temperature ranges, and advantages in eco-friendly compatible operations (Joulié et al., 2014; Mylarappa et al., 2017). Fig. 5 shows waste LIB sources and estimated global amounts along with lifetimes. A typical LIB structure is normally composed of anode materials, cathode materials, an organic solid/liquid electrolyte, and a porous polymer (PE/PP) separator (Li et al., 2010a; Nan et al., 2006). The anode, cathode, and separator are laminated by compressing them together which makes up the electrical connection achievable. The anode typically consists of a Cu-foil that is coated with a porous graphite mixture, a conductor, and an electrolyte with a binder. The binder consists of polyvinylidene fluoride (PVDF). The cathode contains porous CAMs (Li, Co, Ni, Mn, Fe, etc.) with a binder. Some of the LIBs materials, such as heavy metals, toxic electrolytes, and hazardous organic separators and binders, can constitute a significant threat to human health and ecosystems. Thus, it is necessary to safely recycle S-LIBs to recover their major valuable constituents.

LIBs have a shorter lifespan than other batteries. A LIB can last up to 3 years in a small electrical and electronic device, and from 5 to 10 years in a larger device; NiCd batteries last from 15 to 20 years, and lead-acid batteries (LABs) last from 5 to 10 years. At present, 80% of LIBs are used for small EEEs, with EV and solid-state electrolyte (SSE) applications accounting for less than 20%. In 2012, LIB disposal was estimated to be 10,700 tons. This value has increased progressively each year up to 250,000 tons in 2020. Global waste LIB amount will be 464,000 t in 2025. Waste battery collection rate was only 2%–5% in the EU, USA, and Australia by government and

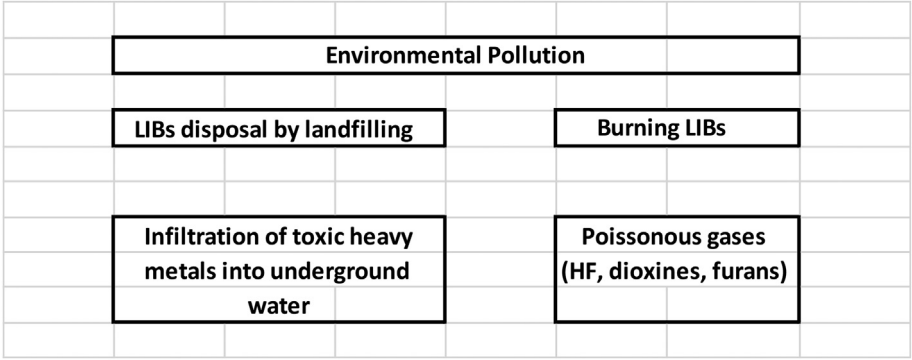


Fig. 3. Environmental hazards of improper LIB disposal and burning.

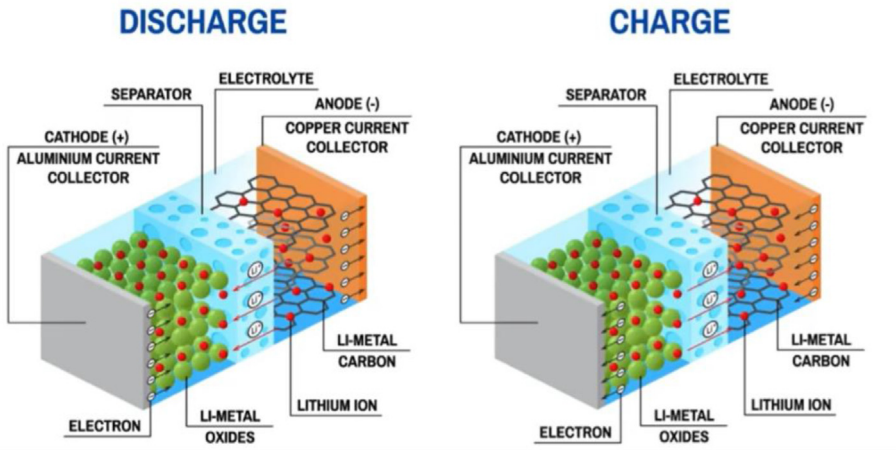


Fig. 4. Charge and discharge of LIBs.

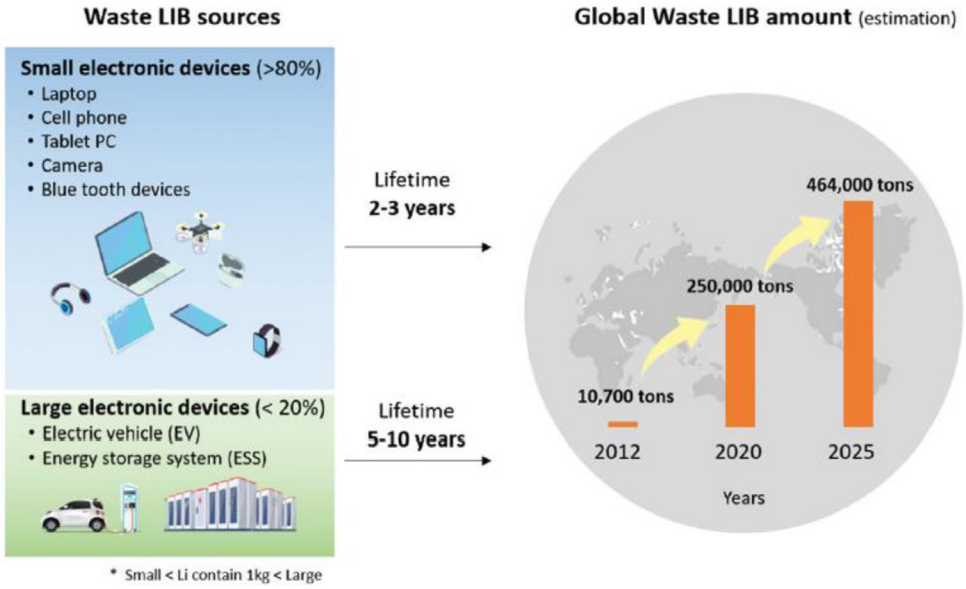


Fig. 5. Waste LIB source types and global amounts.

manufacturer-driven collection (Bae & Kim, 2021). The reason for this low collection rate is the lack of consumer awareness of recycling, the collection habit of consumers, and the tendency to resell electronics. Even though it may vary by country, there is still a lack of legal regulations and physical collection infrastructure for efficient, safe, and economical transportation of S-LIBs. Significant enhancements are necessary to significantly improve the collection rate.

8. LIBs are the backbone of electrical vehicle transportation

In the transition to a low-carbon future under climate change, electrification is a main key element. Globally transportation by EVs is becoming popular; worldwide more than 1 million EVs were sold in 2020, and that number is expected to increase 20 times in 2030. Therefore, the demand for rechargeable LIBs will be rising rapidly. Since 2020, the growth in LIBs demand has caused product requirements to rapidly change. In 2027, demand will exceed 1 Mt of lithium carbonate equivalent (LCE) (https://newenergy.slb.com/new-energy-sectors/sustainable-battery-grade-lithium).

9. LIB recycling

LIB recycling has been continuously researched in the last three decades and has recently gained significant importance. However, most researchers focused on the extraction of the expensive Co than Li. Thus, little importance has been placed on extracting Li from disposed of S-LIBs. Co is the most expensive material in a LIB; thus, there has been considerable research interest in diminishing the Co content or replacing it with Fe, Mn, and Ni in $LiFePO_4$ or $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. However, Li is an irreplaceable main component in LIBs, and it is used in the cathode, anode, and electrolyte. Thus, an extensive review of Li recycling from S-LIBs is necessary.

Harmless treatment for S-LIBs is vital for Li sustainability. Additionally, S-LIBs have a high economic value because they contain a significant amount of valuable/critical metals, some with even higher grades than natural ores. S-LIBs usually contain 5%–20% Co; 5%–7% Li; 5%–10% Ni and other metals (such as Cu, Mn, Al, Fe, etc.); 15% organic compounds, and 7% polymer separators. LIB compositions differ depending on the battery producers and the

types. Valuable metals such as Li, Ni, Co, Cu, Al, and Mn recovery from S-LIBs cause significant economic gains if they can be recycled properly. Fig. 6 shows recycling LIB market growth from 2018 to 2030. There will be a recycling boom until 2030. Discarded LIBs are likely to create a new global market for Li. The market will be more than 1.5 MMt after 2029. As demand grows, LIBs recycling will become an increasingly valuable secondary source of Li and Co metals.

The current LIB recycling ratio is very low and has the following drawbacks:

- There is no mature technology to recycle LIBs yet,
- Environmentally unfriendly,
- Produce extensive liquid and toxic waste by-products,
- Medium to low-grade products,
- Complex processing and purification steps,
- Low Li and Co recovery with little to no recovery of remaining metals, and
- Large consumption of reagents and energy.

Therefore, there is an urgent global need for novel LIB recycling technologies.

9.1. Reasons of the LIBs recycling

As the LIB demand for EVs and electronic industries grows the need for sustainable and circular LIB recycling will become increase. Currently, stockpiling, landfilling, and exporting LIBs is a no longer acceptable choices. Because of:

- Waste and scrap LIBs are considered hazardous waste in many countries (restricted to export to other countries according to the Basel Convention) and pose fire and explosion risks during storage and transportation.
- Once liberated and extracted, LIB constituent materials are economically valuable and there is a serious shortage of these materials in the world. Most of these materials are produced in conflicted areas.
- For most countries, national domestic supply chains can be met by secondary resource recycling only.
- Hydrometallurgical LIB recycling supports electrification with a decreased greenhouse gas footprint at reasonable material recovery rates; and
- Recycling is no more optional for many countries to support circular economic principles.

10. LIB structure

A LIB is mainly made of an anode, a cathode, an electrolyte, and a porous separator. The cathode materials of LIBs are usually Li intercalation oxides, like $LiCoO_2$ (LCO), $LiNiO_2$ (LNO), $LiMn_2O_4$ (LMO), $LiFePO_4$ (LFP), $LiNi_xCo_yMn_{1-x-y}O_2$ (NMC), etc. NMC cathode materials have become the most promising CAM for EV LIBs due to the low cost, large discharge capacity, good cyclic performance, and stable structure advantages. Portable electronics generally have LCO cathodic materials. Heavy Ni and Co metals in cathode materials pose a threat to the ecosystem and human health.

The electrolyte of a LIB usually includes both mixture of organic solvents, like dimethyl sulfoxide (DMSO), propylene carbonate (PC), and diethyl carbonate (DEC), and inorganic solutes, such as $LiPF_6$, $LiClO_4$, and $LiBF_4$. $LiPF_6$ is one of the most common inorganic solutes used in LIBs. Electrolytes can be corrosive and produce hazardous gas such as HF, Cl_2, CO, and CO_2 when heated/burned. The porous separator prevents short-circuiting because of direct contact between the cathode and anode. LIB separators are made of usually single-layer or multi-layer polyethylene (PE) or polypropylene (PP). Polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE) binders are used to bond electrode active materials to the Al/Cu foil and each other and can produce hazardous HF gas when heated. The cathode is an Al-foil with a CAM (like $LiCoO_2$) combination, an electrical conductor, a PVDF binder, and additives. A separator is placed between two electrodes to help in preventing a short circuit between them (Fig. 7).

Recycling processes of the S-LIBs include mechanical/physical, chemical, or physicochemical processes. The mechanical processes are the pretreatment methods while the extraction methods refer to the chemical processes. The LIBs contain several heavy metals, some organic chemicals, and plastics. 25%–35% of the LIB by weight is cathode material, 10%–19% anode material, 9%–15% electrolyte, and 1%–12% separator. The heavy metals mainly include 5%–20% Co, 5%–10% Ni, 5%–7% Li and there are about 15% of organic substances and 7% of plastics (Table 4). The most expensive parts of the S-LIBs are cathode and anode active materials.

Recently, the primary Li resources are depleting and Li is regarded under low to medium supply risk, concerning supply and demand (Meshram et al., 2015; Munir et al., 2020). According to

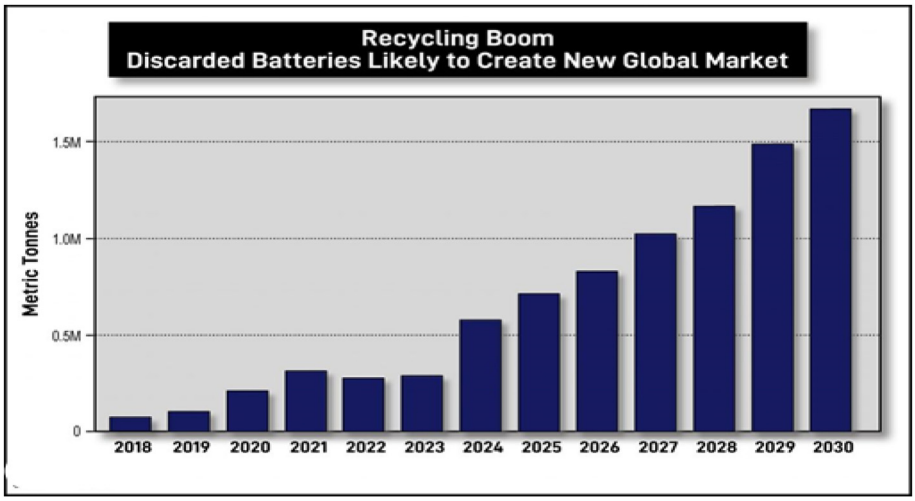


Fig. 6. S-LIB recycling market capacity between 2018 and 2030.

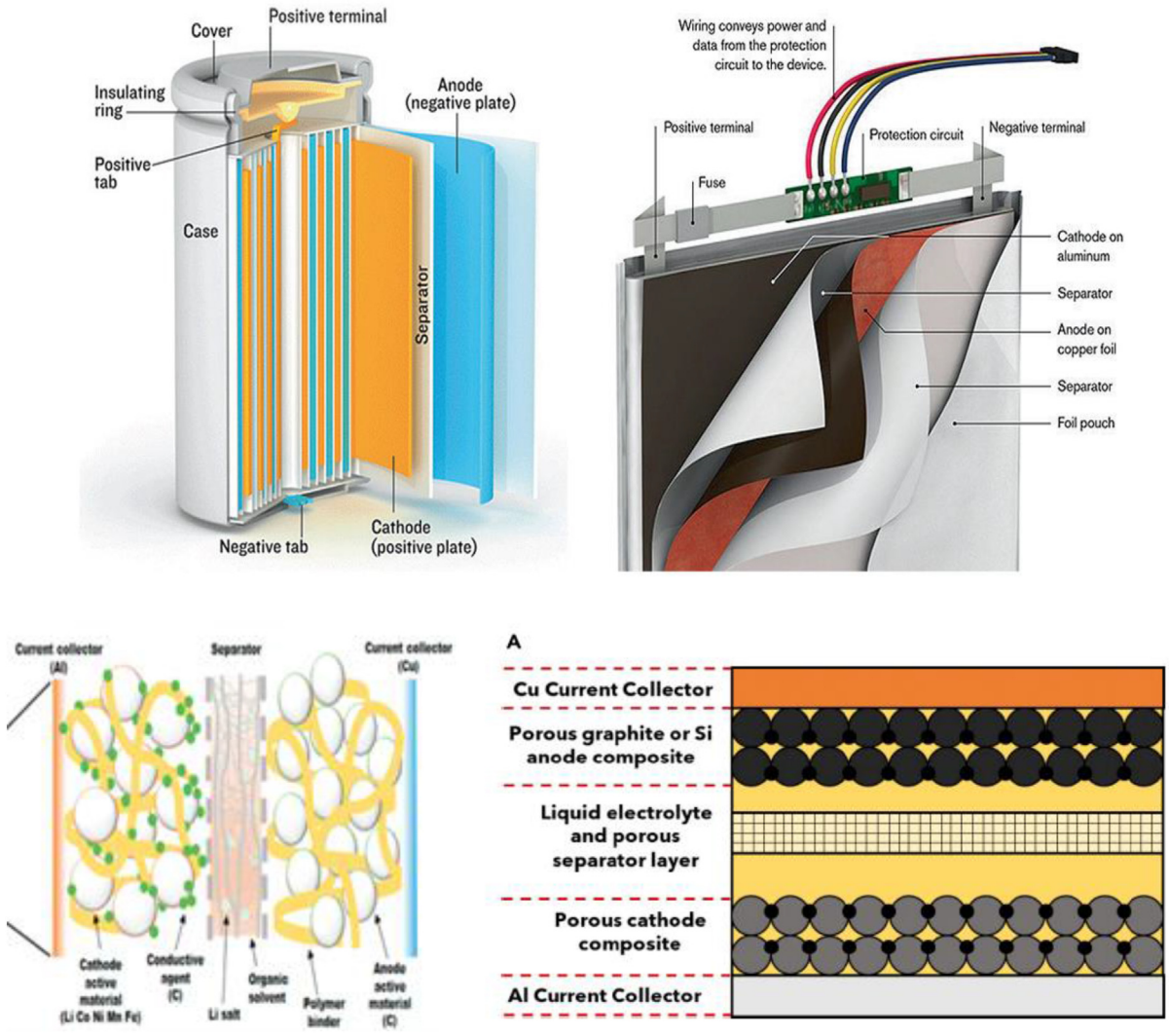


Fig. 7. Illustration of the cylindrical and mobile phone's conventional LIB internal and external structures.

Zhao et al. (2019), the amount of Li content in the S-LiBs is about ten times higher than in a primary spodumene ore and is thirty times higher than in brines. Apart from critical Co and Li, LiBs also contain economically desirable levels of non-ferrous metals like Cu, Al, Mn, and Ni (Sethurajan et al., 2016; Simate et al., 2010; Zhang and Cheng, 2007). When considering them as alternative secondary resources for metals, the proper management and recycling of S-LIBs become even more important. It was found that by the end of 2020, 0.5 Mt of S-LIBs and 25 billion units were generated only in China (Li et al., 2011; Yun et al., 2018). The worldwide LIB cathode market was a $7 billion market in 2018 and is expected to reach about $59 billion by 2024 (https://www.researchandmarkets.com/reports/4745669/lithium-ion-battery-cathodes-market-shares).

Table 5 shows the comparison of the LIB cathode types (such as LCO, LFP, LMO, NCA, and NMC), chemistry structure, year of introduction, energy and power densities, life span, performance, cost, and market share. Portable electronics and EVs contain different cathode types. Portable consumer electronics use LCO-type cathodes which becomes obsolete soon. Electric bikes, buses, and large vehicles use LFP-type cathodes. EVs use the cheap base metal-rich NMC and NCA types of cathodes which deliver strong energy density for the extended driving range. LCO has layered, LFP olivine, LMO spinel, NCA and NMC are layered type structures.

11. Advantages and disadvantages of LIBs

Table 6 shows the pros and cons of LIBs. The life span of the LIBs is between 3 and 5 years if not in use and 1–3 years when in use. Li-ion technology is dominant in the rechargeable battery market for electronics because of its small size, lightweight, high energy density, low discharge rate, no memory effect, etc. High cost, safety concerns, aging, and transportation problems are some of the disadvantages.

12. State-of-the-art S-LIB recycling technologies

S-LIBs contain not only highly valuable and scarce Li, Co, and Ni metals; but also Fe, Cu, Al, P, and other elements with low concentrations. From the economic point of view, the recovery of S-LIBs mainly focuses on recycling highly valuable Co, Li, and Ni metals from CAMs; the recovery of graphite-containing anode materials and the electrolyte is hardly stated. Current metal-recycling processes for S-LIBs are pyrometallurgy, hydrometallurgy, biometallurgy, and direct recycling. State-of-the-art metal recycling processes from S-LIBs can be divided into three processes: namely, pretreatment, metal extraction, and end product preparation processes. Pretreatment is not required for the pyrometallurgical

Table 4
Composition of commercial LIBs estimated material costs and mass percent of battery components.

Battery components	Material	Mass (%)	Estimated costs (%)
Container/housing/packaging foil	Steel or Al	20–25	2
Positive electrode/cathode	LCO, NMC, NCA, LFP, LMO, etc	25–35	49
Negative electrode/anode	Graphite	10–19	16
Electrolyte	$LiPF_6$ dissolved in PC, EC, DMC, or DEC	9–15	6
Cathode current collector foil	Al	5–7	2
Anode current collector foil	Cu	4–9	5
Separator	PE, PP	1–12	16
Binder	PVDF	—	3
Others (additives)	Conducive carbon black, silicon, etc.	Balance	1

process. Metal-extraction processes play the most important role in the entire recovery process and involve one or both of the pyrometallurgical and hydrometallurgical methods.

The main purpose of recycling S-LIBs is to reduce or eliminate potential environmental problems and to recover valuable metals and cheap plastics, therefore promoting the sustainability of the Li battery industry. Even though several R&D studies have been performed globally on S-LIB recycling, the recycling technology remains at the lab scale because of the heterogeneous and complicated structure of the S-LIBs.

Currently, the main industrial S-LIB recycle technologies include hydrometallurgical process, hydrometallurgical process, or the combination of both, and microbial biometallurgy is still in the developing stage at the lab scale (Li et al., 2011). The most frequently used industrial recycling technology for S-LIBs is pyrometallurgical processes. Using the above processes, Ni, Co, and Cu can be extracted effectively, while Li and Al are lost in the slag phase. However, pretreatment of S-LIBs is not used for pyrometallurgical processes, and high energy consumption, equipment cost, and environmental pollution hinder their widespread application. Thus, several industrial hydrometallurgical processes have been globally developed and are being used by various companies, such as Accurec, Toxco/Retriev, Umicore, etc. In these companies, S-LIBs are recycled using the following steps: pretreatment, leaching, and purification by SX, and/or precipitation. Equipment corrosion problems due to the highly acidic or alkaline solutions existed in the hydrometallurgical process, but it is undoubtedly the most suitable method for industrial application at present.

The following steps are the original route of the hydrometallurgical process (Li et al., 2009; Mishra et al., 2008):

- Discharging pretreatment to remove the excess energy
- Dismantling of S-LIBs for removing the plastic and metallic covers/shells
- Size reduction by shredding and grinding
- Leaching with strong acid/alkaline solutions first to remove Al then leaching with strong acids
- Separation of Li, Ni, and Co metals from pregnant leach solution (PLS)

The pros of hydrometallurgical processes are reduced energy consumption and the ability to recycle Li and Al. However the cons of hydrometallurgy processes are their complex and long process flowsheet. This manuscript aims to review the major S-LIB recycling methods and processes, highlight their main problems and provide perspectives for the future development of S-LIB recycling technology.

The general schematic of the methods and processes for recycling S-LIBs includes three stages (Fig. 8). In the pretreatment stage, discharging, dismantling, comminution, classification, and plastic, C, Al, Fe, and Cu separation from cathode and anode materials are carried out. In the metal extraction stage, pyrometallurgical, hydrometallurgical, electrometallurgical, and biometallurgical methods can be performed. Energy input, reagents, reductants, water, and bacteria/microorganisms are used in the process. Concentrate, slag, wastewater, and waste gas are outputs of the process. The last product preparation stage includes the separation and recovery of different materials and synthesis of CAMs for reuse in new LIB production.

Manual dismantling of the individual cells is generally carried out, but not many issues related to this were stated yet. (Kim et al., 2021). An automatic mechanical dismantling methodology for EoL pouch LIBs with Z-folded electrode-separator compounds (ESC) was developed by Li et al. (2019).

Changes in the types of size reduction equipment and the operating conditions, like multiple comminution steps have been made, and it was verified that these changes have a major effect on the yield of black mass and the flotation recovery efficiency. For electrode material concentrations, various screen sizes from μm to mm and the wet or dry screening conditions have been tested for the classification of the LIB comminution products.

13. Environmental problems created by LIBs

Table 7 presents environmentally-related properties (such as vapor pressure, toxicity and hazards to water, and flammability) of materials used in industrial LIB production. Table 8 summarizes the name, chemical formula, flammability limits, and flash points of LIBs. As seen from both tables, the ingredients can pose various types of hazards to the ecosystem, particularly:

- Fire and explosion hazards because of high calorific, highly volatile and self-igniting carbonate electrolytes
- Toxic effects for humans, because of gaseous, sometimes deadly decomposition products (such as HF, benzene, etc.) from LIB components
- The carcinogenic effect through the release of inhalable fine particle (−10 μm) dusts of Ni/Co/Mn compounds

Those potential health hazards should be recognized in handling waste LIBs during recycling. In addition, under certain circumstances thermal runaway (for example overcharged, external/internal short-circuit, overheat, etc.) behaviour can be triggered, releasing rapidly massive heat and toxic off-gases, causing technical hazards and health risks.

Depending on the battery type, charge state, ambient atmosphere (air or inert Ar or N_2 gas use), thermal treatment, and mechanical treatment, toxic HF and/or POF_3 gas emissions from LIBs are generated during the recycling process. As a result, an extensive off-gas cleaning system is required in both thermal and mechanical treatment. The hazardous fluoride gas emissions mainly come from the decomposition of $LiPF_6$ electrolyte, which is promoted by the presence of water/humidity based on the following reactions:

Table 5
Comparison of the LIB cathode types, chemistry, and properties.

Cathode type	LCO	LFP	LMO	NCA	NMC
Chemical formula	$LiCoO_2$	$LiFePO_4$	$LiMn_2O_4$	$Li(Ni, Co, Al)O_2$	$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC111) $LiNi_{0.50}Mn_{0.30}Co_{0.20}O_2$ (NMC532) $LiNi_{0.60}Mn_{0.20}Co_{0.20}O_2$ (NMC562) $LiNi_{0.80}Mn_{0.10}Co_{0.10}O_2$ (NMC811)
Structure	Layered	Olivine	Spinel	Layered	Layered
Introduction year	1991	1996	1996	1999	2008
Safety	2	5	4	3	3
Energy density	4	3	3	5	5
Power density	3	4	4	4	3
Lifespan	3	4	4	4	4
Cycle lifespan	3	4	3	4	3
Performance	4	4	3	4	4
Cost	1	4	4	3	3
Market share	obsolete	e-bikes, buses, and large vehicles	small	steady	NMC111>NMC532>NMC622>NMC811 growing to without Co presence
LIB cathode chemistry	5 (excellent)	4	3	2	1 (poor)

Table 6
Pros and cons of LIBs.

Pros	Cons
• Smaller and lighter than others • Li has the greatest electrochemical potential • High energy density • Low self-discharge rate (5%–10%) • Low maintenance • Fast charging • No priming • Availability of different prices • Reduced use • Shape and size variations • No memory effect	• Cost • Protection required • Ageing • Transportation • Immature technology • Safety concerns • The internal resistance of LIBs is high as compared to other batteries • Due to overcharging and high-temperature capacity will diminish

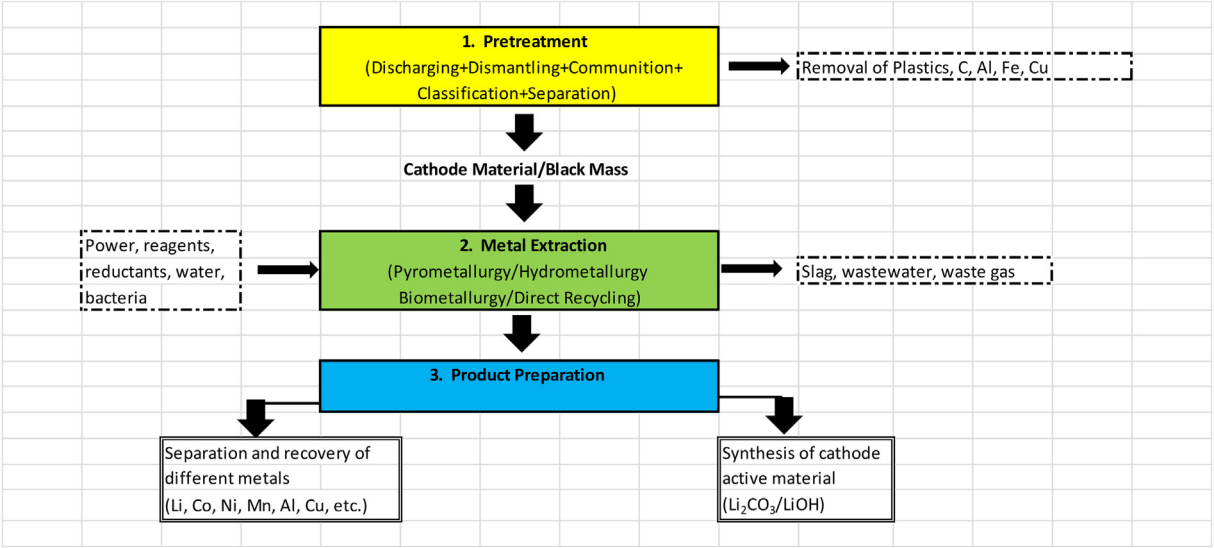


Fig. 8. Main stages in S-LIB active material recycling process.

$$LiPF_6 \rightarrow LiF + PF_5 \quad (1)$$

$$PF_5 + H_2O \rightarrow POF_3 + 2HF \quad (2)$$

$$LiPF_6 + H_2O \rightarrow LiF + POF_3 + 2HF \quad (3)$$

14. Pretreatment methods for S-LIBs

The pretreatment process has been used from the starting stage of LIB recycling research, and several research articles that focused on the S-LIB pretreatment methods have emerged in the last

Table 7
Environmental problems related to the materials used in commercial LIB.

Materials	Properties
Ethylene Carbonate (EC, C_3H_4O) 	• Vapor pressure: 21 Pa (20 °C). • Toxicity and hazard to water: - Causes serious eye irritation - Slightly hazardous to water (German water hazard class: WGK 1)
Propylene Carbonate (PC, $C_4H_6O_3$) 	• Vapor pressure: 4 Pa (20 °C), 130 Pa (50 °C). • Toxicity and hazard to water: - Causes serious eye irritation - Slightly hazardous to water (German water hazard class: WGK 1)
Dimethyl Carbonate (DMC, $C_3H_6O_3$) 	• Highly flammable, highly volatile • Vapor pressure: 5300 Pa (20 °C). • Toxicity and hazard to water: - Irritant effects, nausea, intoxication, unconsciousness, respiratory stop - Slightly hazardous to water (German water hazard class: WGK 1)
Diethyl Carbonate (DEC, $C_5H_{10}O_3$) 	• Highly flammable, highly volatile • Vapor pressure: 1100 Pa (20 °C). • Toxicity and hazard to water: - Low toxicity - Slightly hazardous to water (German water hazard class: WGK 1)
Ethyl Methyl Carbonate (EMC, $C_4H_8O_3$) 	• Highly flammable, highly volatile • Vapor pressure: 3600 Pa (25 °C). • Toxicity and hazard to water: - rritant - Slightly hazardous to water (German water hazard class: WGK 1)
Lithium Hexafluorophosphate ($LiPF_6$) 	• Toxicity and hazard to water: - Causes severe skin burns and eye damage - Highly hazardous to water (German water hazard class: WGK 3)
Lithium Cobalt Dioxide ($LiCoO_2$) 	• At high temperatures, exothermic decomposition reaction with the release of oxygen • Toxicity and hazard to water: - Irritant, hazardous to health - Cobalt salts can lead to cardiomyopathy (heart muscle disease) - Possibly carcinogenic
Lithium—Nickel—Manganese—Cobalt Oxide $Li(Ni_xCo_yMn_zO_2)$ 	• Toxicity and hazard to water: - Toxic, Co, Ni in the compound - Hazard to water: no information
Lithium—Titanate ($Li_4Ti_5O_{12}$) 	• Toxicity and hazard to water: - Slightly irritating to the respiratory tract - Nanocrystals can be toxic due to their small size

decade. Thus, it will be convenient to cover various novel methods in the pretreatment process and summarize the related literature in the present stage. The aim and the order of the pretreatment processes can be categorized into discharge, dismantling, size reduction, classification, separation, dissolution, and thermal treatment stages (Kim et al., 2021). The technological development and the current status of each category are highlighted extensively here.

14.1. Discharging

Determination of the residual power of an S-LIB is not easy. Even after the depleting charge of the LIB, the battery might still have some remaining power. To prevent short-circuiting, burning, explosion or spontaneous combustion, firstly S-LIBs should be discharged. In addition, because LIBs contain various types of materials in their electrodes, it is not efficient to treat the batteries directly. Thus, a pretreatment process is essential before hydrometallurgical treatment. S-LIBs can be pretreated and separated safely only when they are almost fully discharged. Otherwise, the battery can burst, burn or emit hazardous gases because of short-circuiting between anode and cathode. Electronic techniques and conductive liquids/metals can be used for discharging batteries. LIBs can be discharged to a safe voltage (0.3—1.0 V) by connecting with a load (halogen bulb or resistor) (Widijatmoko et al., 2020;

Table 8
Lower/upper flammability limit (LFL/UFL) and flashpoint of LIB electrolytes.

Electrolyte	Name	Formula	LFL, %vol (in the air)	UFL, %vol (in the air)	Flashpoint, °C
EC	Ethylene carbonate	$C_3H_4O_3$	3.6	16.1	143
DMC	Dimethyl carbonate	$C_3H_6O_3$	4.22	12.87	18
EMC	Ethyl methyl carbonate	$C_4H_8O_3$	2	NA	23
DEC	Diethyl carbonate	$C_5H_{10}O_3$	1.4	NA	33
PC	Propylene carbonate	$C_4H_6O_3$	1.7	21	123
EA	Ethyl acetate	$C_4H_8O_2$	2.2	9	−4
DE	Diethyl acetate	$C_4H_{10}O$	2	36	−45
THF	Tetrahydrofuran	C_4H_8O	1.5	12	−17
AN	Acetonitrile	C_2H_3N	3	16	2
DMSO	Dimethyl sulfoxide	C_2H_6OS	2.6	42	89
DME	Ethylene glycol dimethylether	$C_4H_{10}O_2$	1.6	10.4	5
g-GBL	g-Butyrolactone	$C_4H_6O_2$	3.6	16	98

Zhan et al., 2018). S-LIBs are unfolded to separate anode, cathode, separator, and other components under the fume hood to prevent toxic organic solvents (EC or EMC). Immersion of the S-LIBs in a conducive salt (NaCl) solution is the most common and popular discharging method used on the lab scale.

There is still ongoing research on the discharge and corrosion rates of other conductive liquids and/or solids. Unlike other batteries, LIBs often explode during the recycling process because of radical oxidation, which is caused by the mechanical shock of Li metal produced from battery overcharge from exposure to the air. Considering the current crushing and grinding processes, this poses a great danger. Therefore, before the crushing and grinding processes, S-LIBs should be soaked in unsaturated (10%) salt water (like NaCl, KCl, $NaNO_3$, $MgSO_4$, $MnSO_4$, and $FeSO_4$) and the energy inside them should be discharged (Pražanová et al., 2022). Xiao et al. (2020) found that overall discharge efficiency decreased in the order of $MnSO_4$ < $FeSO_4$ < NaCl. This process is the most popular stabilization method and decreases the short-circuiting generation and exothermic reaction occurrence in the anode. For instance, the response of Li to oxygen (air) and water (humidity) causes the inflammation of the highly combustible organic electrolyte solvents. Therefore, preliminary discharging treatment of S-LIBs before hydrometallurgical recycling is necessary (Contestabile et al., 1999). The physical discharge in solid media using Cu and graphite powder may be an adequate large-scale discharge method. But because of the contact problem, the easily oxidized metal surface, and the graphite dust bursting risk cannot make this method be used extensively. Thus, Kim et al. (2021) suggested $FeSO_4$ be the most ecofriendly discharge solution.

The industrial Batrec company generally uses a mechanical treatment to recycle S-LIBs. First of all, the batteries are size reduced in an inert CO_2 gas atmosphere. Thereby, the volatile organic electrolyte evaporates by heat and is collected as condensate without any usage. Then, S-LIBs are dismantled by hand or mechanically separated. Manual dismantling is generally carried out to separate the cathode material, anode material, and other components. Manual dismantling is not suitable for industrial-scale. Graphite particles are weakly attached to the anodic Cu current collector electrode and $LiCoO_2$ particles are strongly attached to the cathodic Al current collector electrode by a binder (Dai et al., 2019). Therefore, graphite generally contaminates $LiCoO_2$ in mixed materials. It is difficult to remove/liberate binder from CAMs mechanically. The CAM is generally bonded to Al-foil via the PVDF or PTFE binder, which makes it difficult to separate the CAM from the foil. To effectively separate the CAM from the Al-foil, solvent dissolution, NaOH dissolution, ultrasonic-assisted separation, thermal treatment, and mechanical methods have been previously tested (Zheng et al., 2018).

14.2. Dismantling

Individual battery cells are often disassembled by hand for laboratory experimental purposes, but manual disassembly is expensive for industrial processing. Automatic/robotic disassembly can be developed for industrial-scale operations, although the large variety of battery cell designs makes that challenging. Thus, most processing flowsheets proposed for small LIBs involve shredding, and then different components are separated before materials can be recovered. The Al-and Cu-foils holding the electrode active materials are usually separated by sieving at 212 μm. However, a portion of the active material may still stick to the foils. Therefore, screening from 38 μm achieves better Li and Co liberation and extraction than Al and Cu foils. The evaporation step of organics removes the binder and reduces the quantity of active material stuck to the foils.

Li et al. (2019) proposed the automatic disassembly technology for the recycling of pouch-type LIBs, which were named Z-folded electrode-separator compounds. The proposed electrode sorting strategy extracted the cathode and the anode sheets without applying any destructive forces. By automatically stretching and feeding the Z folded separators, the cathode and the anode sheets attached on the opposite sides of the separators were scraped off using specialized toolsets.

14.3. Pretreatment methods

Pretreatment methods to separate the CAM and/or anode active material from the disposed of S-LIBs after discharging can be broadly categorized as alkaline dissolution, ultrasonic-assisted operation, SX, mechanical separation, and calcination treatment separation. The pros and cons of various pretreatment methods are compared in Table 9.

14.3.1. Mechanical pretreatment

The disassembled LIBs require size reduction by crushing and grinding to liberate the electrode active materials, and this size reduction stage is especially important for the hydrometallurgical process. Selective liberation depends on the comminution technique being used. Liberation can be provided by impact, shear, abrasion, etc. Attrition scrubbing induces impact and shearing action between particles which promotes surface abrasion and produces fine particles. Inert silica sand was used as an abrasion media by Widijatmoko et al. (2020). Mechanical pretreatment methods are effective processes that involve physical size reduction (crushing by shredders, blade crushers, etc., and grinding by hammer mills) and classification (by sieving and separation) of the discharged S-LIBs. Different parts of the S-LIB have different

mechanical properties, thus a shredder/mill which can uniformly crush/grind all the parts is required. Generally, a closed-circuit gastight grinding is used.

Batenus hydrometallurgical process, which is one of the first large-scale battery recycling facilities, shredded mixed types of batteries in a gastight unit (Fröhlich & Sewing, 1995). The Recupyl process has two-step crushing in an inert gas atmosphere (Pinegar and Smith, 2019). In the first step of crushing, a low-speed two-blade rotor crusher without a sieve, and in the second step of crushing, a high-speed hammer mill with a 5 mm sieve was used for the simultaneous recycling of the LIB, NiMH, and the primary Li batteries (Granata et al., 2012). The second step fine crushing increases the black mass yield from 60% to 75% in the absence of the impurities from the Al and the Cu current collectors (Kim et al., 2021).

After crushing and grinding, the cathode/anode active material and Al/Cu-foils are separated by using the differences in size (by dry/wet sieving), density (by gravity separation like heavy media separation), and magnetic susceptibilities (by magnetic separation). Zhang et al. (2018) generated small battery pieces by shredding from NaCl solution immersed S-LIBs. They used impact crushers fitted with blade crushers and ground the battery for 20 s at 3000 rpm. The crushed pieces were classified into four size groups by dry sieving. The coarse pieces of plastic, Cu, and Al were separated from the CAM and anode active materials at 75 μm. After removing the floating hydrophobic hydrocarbon (HC) material on the water surface, $LiCoO_2$ and graphite were separated by reverse froth flotation. Due to simplicity and scalability, mechanical pretreatment is the most widely used method of S-LIB separation. However, setting up a stable classification setup is essential, and this method can cause noise, dust, and harmful gas production. Additionally, it is not easy to ensure the perfect separation of all materials using this method.

The comminuted LIB products contain three parts: An Al-enriched coarse (>2 mm) fraction, a Cu–Al-enriched medium (0.25–2 mm) fraction, and a Co, Li, and a graphite-enriched fine (<0.25 mm) fraction. It seems that the −212 μm screen is sufficient for Al and Cu foil removal from fine electrode mixture materials. Al and Cu can not be separated from each other by size (Widijatmoko et al., 2020). The mineral phase analysis and the chemical composition analysis revealed that the CAMs obtained from the <0.25 mm fine fraction remained in their original crystalline structure and chemical composition in LIBs. However, the surface of these fine powders was coated with a layer of binder HCs, leading to difficulty in separation by froth flotation. The valuable black mass is in fine fractions, whereas large fractions generally contain less valuable components, such as Al/Cu current collector foils, metallic/plastic cell cases/shells, and plastic separators. Shin et al. (2005) proposed a combined process to recover metals from S-LIBs that used mechanical separation for the collection of CAMs, followed by a hydrometallurgical treatment for metal extraction. Enriched particles of $LiCoO_2$ were obtained through a series of mechanical treatments like crushing, sieving, and magnetic separation; next, $LiCoO_2$ and small pieces of Al-foil were separated by finely ground the $LiCoO_2$-enriched particles. The efficiency of the desired metal recovery can be enhanced by mechanical separation processed before the hydrometallurgical process. The main disadvantage of mechanical methods is that the components of S-LIBs cannot be fully liberated and then separated from each other; in addition, the decomposition of electrolyte components, such as $LiPF_6$, DEC, and PC, during mechanical processes causes a serious threat to the ecosystem. Despite different pretreatment methods that have been suggested by many researchers, challenges still exist regarding the pretreatment of S-LIBs.

There are two types of LIBs crushing and grinding: dry and wet. Dry crushing is carried out in a gastight unit in an inert gas (N_2, Ar, etc.) atmosphere (Kim et al., 2021). Generally, dry crushing can be carried out in two stages (i.e. firstly shear crushing for chopping and secondly impact crushing) after at least 24 h soaking in brine water and chopping into small pieces. Over-crushing is less in the dry crushing than in the wet crushing route (Kim et al., 2021). One-stage cutting mill crushing provides poor liberation. Second-stage milling can achieve the selective liberation of LCO. Wet crushing can be performed with a blade crusher with water addition. Li et al. (2019) found that crushing to 12 mm achieved maximum Co content and minimum total impurity (Al, Cu, and Fe) contamination in the black mass**.** The wet shredding can be conducted at room temperature, so the water can act as both a scrubbing agent and a temperature controller. The shredder output slurry contains both hydrophobic plastics floated on the water surface and can be removed by scrapping manually and the electrode active materials, which can be separated via the sieving operation. The dry crushing selectively crushes LCO and graphite electrode materials to liberate them from the Cu and Al-foils without over-crushing (Kim et al., 2021). CAMs and anode active materials laminate that has been detached from its current collector and is still held together by the binder. This type of particle comes as aggregate for particle sizes 38–850 μm. Guan et al. (2017) suggested that the mechanochemical reduction process via planetary ball mill enhanced the Li and Co leaching efficiency.

Widijatmoko et al. (2020) firstly used a shredder for anode and cathode layers to cut into 5 mm × 12 mm. Retsch SM2000 cutting mill with 8 mm screen size was used for the first stage liberation. 2.5 min attrition scrubbing with 2360–850 μm low Fe silica sand at 1000 rpm was performed as a secondary liberation. The pulp density was around 70% and S-LIBs/silica media ratio was 10%. 2.5 min attrition scrubbing was sufficient for fine CAMs production with wet sieving from 212 to 38 μm screens.

The grinding-assisted flotation process for the separation and recovery of LCO and graphite from the S-LIBs is proposed by Yu et al. (2018). The anode and cathode strips were firstly crushed to 74 μm by an impact crusher. The resulting mixed electrode powder was ground in a ball mill for 5 min. The lamellar graphite structure slides, flakes, and exposes a large number of new fresh hydrophobic

Table 9
Advantages and disadvantages of different pretreatment methods.

Pretreatment method	Advantages	Disadvantages
Alkaline NaOH dissolution	Simple treatment, high separation rate.	Al recovery is difficult; alkali wastewater discharge.
Ultrasonic-assisted operation	The operation is simple, no gas emission.	High noise pollution, high capital investment.
Solvent extraction (SX)	High separation efficiency	Solvents are expensive, environmental hazards are high.
Thermal treatment (Calcination process)	Simple treatment, high capacity.	Energy consumption is high, high device investment, toxic gas emissions.
Mechanical methods	Simple, suitable operation.	Toxic gas emissions, cannot separate mixed and all kinds of electronic components in LIBs

surfaces under the horizontal shear force generated by the grinding media. The organic binder film-coated LCO particles are partially worn down to restore the original hydrophilic surfaces. With the action of the vertical rolling pressure, the adhesion of LCO and graphite could occur and finally become an important separation problem. Even though the adhesion behaviour in the 5-min grinding process may lead some LCO concentrate to follow hydrophobic graphite into the froth phase to reduce the flotation recovery efficiency. High wettability difference between LCO and graphite results in a good flotation concentrate grade. Clean LCO is obtained from flotation tailing.

14.3.2. Flotation

Reverse froth flotation separates fine hydrophobic anodic graphite from hydrophilic cathodic $LiCoO_2$ (Zhan et al., 2018). Kerosene (1–2 kg/t) is used as a collector and MIBC as a frother in flotation. 3 min conditioning for the collector and 2 min conditioning for frother are enough. For a better flotation result, −212 μm particle size and 1%–2% w/w solid slurry are used. Before flotation, fine materials can be rinsed with distilled water to remove excess electrolytes on the surfaces. 4 min flotation time was sufficient for more than 95% graphite recovery in the froth phase. Valuable tailing should contain CAMs with minimum graphite contamination. Kerosene dosage increases CAM contents at the expense of its recovery. Without kerosene, CAM recovery is high but CAM content is low. There are only a few studies on LIBs material flotation. Before flotation, binders should be removed by burning off for one hour at 500 °C. Then flotation is employed. Flotation behaviour of anode, cathode and mixed new and S-LIBs material are different. There are many benefits of using flotation in LIBs recycling. Firstly, physicochemical separation process of flotation effectively preserves the functional integrity of electrode materials during the recycling process. As a result, CAMs can be regenerated through a lithiation process and reused in new batteries (Chen et al., 2016). Secondly, flotation separates fine materials according to chemistry. This significantly increases the energy efficiency of downstream processes while minimizing greatly secondary waste. Flotation produces metal reach products that can be used as a high-value feedstock for the hydrometallurgical or pyrometallurgical processes. Finally, flotation beneficiation of S-LIB materials is easily and economically applicable for full plant-scale production.

Fenton reagent (including H_2O_2 + $FeSO_4$) was used to modify the surface of the crushed electrode materials for the recovery of LCO and graphite in reverse froth flotation (He et al., 2017). Fenton reagent removes the organic hydrophobic binder layer and assists flotation. First of all, the electrode materials from the S-LIBs were immersed in the Fenton reagent to remove the organic binder outer layer from particles. Optimum conditions of 1:120 Fe^{2+}/H_2O_2 ratio and a 1:75 S/L ratio eliminated most of the organic binder layers coated on the surface of the electrode materials. After being modified by the Fenton reagent, the original wettability of hydrophilic LCO and hydrophobic graphite was regained thus the reverse froth flotation could be used for the selective separation of LCO and graphite. After Fenton treatment, electrode particles are wrapped with an inorganic hydrophobic $Fe(OH)_3$ layer which leads to poor flotation (sink). Yu et al. (2017) determined the effect of the secondary product of semi-solid phase Fenton on the floatability of LCO electrode material from S-LIBs. They used 500 mL 0.8 M H_2O_2, 33.3 mL 0.1 M $FeSO_4$, and 7 g LCO sample in 20 min Fenton treatment. After filtration and drying, flotation with 300 g/t kerosene as a modifier and 150 g/L 2-octanol as frother addition after 6 min conditioning time was performed. Pyrolysis at 500 °C and ultrasonic treatment can clean the surface of particles to increase floatability. Ultrasonic-assisted flotation improved LCO grade from 67.3% to 93.9% and recovery from 74.6% to 96.9%. Optimum roasting treatment was achieved at 450 °C for 15 min by Wang et al. (2018). At these conditions, LCO outer layer was eliminated and graphite was protected from combustion which resulted in a 97.7% Co recovery rate. Zhang et al. (2020) used optimum pyrolysis condition at 550 °C using 10 °C/min and pyrolysis time for 15 min. The cathode grade was slightly improved from 94.7% to 94.9%, but its recovery was enhanced from about 84% to 91%, which supports that the wet-ball grinding can remove the residual pyrolytic carbon on the surface of the CAM efficiently. Two-stage pyrolysis treatment enhanced the flotation process and upgraded LCO grade to 98%.

Grinding-assisted flotation (Liu et al., 2020; Yu et al., 2018; Zhan et al., 2018; Zhang et al., 2020) destroy the lamellar structure of hydrophobic graphite, generating fresh surfaces, and abrasion of the organic film coating the hydrophilic LCO particles cause their original surface. Creating a great wettability difference between LCO and graphite leads to very good flotation selectivity. It was reported that fine grinding could produce a purer product than the coarse grinding at the same recovery.

Liu et al. (2020) used froth flotation with single-stage cryogenic ball milling. Liquid N_2 gas was used for cooling recovery and the grade of the LCO concentrates was enhanced after 9 min of cryogenic grinding that removes the hydrophobic organic binding material from the surface of the LCO and graphite. Flotation improvement of LCO and graphite by using cryogenic grinding is achieved by graphite adherence to the air bubbles for flotation and hydrophilic LCO remains in the slurry phase. In the flotation process, kerosene, MIBC, NaOH, and amylum were the best collectors, frother, pH regulators, and depressants (Shin et al., 2020; Zhao and Zhang, 2020). Wang et al. (2019a) also investigated cryogenic ball milling for recovering CAM from LCO-based S-LIBs. Liquid N_2 pretreatment at −196 °C for 5 min and grinding 30 s enhanced peel off fine cathode material from Al-Foil up to 87.3%. PVDF glass transition temperature is about 38 °C. Liu et al. (2020) combined cryogenic ball milling using liquid N_2 with froth flotation for LCO and graphite separation.

14.3.3. NaOH dissolution method for Al removal

He et al. (2019) used an aqueous exfoliating and extracting solution that included NaOH salts without strong acid and alkali for the recycling of the LIBs that contained LFP and NMC. The cathode materials could be peeled off from the Al-foil by dissolving the Al-foil. The resulting recovery efficiencies of the Al-foil and the electrode materials were almost full. In many proposed recycling processes, the cathode materials are separated from the Al-foil by leaching the cathode with an alkaline NaOH solution, which works to separate the materials because of the amphoteric property of Al, which can react with both an acid and a base. In their process to recover the CAM, Nan et al. (2005) used a 10 wt% NaOH solution to separate the LCO-based CAM from Al-foil. Using a NaOH solution with a 100 g/L S/L ratio, 5 h reaction time, at room temperature, about 98% of the Al-foil was dissolved. When a NaOH solution is used to dissolve the Al-foil of the cathode, two substances are dissolved: the protective layer covering the surface of the collector and the Al. Following reactions occur between Al and Al_2O_3 and NaOH in the presence of water:

$$2Al + 2NaOH + 6H_2O \rightarrow 2Na[Al(OH)_4] + 3H_2 \quad (4)$$

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4] \quad (5)$$

This NaOH dissolution method has the advantages of both simplicity and high separation efficiency. However, the recovery of Al is difficult because of the ionic form of Al. In addition, NaOH wastewater is very environmentally harmful to disposal. Molten salt $AlCl_3$–NaCl mixture can also be used for Al dissolution.

14.3.4. Solvent dissolution pretreatment for binder elimination

Unfortunately, some liberated electrode active materials are still attached to the current collectors while other detached active materials are agglomerated by the organic binders after the classification and the separation operations. Thus, the dissolution of the binders or the Al-foils is generally performed with suitable solvents. Solvent pretreatment utilizes solutions and solvents to separate the LCO and graphite from the Al- and Cu-foils/films in the S-LIB. This method eliminates the additive binder material that strengthens the foil contact with the active materials, thereby separating the active materials. By stripping off or dissolving the binder, the active material can be separated from the metal foil. A commonly used method is to immerse the electrode plate into an organic solvent N-methyl-2-pyrrolidine (NMP) at 100 °C to remove the PVDF binder by dissolving and separating the Al- and Cu-foils. He et al. (2019) discharged the LIB by immersing it in an unsaturated NaCl solution and separated the battery manually using pliers. After separating the plastic, metal case, electrode plate, and separator, the cathode was cut into small pieces. The cathode pieces were inserted in NMP solution at 80 °C for 2 h, thereby dissolving the organic binder and separating the Al-foil and CAM. Most batteries use a PVDF binder to attach the active materials, however, some use PTFE binders, which require different organic solvents to use around 100 °C, which increases the operating cost and creates toxic waste products. Table 10 presents previously used solvents for binder dissolutions.

Liu et al. (2006) used N, N-.dimethylacetamide (DMAC), which also dissolves PVDF that is about 10%, for the separation of the LCO CAM from the Al-foil because of its economic edge over NMP. When the S/L ratios were controlled between 1:4 and 1:5, the CAM was separated from the Al-foil, which was followed by the filtration of LCO and graphite conductive agents from the solvent. Because the boiling point of DMAC is 165 °C, DMAC can be evaporated by heating it at 120 °C for 12 h. Zhou et al. (2010), Song et al. (2013; 2014), and Xu et al. (2014) used N, N-dimethylformamide (DMF) to separate the LCO and NMC CAMs from the Al-foil. The cathode scrap materials were immersed in DMF or a mixture of DMF and ethanol at 70 °C.

Wang et al. (2019b) achieved the separation of the CAMs and the Al-foil using a low-temperature $AlCl_3$—NaCl molten salt system, which had a better peeling-off performance than the commonly used NaOH or nitrate systems. The optimum performance was achieved with an S/L ratio of 1:10 g/mL at 160 °C for 20 min. The heat storage of the phase transformation of the $AlCl_3$—NaCl molten salt caused the melting of the PVDF organic binder for the separation of cathode active material and Al-foil. Specifically, when the heating temperature exceeds the phase transformation temperature of 153 °C, the $AlCl_3$—NaCl molten salt mixture is converted from a solid to a liquid compound by absorbing a large amount of heat. If the temperature continues to rise to 160 °C, PVDF melts, which results in the efficient separation of the CAMs from the Al-foil. Zhang et al. (2014) dissolved the PTFE binders in the NMC-based LIBs with trifluoroacetic acid (TFA), which is a strong carboxylic acid with a relatively low boiling point (71.8 °C). The optimum TFA concentration was 15 vol%, S/L ratio 1/8 g/mL, the reaction time 180 min, and temperature 40 °C in the presence of agitation.

14.3.5. Ultrasonic-assisted separation for binder elimination

It is not easy to remove CAM from Al-foil during the S-LIBs recycling due to the strong bonding force of the PVDF binder. Ultrasonic-assisted treatment is considered to be one of the effective methods for stripping CAM from Al-foil because of its strong cavitation effect (He et al., 2015; Li et al., 2015; Zhang et al., 2013). Cavitation breaks the intermolecular bonds. When studying the effects of both agitation and ultrasonic treatment on the separation of CAMs, Li et al. (2015) discovered that most of the CAMs continued to adhere to the surface of the Al-foils when mechanical agitation alone was used. When ultrasonic treatment alone was used, only parts of the CAMs were separated. However, when both methods were used at the same time, almost all of the CAMs could be stripped from the foils. This may be because of the cavitation effect of ultrasonic treatment, which can generate higher pressure to destroy insoluble materials and disperse them in solution. The rinsing effect of mechanical agitation further promotes the separation of CAMs from Al-foils. He et al. (2015) attributed the mechanism by which CAMs were separated from Al-foil by ultrasonic treatment to the dissolution of the binder and the cavitation effect produced by the sonication. Depending on this mechanism, the stripping efficiency of the CAM reached 99% with NMP at 70 °C, 240 W ultrasonic power, and 90 min processing time. CAM that was separated from the Al-foil by ultrasonic treatment exhibited a low degree of agglomeration, which significantly facilitated subsequent leaching processes.

For the separation of the LCO material from Al foils, NMP is the best solvent for PVDF or N, N-dimethylacetamide (DMAC), DMF, NeN- dimethyl sulfoxide (DMSO), ethanol, or molten salt of $AlCl_3$—NaCl can also be used. The peel-off efficiency in any of the solvents did not surpass 10% with an S/L ratio of 1:10 g/mL at 60 °C for 30 min. However, the peel-off efficiency increased by at least six times with the assistance of the ultrasound in the increasing order: ethanol < DMSO < DMF < DMAC < NMP. 100% peeling off was achieved (Liu et al., 2006). Ultrasonic treatment along with solvent dissolution is one of the best solutions for cathode material removed from Al-foil.

14.3.6. Thermal (heat treatment)/Pyrolysis/Calcination pretreatment for binder elimination

The binder materials that bind the active materials and the conductive carbon together and fix them to the current collectors can be also eliminated by heat treatment. The thermal treatment uses high-temperature binder decomposition to decrease the

Table 10
Solvents used for binder dissolutions in S-LIB recycling.

Solvent	Binder	Temp./Time/ S/L	Material removed	Material remained	Reference
NMP	PVDF (Solubility: 200 g/kg solvent; boiling point: 200 °C; price: 5–6 $/kg)	<100 °C/1h /10%	$LiCoO_2$ and graphite	Al and Cu metals by filtration	Contestabile et al. (2001)
DMAC	PVDF (Boiling point: 165 °C; price: 21.5 $/kg)	—	$LiCoO_2$	Al-foil	Liu et al. (2006)
DMF	Suitable for PVDF Not suitable for PVDF (Price: 0.9–2.4 $/kg)	60–70 °C/ –/–	NMC/LCO	Al-foil	Song et al., 2013; Xu et al., 2014; Zhou et al., 2010
TFA	PTFE acetic acid 15 v%, L/S: 8 mL/g with agitation (Boiling point: 71.8 °C)	40 °C/3 h/—	NMC	Al-foil	Zhang et al. (2014)
AlC_3^- NaCl molten salt	PTFE, 1/10 g/mL (price: 10–25 $/kg) PVDF	160 °C/ 20 min/—	Cathode material	Al-foil	Wang et al. (2019b)

bonding force between particles of cathode/anode active material that can then be easily separated by screening. Calcination pretreatment occurs in the temperature range of 150–650 °C to remove conductive carbon, acetylene black, and organic material from the S-LIB. In addition, by calcination at 250 °C–350 °C, the organic PVDF binder can be removed, thereby reducing the adherence of the active materials on the Al- and Cu-foils. Yang et al. (2016) cut the cathode parts into small pieces and placed them in a tube furnace in an inert N_2(gas) atmosphere at 550–650 °C. Then, the CAM and the Al-foil were easily separated using gravity separation. However, calcination pretreatment requires expensive furnaces, is an energy-intensive process and can emit hazardous gases (Bae & Kim, 2021).

The LCO CAMs were separated using a thermal treatment of the S-LIBs in two steps. After drying at 60 °C for 24 h, the first thermal pretreatment was performed at 300–500 °C for 1–2 h to eliminate carbon, PVDF binder, and the organic additives in the CAMs. The second thermal treatment was conducted at 700–900 °C for 1.5–2 h to remove carbon by burning off the residual unburned organics. PVDF and the carbon powder in the anode materials were removed with the high temperature calcining after LCO was initially separated from the Al-foil (Li et al., 2010a, 2013; Liu et al., 2006; Meng et al., 2017; Natarajan et al., 2018; Zhang et al., 2014).

A vacuum pyrolysis method to separate CAM was proposed by Sun and Qiu (2011). The electrolyte and binder were evaporated or decomposed, which reduced the adhesion between the CAM and Al-foil during the process of pyrolysis, If the pyrolysis temperature was lower than 450 °C, the CAMs did not peel away from the Al-foils. When the temperature was between 500 and 600 °C, the separation efficiency improved with an increase in the temperature. However, the Al-foil became fragile at temperatures above 600 °C, making it difficult to separate the CAM from the Al-foil. A reducing thermal treatment process to separate the CAMs from the Al-foil collectors was proposed by Yang et al. (2016). It was shown that controlling the reduction reaction temperature allows the CAMs to be separated from the Al-foils. Besides, this process changes the CAMs molecular structures, which enhances the leaching of metals during the leaching steps. Thermal treatments are straightforward operations and have high throughputs. However, they generate toxic gas emissions during the thermal treatment process.

14.3.7. Classification

After comminution, classification can be performed by sieving or zigzag air classifier. Air separation in a zigzag classifier can be utilized after two-stage of crushing of the discharged cells from the S-LIB. Screening from 212 to 38 μm significantly separates Li & Co from Al & Cu. The finer the screen size the better the separation.

15. Separation

After the classification of the S-LIB comminution products, the physical/mechanical/physicochemical separation based on the particle size, density, magnetic susceptibility, electrical conductivity, and surface chemistry properties (such as gravity, magnetic, eddy current, electrostatic, and froth flotation separation) are employed. Magnetic separation has been often used for the removal of the Fe and steel casing, in the S-LIB recycling process. Shin et al. (2005) used magnetic separation after vibration sieving to separate the CAM from the LCO and the Al-foils, the anode, the steel casings, and the plastic packaging. The eddy current separation allows the electrical conductors (Cu^{-}, Al-foils) to be separated from the non-conductors (plastics) or the minimally conductive materials and an eddy current separation apparatus is used for the recycling of the LFP-based LIBs. Cu and the Al foils are conductive metals and generate a high-intensity eddy current in an alternating magnetic field, they could be separated in the particle size range of 2.0–20 mm. Cu and PE separators and NMC active material and Al-foil can be separated by gravity separation. In the commercial-scale Recupyl process, non-magnetic materials are separated based on density differences (Pinegar and Smith, 2019). For the +2.0 mm fraction, Al-shell and separators can be separated by air separation. For −2.0 + 0.5 mm size fraction, Al–Cu and separator can be separated by electrostatic separation. For −0.5 + 0.075 mm size fraction, grinding and dry sieving from 0.075 mm is performed. +0.075 mm size fraction is sent to the electrostatic separation and −0.075 mm is sent to the froth flotation which is carried out after surface modification to separate $LiCoO_2$ and graphite (Gratz et al., 2014; Kim et al., 2021). Surface modification can be achieved by either Fenton-assisted flotation (Yu et al., 2017) or roasting-modified flotation. Fenton-assisting flotation increased $LiCoO_2$ grade to 60% from 55.6% with direct flotation. Treatment with Fenton reagents removes the organic hydrophobic binder from both graphite and CAMs. Hydrophobic graphite floats and hydrophilic LCO sink during flotation. The roasting-modified flotation exhibited an 89.6% LCO concentrate grade with the highest selectivity between tailings and concentrate (Zhang et al., 2018).

16. Metal-extraction processes for S-LIBs

Metal extraction from S-LIBs is an important part of the whole recycling process. This recovery process focuses on changing the solid metals into their alloy form or solution form, which facilitates the subsequent separation and recovery of metal components. There are four main different extraction processes including pyrometallurgy, hydrometallurgy, biometallurgy, and direct recovery. From these approaches, hydrometallurgy has become a promising novel process because of its attractive recovery rates and the high purity of the final products.

Although most of the previous researchers so far have firstly concentrated on the recovery of expensive CAMs and secondly Al- and Cu-foils, it is also possible to recover anodic graphite and even electrolytes using low-temperature processes. Both graphite and electrolytes, of course, burn in a smelter, supplying some of the process fuel energy. Plastic polymeric separators (thin porous film) also burn in the smelter. There is no suggested process proposal for recovering separators. Polymeric plastics could be recovered, but they are cheap. Recovery of anode material (graphite) using simple physical separation processes has been proved as part of direct recycling; anode material is cheaper and weakly attached to the Cu-foil than CAM but must be separated to obtain useable CAM. Different methods of separating the black mass into anode and cathode fractions have been studied, including heavy media gravity separation using toxic bromoform and froth flotation. Gravity separation between $LiCoO_2$ (4.9 gr/cm^3) and graphite (2.26 gr/cm^3) can also be used for further purification of flotation tailing. Anode material could also be recovered using hydrometallurgical processes. Graphite is not soluble in acids, which would remain as a solid residue while the CAM dissolves. The anode material could then be recovered by filtration, but its quality becomes low. Gaines (2018) investigated the recovery of the Li-salt-containing electrolyte, by extraction of breached cells with supercritical CO_2 and SX. Even though the recovered electrolyte performed well in recycled cells, the process is not found to be cost-effective. Interest may increase when large volumes of material are being processed. Current research has been concentrated on the extraction of high-value metals from CAMs using pyrometallurgy and hydrometallurgy. Before being fed into metal extraction processes, the separation of mixed materials from LIBs using low-cost and energy-efficient methods is critical to lower processing costs, minimize

secondary waste, and increase product values. The main objective of LIB recycling is to recover as many materials as possible, in a useful and reusable condition, and in an environmentally friendly and economic manner. Throughout this paper, shortcomings of existing processes are highlighted for improvement of the current practices.

16.1. Pyrometallurgy

A typical pyrometallurgical S-LIB process for recycling valuable metals is high-temperature smelting reduction in a furnace without any pretreatment to produce mixed alloys. In the pyrometallurgical process, charcoal (reductant) and slag-forming agents (fluxes) are added in the reductive smelting. Umicore in Belgium developed a combination of pyrometallurgical and hydrometallurgical processes to recycle waste battery mixtures. The plastics, organic binders, solvents, and graphite in the LIBs provide additional excess fuel heat during combustion, while the metal components are reduced and converted to their alloys. The obtained alloys can be further purified by H_2SO_4 leaching and SX to obtain cobalt oxides and $Ni(OH)_2$. Although pyrometallurgy does not require any pretreatment, it losses all Li in the slag phase. To reduce the Li loss in the recycling process, a novel process that combines pyrometallurgy and hydrometallurgy to recycle valuable metals from S-LIBs was proposed by researchers.

Pyrometallurgy uses high temperatures to remove organic material by evaporation and causes reactions in the CAM and anode active materials to solubilize Li in the aqueous solution in which Li is recovered. The CAMs were powdered and subjected to calcination above 700 °C, and the lithium metal oxide of the cathode and anode react to form Li_2CO_3 and metal oxides. The possible reactions that occur are given in Eqs. (6)–(10).

$$C(s) + 12LiMO_2 \rightarrow 6Li_2O + 4M_3O_4 + CO_2(g) \quad (6)$$

$$C(s) + 4LiMO_2 \rightarrow 2Li_2O + 4MO + CO_2(g) \quad (7)$$

$$2M_3O_4 + C(s) \rightarrow 6MO + CO_2(g) \quad (8)$$

$$Li_2O + CO_2(g) \rightarrow Li_2CO_3 \quad (9)$$

$$2MO + C(s) \rightarrow 2M + CO_2(g) \quad (10)$$

Water leaching is applied to the calcined powder to dissolve the Li. The metal oxide does not dissolve in the water. After water leaching, the filtration process separates the undissolved metal oxide and the aqueous solution to produce a rich Li_2CO_3 solution, followed by water evaporation to finally obtain Li_2CO_3 powder (Bae & Kim, 2021). Some researchers used additional acids (HNO_3, HCl, and H_2SO_4) during the roasting for higher Li extraction rates. Peng et al. (2019) used HNO_3 to nitrate the S-LIBs and roasted them at 250 °C for 1 h. After roasting, by water leaching, Li solution was produced and with carbonation, Li_2CO_3 was produced with low-temperature roasting. Sulphating roasting with H_2SO_4 and chlorination roasting with HCl can also be used. However, the low solubility (13 g/L) of Li_2CO_3 requires a large amount of solvent consumption. Besides, the pyrometallurgical treatment requires complex calcination equipment and can create toxic gas emissions.

A reduction smelting method to recover valuable metals from S-LIBs was used by Georgi-Maschler et al. (2012). Valuable Fe, Co, Ni, and Mn metals were converted to alloys. However, Li is lost as slag or dust during this process. With further slag leaching with H_2SO_4, purified Li was obtained. In addition, Träger et al. (2015) proposed a vacuum evaporation process and selective carrier gas evaporation at high temperatures to evaporate Li from S-LIBs. However, the temperature was higher than 1400 °C, which is very high. Li et al. (2016) roasted $LiCoO_2$ and graphite at 1000 °C for 30 min under an inert N_2 gas environment. The roasting products were Li_2CO_3, carbon, and Co which were then water leached and separated by magnetic separation. The concentration of the Li solution was only 337.4 mg/L which is low for Li recovery. Depending on previous studies, a novel method to recover S-LIBs by low-temperature roasting under an inert Ar gas atmosphere, followed by the recovery of Li_2CO_3 from the roasting product using water leaching was proposed by Hu et al. (2017). The results showed that the roasting products were Li_2CO_3, Ni, Co, and MnO when the cathode was reduced to 650 °C for 180 min with a 19% C dosage. The roasting products were then dissolved in water and fed with CO_2; this created the conversion of insoluble Li_2CO_3 into $LiHCO_3$. The Li_2CO_3 was then recovered by evaporation crystallization. The concentration of Li in the leaching solution reached 4.36 g/L when the S/L ratio was adjusted to 1/10 (g/L) the CO_2 flow rate was confined to 20 mL/min, and the leaching time was 120 min. Even though recycling valuable metals from S-LIBs by pyrometallurgy is easy, it is not ecofriendly because of its high energy consumption and secondary pollution (Golmohammadzadeh et al., 2017; Wang et al., 2017a). Besides, the loss of Li in the slag during the recycling process is a significant problem that needs to be solved in pyrometallurgical treatment.

16.2. Hydrometallurgy

Recycling Li and Co metals from S-LIBs using hydrometallurgy involves leaching, which dissolves the metallic fraction and recycled metal solutions for subsequent separation. Typical leaching agents are inorganic/organic acids, alkaline solutions, and ammonia-ammonium salt systems. From the mineral acids, HCl (Barik et al., 2017; Takacova et al., 2016; Zhang et al., 1998), H_2SO_4 (Chen et al., 2011; Dorella & Mansur, 2007; Ferreira et al., 2009; Kang et al., 2010; Nan et al., 2006), HNO_3 (Lee & Rhee, 2002), and H_3PO_4 (Chen et al., 2017; Pinna et al., 2017) were generally used as lixiviants to leach valuable metals from S-LIBs. With the help of reducing agents such as hydrogen peroxide (H_2O_2) (Chen et al., 2011; Dorella & Mansur, 2007; Ferreira et al., 2009; Kang et al., 2010; Lee & Rhee, 2002; Li et al., 2009), sodium bisulfite ($NaHSO_4$) (Meshram et al., 2015), or glucose ($C_6H_{12}O_6$) (Pagnanelli et al., 2014), Co or Mn with a high-valent state in the solid phase is reduced to easily soluble Co^{2+} or Mn^{2+}. The main factors affecting the metal leaching process include the leaching time, reaction temperature, leaching agent concentration, S/L ratio, and concentration and type of reducing agents.

Takacova et al. (2016) studied the Co and Li recovery from CAM of spent mobile phone and laptop LIBs using H_2SO_4 and HCl. Co, Li, Ni, and Cu contents in the sample for −0.71 mm size fraction were 22.4%, 3.7%, 1.5%, and 1.3%, respectively. HCl was found as a better leaching reagent than using H_2SO_4. The optimal conditions for Co and Li recovery were: 2.0 M HCl concentration, 60–80 °C temperature, and 90 min leaching time.

The following equations describe the possible reactions of Co and Li in an H_2SO_4 solution, with values of ΔG^0_{80}(kJ):

$$4LiCoO_2 + 6H_2SO_4 \leftrightarrow 2Li_2SO_4 + 4CoSO_4 + 6H_2O + O_2$$
$$\Delta G^0_{80}: -608.96 \quad (11)$$

$$Li_2O + H_2SO_4 \leftrightarrow Li_2SO_4 + H_2O \quad \Delta G^0_{80}: -306.69 \quad (12)$$

$$2Co_3O_4 + 6H_2SO_4 \leftrightarrow 6CoSO_4 + 6H_2O + O_2 \quad \Delta G^0_{80}: -188{:}42 \quad (13)$$

$$Li_2CO_3 + H_2SO_4 \leftrightarrow Li_2SO_4 + H_2O + CO_2 \quad \Delta G^0_{80}: -126{:}61 \quad (14)$$

$$CoO + H_2SO_4 \leftrightarrow CoSO_4 + H_2O \quad \Delta G^0_{80}: -114.12 \quad (15)$$

$$2Co_2O_3 + 4H_2SO_4 \leftrightarrow 4CoSO_4 + 4H_2O + O_2 \quad \Delta G^0_{80}: -94.17 \quad (16)$$

For H_2SO_4, all calculated values of ΔG^0 are negative at all ranges of temperatures (20–80 °C). It follows that the reactions occur in the direction of product formation with a high probability.

The following equations describe the possible reactions of Li and Co in an HCl solution, with values of ΔG^0_{80} (kJ):

$$2LiCoO_2 + 8HCl \leftrightarrow 2LiCl + 2CoCl_2 + 2H_2O + Cl_2 \quad \Delta G^0_{80}: -358.60 \quad (17)$$

$$Li_2O + 2HCl \leftrightarrow 2LiCl + H_2O \quad \Delta G^0_{80}: -195.87 \quad (18)$$

$$CoO + 2HCl \leftrightarrow CoCl_2 + H_2O \quad \Delta G^0_{80}: -42.95 \quad (19)$$

$$Co_2O_3 + 6HCl \leftrightarrow 2CoCl_2 + 3H_2O + Cl_2 \quad \Delta G^0_{80}: -34.02 \quad (20)$$

$$Li2CO3 + 2HCl \leftrightarrow 2LiCl + H2O + CO2 \quad \Delta G080: -28.12 \quad (21)$$

$$Co_3O_4 + 8HCl \leftrightarrow 3CoCl_2 + 4H_2O + Cl_2 \quad \Delta G^0_{80}: +24.05 \quad (22)$$

For HCl, all calculated values of ΔG^0 are negative at all ranges of temperatures (20–80 °C), except for the reaction (22). It follows that the reactions occur in the direction of product formation with a high probability. The reaction (22) with a positive value of ΔG^0 probably occurs in the opposite direction. If only values of ΔG^0 are taken into account, neglecting kinetics, system complexity, and side effects factors, the probability of Li and Co extraction in both leaching agents increases with increasing temperatures from room temperature to 80 °C.

In the leaching process, the major aim is to obtain maximum % Li/Co/Ni dissolution in PLS under optimum conditions (minimum energy and reagent consumption, maximum efficiency, and high percent solid), while keeping the content of other impurities to a minimum. Leaching can be explained as the diffusion of the desired solid content into the liquid with heterogeneous reactions occurring at the interface between solid particles and the liquid medium. Leaching can be done with different reagents. Although strong mineral acids (like H_2SO_4, HCl, and HNO_3) have high efficiency, their wastes are harmful to nature. Weak organic acids (like citric, oxalic, malic, ascorbic, etc.) have lower efficiency, although their wastes are not harmful to nature. During the leaching process, an H_2O_2 reducing agent is usually added to convert all Co or Mn to their divalent states, which are easily leached out by acid solution. Table 11 shows some of the previous LIB leach performances using organic and inorganic acids.

The leaching of NCA cathodes in H_2SO_4, HCl, and HNO_3, was investigated by Joulié et al. (2014). It was found that HCl provides the best leaching efficiency and the nature of the acid has a significant effect on the leaching rate of the metals. The optimum conditions for HCl leaching are 4.0 M concentration, 90 °C temperature, 18 h leaching time, and 5 g/L S/L ratios. Almost 100% of the valuable metals in the CAM could be dissolved under experimental conditions. Leaching Co^{3+} from the NCA cathode without a reducing agent is generally very difficult because of the conversion of Co^{3+} to Co^{2+}. As a result, when H_2SO_4, HNO_3, or HCl is used, HCl should be chosen as the leaching agent in the absence of other reducing agents, HCl provides a higher leaching efficiency due to its Cl ions, which enhance the dissolution. $Co_2O_3.H_2O$ was precipitated at pH: 3 with NaOH and NaClO at a purity of 99.3% and $Ni(OH)_2$ was precipitated at pH: 11 with NaOH at a purity of 96.4%.

According to Eqs. (17) and (20), lithium and cobalt chloride and halogen Cl_2 gas are generated during the leaching process, which may result in significant environmental issues. Therefore, some researchers used HNO_3 or H_2SO_4 instead of HCl to leach LCO. For instance, Lee and Rhee (2002) treated $LiCoO_2$ CAM with 1.0 M $HNO_3 + H_2O_2$ reductant at 75 °C. 75% Li and 40% Co were achieved in the absence of H_2O_2. However, the leaching rates of Co and Li exceeded 99% in the presence of H_2O_2 mainly because insoluble Co^{3+} was reduced into soluble Co^{2+}.

Chen et al. (2011) proposed a hydrometallurgical approach for recycling from S-LIBs to produce cobalt oxalate (CoC_2O_4); this process consists of alkali leaching, acid leaching, SX, and chemical precipitation. $H_2SO_4 + H_2O_2$ were applied as the leaching agent and as the reductant, respectively. The results showed that the leaching rates of Co and Li were 95% and 96% under the following conditions: 85 °C temperature, 100 g/L S/L ratios, 120 min leaching time, 4.0 M H_2SO_4, and 10% (v/v) H_2O_2 concentration. The solution pH was adjusted to remove ionic impurities from the leachate. Co was then extracted with the solvent extractant P507, followed by precipitation with ammonium oxalate ($(NH_4)_2C_2O_4$) to obtain the CoC_2O_4 compound, which resulted in a purity higher than 99% according to the leaching reaction given below:

$$2LiCoO_2 + 6H^+ + H_2O_2 \rightarrow 2Li^+ + 2Co^{2+} + 4H_2O + O_2 \quad (23)$$

It is relatively easy to achieve high metal-leaching efficiencies using mineral acids. However, these strong acids will produce highly acidic wastewater, Cl_2, SO_2, NO_x, and other harmful gas emissions, which will create environmental pollution (Yao et al., 2015). Therefore, ecofriendly weak organic acids have been used as the leaching agents for metal recovery from S-LIBs; these organic acids include ascorbic acid ($C_6H_8O_6$) (Li et al., 2012; Nayaka et al., 2015; 2016a; 2016b), citric acid ($C_6H_8O_7$) (Chen et al., 2016; Golmohammadzadeh et al., 2017; Li et al., 2013; Yao et al., 2015), oxalic acid ($C_2H_2O_4$) (Sun and Qiu, 2012; Zeng et al., 2015), formic acid (CH_2O_2) (Gao et al., 2017; Zeng et al., 2015), acetic acid (CH_3COOH) (Gao et al., 2018; Golmohammadzadeh et al., 2017), succinic acid ($C_4H_6O_4$) (Li et al., 2017), tartaric acid ($C_4H_6O_6$) (Zhang et al., 2015), etc.

Li et al. (2012) developed a combined process consisting of ultrasonic cleaning, roasting, and ascorbic acid leaching to recycle valuable Li and Co metals from S-LIBs. $C_6H_8O_6$ was chosen as the leaching agent as well as the reducing agent to increase the leaching rate of Co. Using 1.25 M $C_6H_8O_6$ and a 25 g/L S/L ratio, the leaching rates of Li and Co reached 98.5% and 94.8%, respectively. When LCO is leached under these conditions, it first dissolves to produce soluble $C_6H_6O_6Li_2$; the insoluble Co^{3+} in LCO is converted to the easily soluble Co^{2+} by the ascorbic acid, and the $C_6H_8O_6$ is oxidized to $C_6H_6O_6$. The leaching reaction can be given as follows:

$$2LiCoO_2 + 4C_6H_8O_6 \rightarrow C_2H_6O_6Li_2 + 2C_2H_6O_6Co + C_6H_6O_6 + 4H_2O \quad (24)$$

An economically efficient method for metals recycling from S-LIBs that combined reduction leaching with selective precipitation was developed by Chen et al. (2016). $C_6H_8O_7$ was used as the leaching agent, and D-glucose was selected as the reducing agent to dissolve the waste CAM. About 99% of the Li, 94% of the Mn, 92% of the Co, and 91% of the Ni were dissolved using 1.5 M $C_6H_8O_7$ concentration, 20 g/L S/L ratios, 0.5 g/g reducing agent, 120 min reaction time, and 80 °C temperature. The selective precipitation

Table 11
Previous S-LIB leaching optimum conditions.

Reagent-acid	Oxidant	T (°C)	T (min)	S/L (g/L)	Recovery (%)	Reference
1.25M citric	1% H_2O_2	90	30	20	Li: 100%; Co: 90%	Li et al. (2010b)
1.5M Citric+0.5 g/g D-glucose	—	80	120	20	Li: 99%; Co: 92%; Ni: 91%; Mn: 94%	Chen et al. (2016)
1.5M DL-malic	2% H_2O_2	90	40	20	Li: 100%; Co: 90%	Li et al., 2010a
1.0M oxalate	—	80	120	50	$LiCoO_2$ 98%	Sun and Qiu (2012)
1.25M Ascorbic	—	70	20	25	—	Li et al. (2012)
4M HCl	—	80	120		Li: 97%; Co: 99%	Li et al. (2009)
4M HCl (NCA)	H_2O_2	90	1080	50	Li: 100%; Co: 100%	Chen et al. (2011)
HNO_3/H_2SO_4	10% H_2O_2	75	120	—	Li: 99%; Co: 99%	Chen et al. (2016)
1M H_2SO_4 (LCO)	—	85	—	—	Li: 96%; Co: 95%	Chen et al. (2011)
4M H_2SO_4					$CoC_2O_4\downarrow$	

method was then used to separate and recycle the valuable metals. It was also decided that the residue leachate after precipitation could be reused as a leaching agent, which revealed about 98% similar leaching performance when compared with the fresh leaching agent.

$$24LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 + 24H_3Cit + C_6H_{12}O_6 \rightarrow 6CO_2 + (8/3)Ni_3(Cit)_2 + (8/3)Co_3Cit_{(2)} + (8/3)Mn_3Cit_{(2)} + 8Li_3Cit + 42H_2O \quad (25)$$

Organic trichloroacetic acid (TCA), which is a biodegradable leaching agent and reducing agent H_2O_2, was used to selectively leach $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (Zhang et al., 2015) Under optimum conditions (3.0 M TCA concentration, 50 g/L S/L ratios, 4 vol% H_2O_2 concentration, 60 °C leach temperature, 30 min leaching period), the leaching rates of Li, Co, Ni, and Mn were 99.7%, 91.8%, 93.0%, and 89.8% respectively, whereas the leaching rate of Al was only 7.0%. In addition, the leaching rate of Al could be further controlled depending on the use of the leachate. Currently, the CAM used for leaching is obtained from waste LIBs by manual dismantling or in the form of cathode scraps from battery production plants, that have higher purity. Industrial raw materials recovered from S-LIBs recycling are usually more complex than the cathode scraps from LIB production processes, and the cathodes that are obtained after pretreatment usually contain heterogeneous metal components. Leaching the CAM using acid may not manifest ideal selectivity; the leachate generally contains many ionic impurities, which increases the difficulty of downstream purification and separation. Thus, ammonia (NH_3)-ammonium sulfate ($(NH_4)_2SO_4$) is used as the leaching lixiviate and Na_2SO_3 is used as the reducing agent to selectively leach valuable Li, Co, and Ni metals from $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (Zheng et al., 2017). Optimum operating conditions were searched, and it was found that in the presence of 4.0 M NH_3, 1.5 M $(NH_4)_2SO_4$, 0.5 M Na_2SO_3, 500 rpm mixing speed, and 10 g/L S/L ratio, the leaching rates of Li, Ni, Co, and Al were 95.3%, 89.8%, 80.7%, and 4.3%, respectively. During the leaching process, the total selectivity of Li, Ni, and Co was more than 98.6%. It was also observed that Mn from $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was co-leached into the PLS during the leaching process and then precipitated from the solution in the form of $(NH_4)_2Mn(SO_3)_2H_2O$.

A combined process of dismantling, size reduction, physical dissolution, thermal treatment, and organic acid leaching was used by Li et al., 2010a; b). Firstly, both the plastic and steel cases that cover the batteries were manually dismantled from the S-LIBs. Once dismantled by hand, the cathode and anode were manually uncurled and separated, followed by soaking in N-methyl-pyrrolidone (NMP) at 100 °C for 60 min period. According to Or et al. (2020), NMP dissolution is not polar; therefore, it can not be used for electrodes that contain a poly (tetrafluoroethylene)-based binder. The CAMs were effectively separated from their Al- and Cu-foils. Secondly, after being dried at 60 °C for 24 h, the separated CAMs were calcined at 700 °C for 300 min to remove the C and residual organic PVDF binder. Li et al. (2010b)'s results showed that nearly 100% Li and more than 90% Co were leached by using a 1.25 M $C_6H_8O_7$ solution containing 1.0 vol% H_2O_2 reductant, leaching at 90 °C temperature for 30 min period and the S/L ratio of 20 g/L.

A thermal treatment or pyrolysis was also suggested for the full recovery of the CAMs. The organic PVDF binders generally decompose at above 500 °C and the volatilization of the electrolyte occurs at lower temperatures and the C conductive agents are burnt off at higher temperatures. Thermal treatment is harmful to the environment. The inorganic acid leaching of S-LIBs has previously been investigated using H_2SO_4, HCl, and HNO_3 by many researchers (Takacova et al., 2016; Wang et al., 2016; Zhang et al., 2014; Zhou et al., 2010). It was reported that the leaching rate of Co is higher when the existence of $Na_2S_2O_3$ is compared with H_2O_2 and the absence of a reducing agent (Guo et al., 2016; Shin et al., 2005).

Industrial Li recovery from batteries is limited. Today, most industrial plants (Xstrata, Umicore, Accurec, Recuply, OnTo, Dowa, Sony, AEF, etc.) recover Li by hybrid (pyro + hydro + electrometallurgy) processes with all types of mixed and various sizes of batteries (NiCd, NiMH, LIBs, etc.). The current LIB recycling ratio is very low and has the following drawbacks: Environmentally unfriendly; Produces extensive liquid and toxic waste by-products; Medium to low-grade end products; Complex processing and purification steps; Low Li and Co recovery with little to no recovery of remaining metals, and large consumption of reagents and energy. Table 12 shows the possible impurities and their consequences on the hydrometallurgical refining process. For the hydrometallurgical flowsheet, ionic species in the PLS must be separated from each other once they are in solution. The most commonly applied methods cover precipitation, SX, electrochemical processing, membrane separation, etc. (Gaines, 2018).

Biometallurgical processes, with simple operation and mild reaction conditions, have the benefits of being cost-effective; less pollution and corrosion; but, their drawbacks are the difficulty in bacteria development, long leaching time due to the slow kinetics, and poor leaching efficiency. Also, very low percent solid is used in bioleaching operations.

16.3. Precipitation

The precipitation method utilizes the difference in the solubility of metal compounds, which is dependent on the specific pH and medium temperature. Precipitation is the most commonly used purification method for separating Li from leached PLSs. Materials with low solubilities, such as transition metal hydroxides, carbonates, or oxalates, are easily precipitated. Thus, NaOH, Na_2CO_3, and Na_3PO_4 types of precipitants are mainly used to precipitate other dissolved metals in the PLS, followed by Li extraction in the form of Li_2CO_3, LiOH, or Li_3PO_4. For instance, Li_2CO_3 has a higher tendency

Table 12
Impurities and their consequences for hydrometallurgical purification refining (adapted from https://accurec.de/publications-downloads?lang=en).

Accompanying material	Problem formation in hydrometallurgy	Troubleshooting
Electrolyte (EMC, DMC)	Formation of organochlorine compounds, toxic gases, increased acid consumption, costs for pre-wash required	Evaporation/decomposition by thermal pretreatment
PVDF (Adhesive; 100% in AM)	Insoluble in acids and remains in the filter cake, increases disposal costs	Decomposition by thermal pretreatment
$LiPF_6$ (conducting electrolyte salt; 100% in AM)	The HF(g) formation, fast corrosion to the equipment; LiF formation, thus, Li depletion in aqueous and metal-containing phase	Decomposition by thermal pretreatment
Mn	Increased operating costs because of necessary precipitation and disposal, as well as cross-contamination in Fe and Al fraction, more difficult recycling opportunity	Slagging Pyrometallurgy
Al and Fe	Increased operating costs because of necessary precipitation and disposal of waste. Al reduces filtering efficiency.	Slagging Pyrometallurgy
Plastic residues (separator, sleeve, cable covers, etc.)	Additional filter expenditure; disposal costs for incineration	Decomposition by thermal pretreatment
Graphite (100% in AM)	Foam formation with an impact on the plant construction and cost of process additives	Reducing agent Pyrometallurgy
$LiFePO_4$ (100% in AM)	Formation of stable Ni and Co PO_4's, hazardous wastewater with PO_4, corrosion because of gas formation, HF favouritism, basic safety concerns, filtration difficulties	Slagging Pyrometallurgy
Silicon (LiB Gen. Si Anode)	Gel formation increased filtration efforts and high waste disposal cost	Slagging Pyrometallurgy

to form low-solubility Li_2CO_3 under high pH conditions because of the formation of carbonate ions. Also, the Li_2CO_3 solubility decreases at higher temperatures (12.9 g/L at 25 °C, 10.8 g/L at 40 °C), which makes precipitation easier. Compared to other Li compounds (LiOH − 129 g/L, LiCl − 815 g/L at 25 °C) Li_2CO_3 has a substantially lower solubility, which makes it easier to precipitate. The precipitation method is the safest, cheapest, and most efficient refining process for hydrometallurgical treatment. Table 13 summarizes the previous results of some studies. Detailed results are given by Bae and Kim (2021).

For fine-tuning of the precipitation methods, operating conditions (such as medium pH, Li concentration, temperature etc.) should be studied more to produce the required property products.

16.4. Solvent extraction (SX)

SX uses a two-liquid phase system to separate Li from the leached CAM. It utilizes relative solubility to separate ions from polar and nonpolar liquids. Nonpolar extractants are mainly used to separate valuable metals (Co, Ni, and Mn), and Li is separated from the stratified aqueous solution. Non-aqueous solutions dissolve Co^{3+}, Ni^{3+}, and Mn^{3+} while aqueous solutions dissolve Li^{+}. Cyanex 272, PC-88a, Cyphos IL-101, and D2EHPA can be utilized to separate Co, Ni, and Mn. Table 14 shows previous SX conditions and results for $LiCoO_2$ CAM.

16.5. Selective adsorption

Selective adsorption separates Li-ions using a Li-ion sieve to absorb the dissolved Li. Spinel-structured Mn-type Li-ion sieves are inorganic bead-type adsorbents that are extremely selective for Li-ions in a Li-containing PLS and originate from the technology used to extract Li from brines. Since Li is the smallest metal ion, Li-ion sieves use a vacancy to allow only Li-ions. Li—Mn oxide spinel has the highest selectivity, capacity, and stability among the inorganic solvents. Because of the low toxicity, it is the most commonly used material. Wang et al. (2017b) leached Li from S-LIBs using an NH_3—H_2O—NH_4HCO_3 solution in the presence of an H_2O_2 reductant. An Mn-type Li-ion sieve can be used to selectively adsorb Li with the leached Li, Co, and Ni solutions. The Li-adsorbed Li-ion sieve can be separated and dissolved with HCl. Then, NaOH and Na_2CO_3 can be added to separate Li_2CO_3. Li-ion sieves are quite costly and requirement of an additional HCl leaching process to separate the Li combined with MnO_2. Currently, there are some patents for bead-shaped Li-ion sieves.

16.6. Direct recycling

For direct recycling, the CAM and anode active materials must be separated from each other without changing the particle morphology using physical/mechanical separation processes. Heavy media separation and froth flotation can be used. The most efficient methods to separate single/mixed batch cathode and anode from each other, and to remove Al/Cu-foils should be determined before direct recycling. For mixed batch, the CAMs must be separated from each other to obtain the highest possible production value. Although there is a patent for magnetic separation, it may not be economical, and it is unknown whether similar formulations (like two different NMCs) could be separated from each other. Methods for separating cathodes from each other or for using a mixed product would open up possibilities for direct recovery of high-value cathode products (Gaines, 2018).

After disassembly, shredding, screening and physical anode and electrolyte materials separation, Li_2CO_3 is added to the depleted NCM black mass powder in direct recycling. Calcination produces regenerated CAM for new batteries. In this method, Li is replenished (i.e. relithiation) with the thermal treatment.

There are many differences between direct recycling and hydrometallurgical processes. Direct recycling retains the cathode crystal morphology, while hydrometallurgy uses strong mineral acids to dissolve the CAM into its constituent ions. Working with inorganic acids increases process costs and complexity. There are some attempts for using weak and biodegradable organic acids. After leaching with acid, the dissolved constituents can be separated from each other and reused to manufacture new CAM in the LIBs. Several stages of SX are generally used to separate the Co and Ni ions, which have very similar properties and are thus difficult to separate from each other (Gaines, 2018). Worcester Institute of Technology used the mixture without separation by adding sufficient virgin materials to obtain relative proportions suitable for the production of the desired CAM formulation (Gratz et al., 2014). For most CAM chemistries, the constituents in the PLS have some intrinsic value, and their recovery after leaching makes economic sense. However, for LFP and LMO materials, the constituent value is so low that hydrometallurgy does not pay. BYD Co. claimed an economical direct recovery of LFP in China. Direct recovery of LFP has been also reported by Li et al. (2017).

17. Current situation of Li extraction worldwide

- Demand is very high but supply is inadequate.

Table 13
Some previous precipitation test conditions and results.

Electrode material	Leach reactive and conditions	Temp. (°C) /Time	Precipitant	References
$Li_{0.3}Ni_{0.3}Mn_{0.3}Co_{0.3}O_2$	2.0 M formic acid + H_2O_2 reductant	70/—	NaOH and NH_4OH for Co, Mn, Mn (OH)↓ Saturated Na_2CO_3 for Li_2CO_3↓ 98.2% Li efficiency, 99.9% Li purity	Gao et al. (2017)
$LiFePO_4$ calcined before leaching, ball- milled with DEDTA-2Na	0.6 M H_3PO_4 (50 g/L) Mechanochemical activation 20 min	90/9h	5.0 M NaOH $FePO_4$↓+Li_3PO_4↓ 82.6% Li efficiency, 96.5% Li purity	Yang et al. (2017)
LCM	3.5 M CH_3COOH (40 g/L) + 4 vol % H_2O_2	60/—	$(NH_4)_2S$ for CoS↓ Na_2CO_3 for Li_2Co_3	Natarajan et al. (2018)
Anode active material (graphite)	Two-stage calcination 1.5 M HCl leach	—	Na_2CO_3 for Li_2CO_3↓ 100% Li	Yang et al. (2018)

- Li, Co, and Ni are not distributed homogenously throughout the world.
- Secondary resources (such as LIBs) should be recycled efficiently and ecofriendly as much as possible.
- The consequence is the increased pressure on EVs.
- Higher LIB prices will demotivate people to replace fossil fuel (oil or kerosene) based transportation systems.
- For our climate security, it is essential to replace fossil fuel-based systems.
- There are many environmental consequences of current Li extraction methods.

Everyone like Li but not mined in their own country. Mining and recycling are not everything, but without mining and recycling, everything is nothing.

18. Energy saving from different recycling methods

Energy consumption comparison between pyrometallurgical, hydrometallurgical and direct physical recycling and without recycling is given in Fig. 9. There is about 73% energy saving with direct physical recycling for an electrolyte. Anode component recycling with hydrometallurgy and direct physical recycling saves about 69% energy. Cu component recycling saves more than 34% of energy with pyrometallurgy, hydrometallurgy and direct physical recycling. $LiCoO_2$ component recycling also saves more than 42% for hydrometallurgy and direct physical recycling and 30% for pyrometallurgical recycling. The use of recycled material significantly reduces cell production energy and costs.

19. Prices for different cathode materials

CAM prices range according to purity. LCO prices changes 40–77 $/kg, NMC prices changes 50–95 $/kg, NCA prices changes 75–107 $/kg, LMO prices changes 23–40 $/kg, and LFP prices changes from 35 to 50 $/kg. Al foil costs about 15–20 $/kg, Cu costs 4.4–4.5 $/kg and high carbon graphite powder costs 200–240$/kg (www.alibaba.com). There is a significant variation in the cathode cost constituents. Cathode cost is significantly higher than element costs. LMO and LFO cathode material costs are lower than LCO, NMC, and LMO costs.

20. Some of the current industrial S-LIB recyclers in the world

LIB recyclers can be classified into three different categories according to their current production capacity:

- Industrial-scale recyclers: > 1000 t/y (commercialized)
- Pilot-scale recyclers: < 1000 t/y (a few hundred tons/y) (commercialized)
- Lab-scale recyclers: small-scale trials (some grs or kgs), or sometimes pilot-scale trials (some hundred kgs or more) but not commercialized yet

The current global LIB recycling companies and their recycling technologies are compared in Table 15.

Globally, Umicore, Sumitomo-Sony, DK Recycling und Roheisen GmbH, and SNAM companies recycle batteries using the combination of pyrometallurgy and hydrometallurgy methods focusing on recycling mainly Co and Ni metals, rather than Li. In a converse manner, Accurec and Retriev use both pyrometallurgy and hydrometallurgy methods to produce Li compounds from S-LIBs.

Accurec Recycling GmbH collects both household LIB packs and cells and automotive/industrial LIB packs. R&D on LIBs started in 2011. R&D on automotive LIBs started in 2013. LIB recycling facility construction in Krefeld-Germany started in 2015. The company recycled 4300 t/y LIBs, 3100 t/y mixed batteries, 2200 t/y NiCd, and 700 t/y NiMH batteries in 2021. Key characteristics of the process are (https://accurec.de/lithium?lang=en):

- Batch-type flexible processing of each Li sub-chemistry
- No battery discharge requirement
- Highest safety at processing
- No HF/F emissions
- Without emission of environmental hazard electrolytes
- Nearly 0% of gas emissions
- Low energy consumption
- Energy neutral treatment
- Robust process safety: no emissions of carcinogenic Co/Ni micro-powder to workplaces
- Disintegration & metal transformation technology (DTM) is used
- Comminution and multistep mechanical treatment to separate materials are used to produce Al, Cu
- Battery active materials (BAMs), steel and stainless steel

Accurec Recycling GmbH pretreats the disposed of batteries mechanically to separate the polymers, followed by vacuum thermal treatment to remove the electrolyte and solvent by evaporation. The material is then size reduced by crushing, classified by sieving, magnetically and air separated to remove Fe, Al, Cu, and plastic. The pretreated material then undergoes reductive pyrometallurgical treatments to separate Co and Mn, followed by hydrometallurgical acid leaching to precipitate LiCl.

Table 14
Previous SX results for $LiCoO_2$ materials.

Electrode material	Leach reactive and conditions	SX reagent	References
$LiCoO_2$	600 °C/2h 2.25M H_2SO_4 (80 °C/30 min) Leaching: 100%, purity 99.5%	PC88a Residue: $LiSO_4$	Dang et al. (2018)
$LiCoO_2$	0.5 M HCl(60 °C)	Cyphos IL-101 Saturated Na_2CO_3 (60 °C) Residue: Li_2CO_3	Xu et al. (2020)

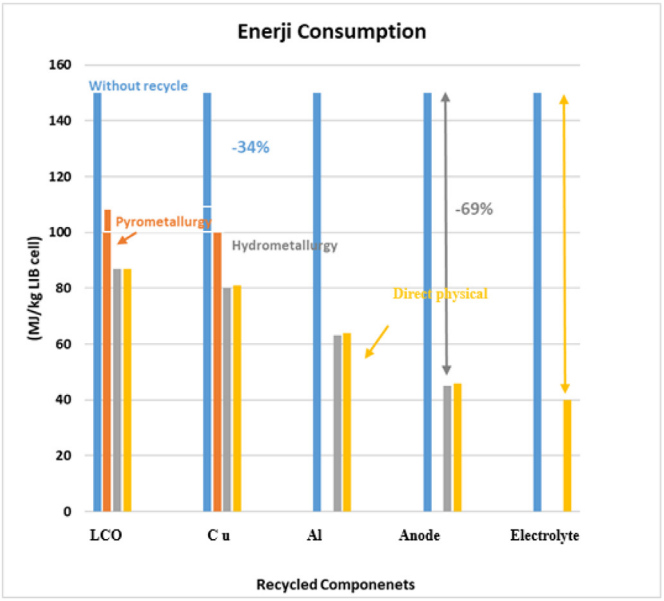


Fig. 9. Energy savings for production of a cell from recycled materials.

In general, current industrial recycling processes for discarded LIBs can be divided into four different process steps, namely Preparation, Pretreatment, Main treatment with Pyrometallurgy and/or Hydrometallurgy, which can be combined in different possible orders. Currently, only two of these (Pyrolyse LIB cells + Pyrometallurgy + Hydrometallurgy) and (Pyrolysis + Mechanical Processes + Pyrometallurgy + Hydrometallurgy) have proven their technical feasibility and industrial maturity and compete with each other after implementation in commercial plants. Both of them involve the sub-steps of thermal pyrolysis and pyrometallurgy, which only appear to be disadvantageous considering their higher energy consumption. However, an active mass (AM) obtained from only mechanical pretreatment cannot be refined directly into the end product in a hydrometallurgy process. Without the precleaning in the two thermal stages, its impurity content and high load of organics and F_2 may cause uneconomical operating costs in hydrometallurgy. Besides, the widely changing composition of the battery AMs (like LCO, NMC, LMO, LFP, NCA, etc.) requires thermal selection and homogenization for the feed material of the hydrometallurgical process. This minimizes the operating costs of the all-process route with relatively low losses of Co, Ni, and Cu targeted metals and also has a positive effect on the environment because the production and use of additional operating materials are unnecessary. A further enhancement or variation of the possible process steps, particularly with the target of

Table 15
Some global LIB recycling plants and their recycling technologies (adapted from https://accurec.de/publications-downloads?lang=en).

Scale	Company	Process
Industrial scale (>1000 t/a)	Umicore (BE)	Pyrometallurgy + Hydrometallurgy
	Accurec (DE)	Thermal + Mechanical + Pyro-metallurgy + Hydrometallurgy
	Nickelhütte (DE)	Thermal + Pyrometallurgy + Hydrometallurgy
	SungEel (KR)	Mechanical + (Thermal+) + Hydro-metallurgy
	Kyoei Seiko (JP)	Pyrometallurgy
	Brunp (CN)	Thermal + Mechanical + Hydrometallurgy
	GEM (CN)	Mechanical + Hydrometallurgy
	Huayou Cobalt (CN)	Mechanical + Hydrometallurgy
	Ganzhou Highpower (CN)	Mechanical + Pyrometallurgy + Hydrometallurgy
Pilot scale (<1000 t/a)	SNAM (FR)	Thermal + Pyrometallurgy + Hydrometallurgy
	EDI (FR)	Mechanical (wet shred)
	TES-AMM (Recuply) (FR)	Mechanical (inert gas)
	Akkuser (Fl)	Mechanical + unknown
	Duesenfeld (DE)	Mechanical + Hydrometallurgy
	Promesa (DE)	Mechanical + (wet shred) + unknown
	Redux (DE)	Thermal + Mechanical + unknown
	Retriev (US)	Mechanical (wet) + Hydrometallurgy
	Kobar (KR)	Mechanical + Hydrometallurgy
	JX Nippon (JP)	Thermal + Mechanical + Hydrometallurgy
	Telerecycle (CN)	Mechanical + Hydrometallurgy
	Guanghue (CN)	Mechanical + Hydrometallurgy
Laboratory scale	Erlos (DE)	Mechanical + recontioning (direct recycling)

A comparison of different LIB recycling methods (i.e. pyrometallurgy, hydrometallurgy, biometallurgy, and direct recycling) from industrial applicability and product recovery is given in Table 16. From an industrial applicability point of view, the highest total process score (5 is the best and 1 is the worst) changes in the following order: **hydrometallurgy** > **biometallurgy** > **pyrometallurgy** > **direct recycling**; and from a product recovery point of view, the highest score order changes: **direct recycling** > **hydrometallurgy** > **pyrometallurgy.**

Table 16
Comparison of different LIB recycling methods. Comparison of LIB recycling methods: Best: 5 and Worst:1.

	Technology readiness	Complexity	Quality of recovered material	Quantity of recovered material	Waste generation	Energy usage	Capital cost	Production cost	Total process score
Pyrometallurgy	5	5	1	3	2	1	1	5	23
Hydrometallurgy	4	3	3	4	3	3	3	3	26
Biometallurgy	2	3	3	3	3	4	4	3	25
Direct recycling	2	1	2	5	4	3	3	1	21

	Presorting requirement	Cathode morphology preserved	Direct reuse suitability	Li recovery	Co recovery	Cu recovery	Al recovery	Mn recovery	Ni recovery	Total process score
Pyrometallurgy	5	–	–	1	5	5	–	3	5	24
Hydrometallurgy	4	–	–	3	5	4	5	3	5	29
Biometallurgy	–	–	–	–	–	–	–	–	–	–
Direct recycling	1	5	4	5	5	5	5	5	5	40

additional recycling products (Li, Co, and graphite), energy savings or lowering losses, is to be technologically aimed at in the future. It is noted that only when the quantity of AM generated has augmented to a certain extent, the installation of an overall process chain with hydrometallurgy specifically designed for the S-LIB sector becomes economically feasible (https://accurec.de/publications-downloads?lang=en).

Neometals has developed a sustainable recycling process for the recovery of valuable components from LIB production scrap and EoL LIBs. The Neometals processing flowsheet aims at the recovery of more than 90% of all battery materials from LIBs that might otherwise be disposed of in a landfill or processed in pyrometallurgical recovery circuits. Specifically, the Neometals' recycling process targets the recovery of valuable materials from LIB with LCO cathodes, Ni-rich EVs, and stationary storage batteries with NMC cathodes. Neometals aims to make revenue from the provision of recycling services, licensing and sale of recovered Co, Ni, Li, Co, Fe, Al, Mn, and graphite into saleable products. While the use of LIB anode materials generally remains constant, cathode compositions tend to differ based on end-use application and performance requirements. The Neometals LIB recycling process aims at the predominant LIB chemistries, with LCO and NMC/NCA cathode batteries targeted from EVs, energy storage systems and consumer electronics (https://www.neometals.com.au/our-projects/core-projects/recycling/). Plastics, Al- and Cu-foil are separated early. The balance of materials is recovered and refined into industrial and high purity chemicals for sale, where possible, directly back into the LIB supply chain.

Fig. 10 shows the closed LIB value chain diagram in which the relationship between components starts at chemical manufacture (using recycled material feed or refined minerals) and works its way to consumer products, disposal, and recycling to support the notion of a "circular economy". Therefore, the value chain of the EV batteries should be closed for sustainability, which is a prerequisite, not an option, in extracting and processing Li.

Most of the battery components can be recycled by more than 90% with minimum toxic waste by-products, environmentally friendly way, and with low energy requirements. Produced valuable metals/compounds should have a high purity for reusing in new batteries. Therefore, the battery supply chain loop is closed and LIBs circular economy can be realized. By recovering secondary Li, Co, and Ni compound sources into the economy, an alternative strategic way will be provided to the scarce resources. In this strategic way, new employment areas will be opened in the production of Li/Co/Ni and their compounds with high added value products.

21. Conclusions and perspectives

Increasing demand and pressure on the Li market are expected in the future. Widening the portfolio both from primary Li deposits to brines and S-LIB recycling may generate significant alternative Li resources. Li demand is expected to grow continuously and dramatically in the coming years as different types of Li batteries are the most promising candidates for powering EVs or hybrid vehicles. Li batteries include both current technologies such as Li-ion and growing battery technologies (such as Li-sulfur or Li-air). Extraction of Li from primary mineral ore deposits is expensive and energy-intensive. The solar brine evaporation pond process is cheap, slow, and requires a large surface area and a large amount of water consumption at lower Li recovery rates. The latest promising development of the DLE process from brines is fast and cost-effective; has a lower water consumption, not weather dependent on very high Li recovery rates. Leveraging recycling technology development, processing, and operational management, subsurface expertise, and strategic partnerships, a sustainable DLE process from brines to enable new production and supply ecosystem can be designed, but this process is not industrially mature yet. Therefore, there is an urgent need for secondary resources of battery materials like Li and Co from S-LIBs.

LIBs have been considered to be greener and cleaner energy storage devices than other battery types due to their higher voltage, high energy density, low self-discharge efficiency, and lower environmental impacts. However, LIBs still pose a threat to the ecosystem and human health due to the hazardous materials they include. There are no simple ways and industrially mature

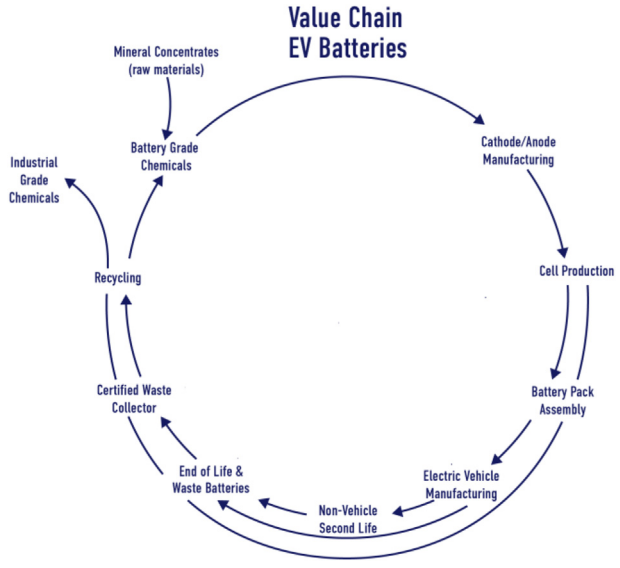


Fig. 10. Closed value chain of EV batteries.

technology for LIB recycling. These are varied and complicated products, whose design continues to evolve. LIB recycling processes should be environmentally friendly and economic feasible, but none of the many methods for their recycling is ideal; each has its disadvantages and advantages. Focusing on the Li market's growth potential, LIBs recyclers should be taking a technology-driven approach that lets researchers explore new ways to produce and process high-purity Li with the entire production ecosystem in mind. This approach enables a cost-effective, sustainable, on-demand response to the growing high-grade Battery-Li market. Since Li helps the transition to a low-carbon economy, consumers are demanding the highest environmental standards and compliance—so sustainability in the supply chain is crucial.

While several industrial S-LIB recycling processes adopt a discharging/stabilization step of dismantling the S-LIBs in an inert environment using CO_2, Ar or liquid N_2 atmosphere, discharging the LIB cells soaked in conductive unsaturated NaCl or other solutions is the most common discharging method. Dismantling the individual battery cells is usually conducted by hand, and not many issues have been reported related to this so far. Automated dismantling is more suitable for industrial-scale operations. Among the three existing major approaches to recycling the S-LIBs, the pretreatment process is especially vital for hydrometallurgical technologies and direct recycling. The pretreatment process can improve the recovery rate of the valuable metals from the LIBs and decrease the energy consumption in the following processes. The pretreatment process can be classified as discharge, dismantling, size reduction, classification, separation, dissolution, and thermal treatment.

Changes in the types of size reduction equipment and their operating conditions, such as multiple comminution steps have been tested, and it was found that these changes have a major effect on the recovery of black mass and the flotation performance. Various screen sizes from μm to mm and the sieving conditions, such as wet or dry sieving have been tested for the classification of the LIB comminution products. Electrode AMs are mainly concentrated in fine fractions, whereas coarse fractions generally contain less valuable components, such as current collectors of Al and Cu-foils, cell cases, and plastics. A variety of physical-chemical reactions occur during the pretreatment of S-LIBs. These reactions always produce environmentally hazardous, human-toxic, highly corrosive, process-relevant substances, as well as explosive gas emissions, which must be handled safely during the LIB pretreatment process.

Various physical/mechanical and physico-chemical separation methods, that include magnetic separation, electrostatic separation (eddy current separation), gravity separation (heavy medium separation, air separation), ultrasonic separation, and froth flotation (reverse flotation), have been suggested in the S-LIB recycling process in the last decades. For the improvement of the froth flotation performance, additional treatments, such as ultrasonication, grinding, mechanical activation, and roasting have been combined with the froth flotation process. Because most liberated AMs are held together by organic binders or attached to the Al/Cu-foils, the dissolution of the PTFE and PVDF binders by NMP or other kinds of solvent is considered as well as the dissolution of the Al-foil by alkaline NaOH solutions. For the complete recovery of the CAMs, a thermal treatment or pyrolysis can also be used. The PVDF binders are generally decomposed at around 500 °C, the C conductive agents are burnt off at higher temperatures and the volatilization of the electrolyte occurs at lower temperatures.

To address the environmental problems, sustainable resource management, and enhance the circular economy, it is important to properly manage and recycle S-LIBs. Conventional methods based on thermal pyrometallurgical routes together with hydrometallurgical leaching processing have been widely studied and used for the recovery of metals from S-LIBs. However, hydrometallurgical approaches have an edge over their counterparts because of their easily industrial applicability and ecofriendly nature. Building on state-of-the-art recycling processes, the ambition is to design and realize a new and environmentally friendly recycling approach for LIBs with the maximum recycling rate and minimum operating costs. Generally, the hydrometallurgy method guarantees high recovery rates and does not require additional equipment, making it quite popular in the laboratory and this method is closest to industrial application. However, this method requires a high acid and base reagent consumption proportional to the LIB for leaching, which can incur additional chemical costs. In addition, the backend costs of disposing of the used solutions can be high. In the future, there will be a global increasing interest in LIB recycling on both laboratory- and industrial-scales.

Declaration of competing interest

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

Abbreviations

AN	Acetonitrile
Bt	Billion tonne
EV	Electrical Vehicle
Mt	Million tonne
AM	Active Mass (Powder)
CAM	Cathode Active Material
CRC	Concentrating, Refining, and Converting
DE	Diethyl Acetate
DEC	Di Ethyl Carbonate
DLE	Direct Li Extraction
DMAC	N,N-dimethylacetamide
DMC	Di Methyl Carbonate
DME	Ethylene Glycol Dimethylether
DMF	N, N-dimethylformamide
DMT	Disintegration & Metal Transformation
DMSO	Dimethyl Sulfoxide
EA	Ethyl Acetate
EC	Ethylene Carbonate
EEE	Electrical and Electronic Equipment
EMC	Ethyl Methyl Carbonate
EoL	End-of-Life
ESC	Electrode-Separator Compounds
g-GBL	g-Butyrolactone
IoT	Internet of Thinks
IX	Ion Exchange
LCE	Lithium Carbonate Equivalent
LCO	Lithium Cobalt Oxide, LiCoO2
Li	Lithium
PC	Propylene Carbonate
PE	Polyethylene
PLS	Pregnant Leach Solution
PP	Polypropylene
ppm	Part per million
LIB	Li-ion Battery
LFP	Lithium Iron Phosphate, LiFePO4
LMO	Lithium Manganese Oxide, LiMn2O4
NCA	Lithium Nickel Cobalt Aluminum oxide, LiNixCoyAlzO2
NiCd	Nickel Cadmium
NiMH	Nickel Metal Hydride
NMC	N-methylpyrrolidone

NMP	N-methyl-2-pyrrolidine
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene Fluoride
SSE	Solid-State Electrolyte
SX	Solvent Extraction
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
USGS	United States Geological Survey

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