Supplementary Information

Recycling of Spent Lithium-ion Batteries for a Sustainable Future: Recent Advancements

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Supplementary Text

1. Aim of the recycling of spent LIBs

1.1 Recycling of spent LIBs for recovery of high-value resources

The LIBs need to be replaced when its capacity decreases to nearly 70 – 80% of the original capacity (called life threshold) since continued use of batteries beyond the life threshold may cause grave safety issues.[1] The key components (wt %) of spent LIBs include battery case (25–30%), cathode (35%), anode (15–18%), electrolyte (11–12%) and plastics (5–6%).[2,3] Spent LIBs contain several mineral resources including valuable metals namely cobalt (Co), lithium (Li), nickel (Ni), manganese (Mn) and iron (Fe) as well as graphite.[4] The major elements namely Co and Li are detected in the range of 5 - 25% and 5 - 7%, respectively, while other elements including Ni, Mn and Fe are found between 5 - 10%, 5 - 11% and 0.04 – 2.3%, respectively, largely depending on the cathode materials used in LIBs.[4,5] The metal contents in spent LIBs sometimes surpass that of the natural deposits (e.g., mining).[6] The spent LIBs are regarded as the secondary source for valuable metals.[5] It is estimated that with the recycling of 500,000 tons of LIBs, several valuable metallic resources can be recovered including 60,000 tons of Co, 75,000 tons of Li, 90,000 tons of Fe, 45,000 tons of Cu, 15,000 tons of Al as well as 35,000 tons recovery of plastics.[7] Additionally, based on the average market price related to these resources, these recycled materials can bring an economic value of US$3.18billion (Fig. S6a).[8] Another study reported a profit of US$30.4 million for the recycling of 3,974 tons spent LIBs (Fig. S1a).[9] Recycling of spent LIBs can help to reduce the demand for 51.3% natural resources, 45.3% fossil fuels and 57.2% nuclear energy.[10]

1.2 Recycling of spent LIBs for improvement of cost-effectiveness

A few studies have reported that the cost of LIBs is reduced over the years which is mainly due to their large-scale production and utilization for various applications.[11,12] From 2005 – 2016, the price of LIBs decreased by nearly five-times i.e., from ~US$1,000/kWh (2005) to ~ $200/kWh (2016) (Fig. S6b).[11] Another study reported that between 2007 – 2014, the cost of LIBs declined by 14% annually, i.e., the price was dropped from US$1,000/kWh to ~US$410/kWh (Fig. S6b).[12] Although the price of LIBs is reduced with the advancement of LIBs production technology, the price of some of their key components highly fluctuated in the past years, and in recent years, the cost of raw materials used for the production of LIBs is mostly increasing.[11] Within a year (2017 – 2018), the price of Co increased by three-folds, i.e., from $30 to $90 per kg.[11] The Li price increased by around four times (from $5 to $20 per kg) between 2010 – 2017.[11] According to the recent London Metal Exchange data (https://www.lme.com/) (Fig. S6c), the Co price is projected to increase from US$28,665.10/ton in June 2023 to US$30,285.09/ton in Aug 2024. However, the Li cost is estimated to rise from US$45,918.18 in June 2023 to US$46,680/ton in August 2024. The current (June 2023) price of Ni is US$23,140/ton, which is expected to rise to US$24,290/ton by the end of 2024. Lithium carbonate (Li_2CO_3) is commonly used as the source of Li for the production of LIBs.[13] In 2021 – 2022, the price of Lithium carbonate in USA increased by nearly three times, while the price almost doubled in China.[14] It should be noted that the global reserve of these minerals is limited. According to the USGS report, the global reserve for Co is 8.3 million tons, whereas the world reserve for Li is 26 million tons.[14] China is the top consumer of Co with ~80% of Co being used for the manufacturing of rechargeable batteries.[14] The global Li consumption in 2021 – 2022 increased remarkably by 41%, i.e., from 95,000 tons in 2021 to 134,000 tons in 2022.[14] It is reported that 25% and 35% of globally produced Co and Li, respectively are used for the manufacturing of LIBs, and Li consumption is projected to be doubled (66%) by 2025.[15,16] To meet the high demand of Li, in addition to the primary sources such as mining, Li extraction from the secondary sources namely brine/seawater has been explored.[17,18] The global reserve for the natural graphite is 330 million tons.[14] To reduce the dependency on natural graphite, a blending of natural and synthetic graphite is used in LIBs industry. However, synthetic graphite is expensive (nearly double) than natural graphite.[19] The recycling of valuable metals from secondary sources like spent batteries would alleviate the shortage of these metals as well as reduce their market price.

1.3 Recycling of spent LIBs for environmental protection

Spent LIBs contain several hazardous materials including toxic metals from cathode (e.g., Co, Ni and Mn), corrosive and organic electrolytes (e.g., $LiBF_4$ and $LiPF_6$), polymer binders, metal castings which could pose adverse effects on both the human health and ecosystem.[20] Spent LIB can enter the municipal solid waste stream, causing environmental pollution. Landfilling and incineration are commonly used for the management of solid waste.[21] Landfilling of solid wastes containing spent LIBs could cause groundwater and soil pollution due to leakage of toxic metals from cathode materials by breakage of LIBs outer case by mechanical, chemical and/or microbial actions.[22,23] In additional to environmental pollution, there is a possibility of occurrence of food chain risks.[24] Incineration of solid wastes containing spent batteries could release several toxic gases (CO, SO_2, HF, volatile organic compounds (VOCs), etc.) as well as airborne particulate matter to the atmospheric environment.[23,25]

1.4 Recycling of spent LIBs for conservation of natural resources

Natural resources in the lithosphere are being greatly exploited due to massive mining of critical metals which are required for the production of LIBs.[26] Since the mineral mining is not renewable, there is a growing concern worldwide for the depletion of natural resources. According to the recent United States Geological Survey (USGS) Mineral Commodity data, the global reserve of various metals including Co, Li, Ni, Mn, Fe and Cu are 8.3 million ton, 26 million ton, >100 million ton, 1.7 million ton, 0.1 8 million ton, and 0.89 million ton, respectively.[14] The requirement for cobalt in China is estimated to raise from 47,300 tons in

2017 to 115,600 tons in 2025.[7] Additionally, the global nickel consumption was forecast to reach nearly 2.4 million tons in 2020.[7] In 2014, nearly 42.5% of Co and 40% of Li produced globally were used for the battery manufacturing.[27] The optimum recycling of spent LIBs would help to conserve the natural resources by reduction of mining activities for extraction of metals.

1.5 Recycling of spent LIBs for sustained production and distribution of resources

The global mineral commodity report published by the USGS shows that mineral resources are unevenly produced (e.g., by mining) and/or distributed globally.[14] The global production of raw materials used in cathodes (e.g., metals namely Co, Li, Ni, Mn, etc.) and anodes (e.g., graphite) is mainly concentrated in specific countries in the world (Fig. S7). More than half of Co (59%) is produced from the Demographic Republic of Congo, whereas Australia (44%) and Chile (34%) are the top countries for Li production.[28]. South Africa (33%) is the main producer of Mn, while Philippines (11%) and Canada (10%) are the top countries for the Ni production. The natural graphite which is used as anode in LIBs is mainly produced in China (67%) followed by India (12%) and Brazil (8%). Overall, these statistics suggest that among various countries, China contributes the major production of several critical elements which are needed for the synthesis of LIBs including graphite, Co and Mn. Geopolitical conflicts may disrupt the supply chain of raw materials for specific countries which would ultimately impact the production of LIBs. The disruption of supply chain may cause the increase of cost of raw materials. Therefore, recycling of spent LIBs is needed for optimum recovery of resources with high purity and quality to reuse in LIB production. The reuse of recycled materials for LIBs production would help to achieve the sustainability and circular economy.

Supplementary Figures

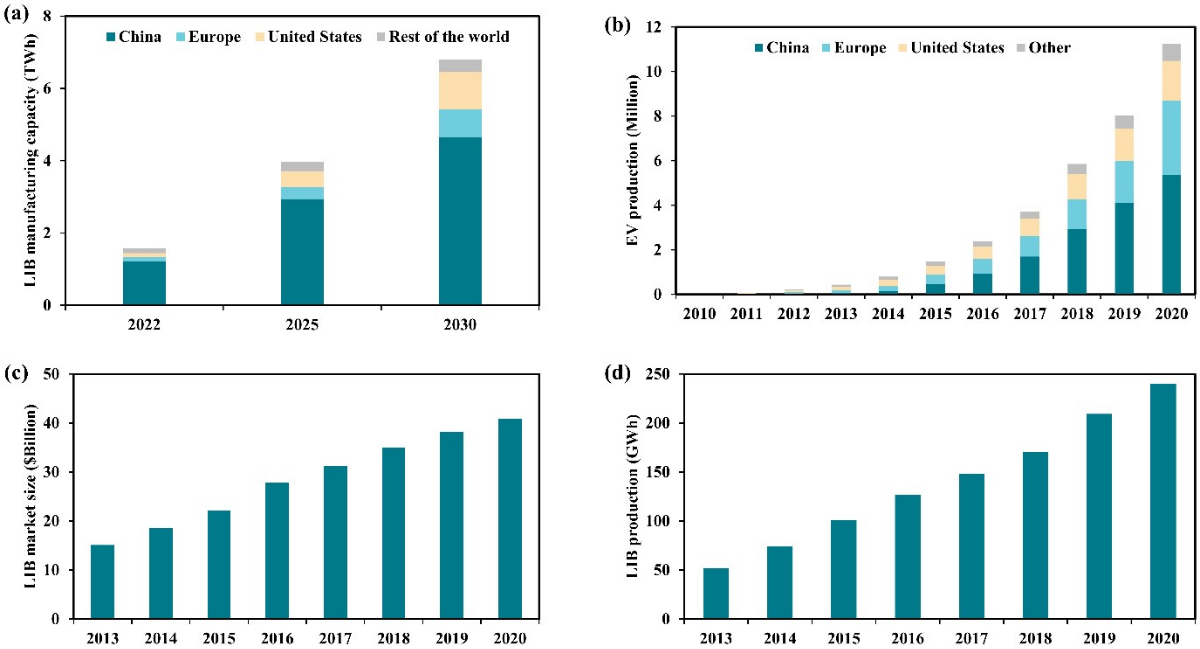
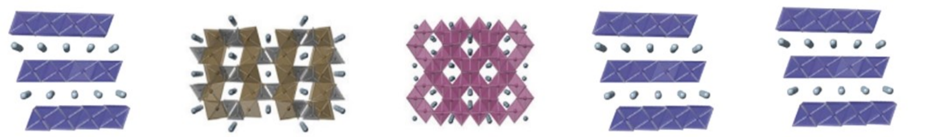


Fig. S1 Global LIB manufacturing capacity (a), **g**lobal EV production (b), global LIBs matter size (c) and global LIB production (d). Adapted and modified from ref. [29–31]

Cathode types	LCO	LFP	LMO	NCA	NMC
Cathode formula	$LiCoO_2$	$LiFeO_4$	$LiMn_2O_4$	$Li(Ni,Co,Al)O_2$	$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC111) $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811)
Year introduced	1991	1996	1996	1999	2008
Structure	Layered	Olivine	Spinel	Layered	Layered
Safety	••	••••	••••	•••	•••
Energy density	••••	•••	•••	••••	••••
Power density	•••	••••	••••	••••	•••
Calendar lifespan	•••	••••	••••	••••	••••
Cycle lifespan	•••	••••	•••	••••	•••
Performance	••••	••••	•••	••••	••••
Cost	•	••••	••••	•••	•••
Market share	Obsolete	Electric bikes, buses and large vehicles	Small	Steady	Growing (from NMC 111 > NMC532 > NMC622 > NMC811 to no-cobalt chemistries)



LIB cathode chemistries Ideal •••• (dark) | •••• | ••• | •• | • Poor

Fig. S2 Key characteristics of different cathode materials used in LIBs. Reproduced with permission from ref. [32]; Copyright 2019. Nature.

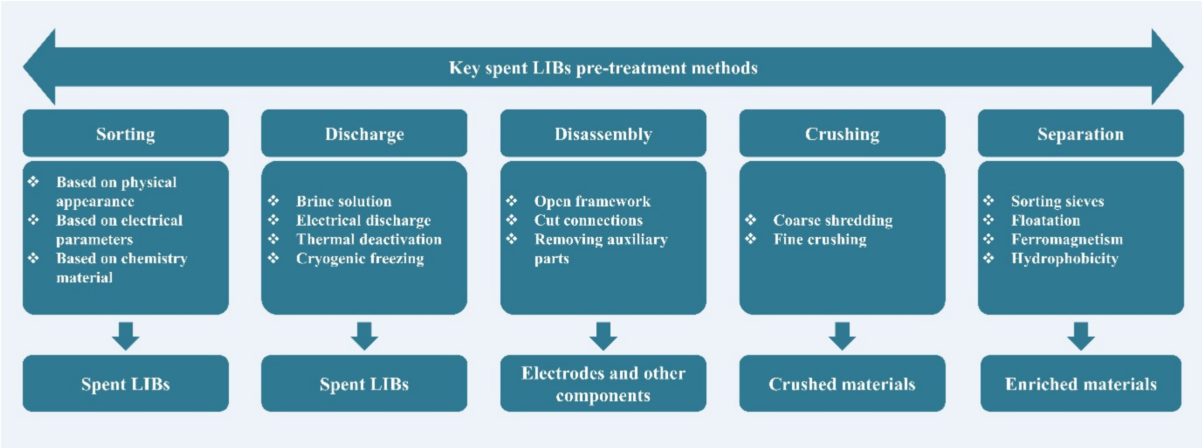


Fig. S3 Key pre-treatment methods for spent LIBs. Adapted and modified from ref. [33].

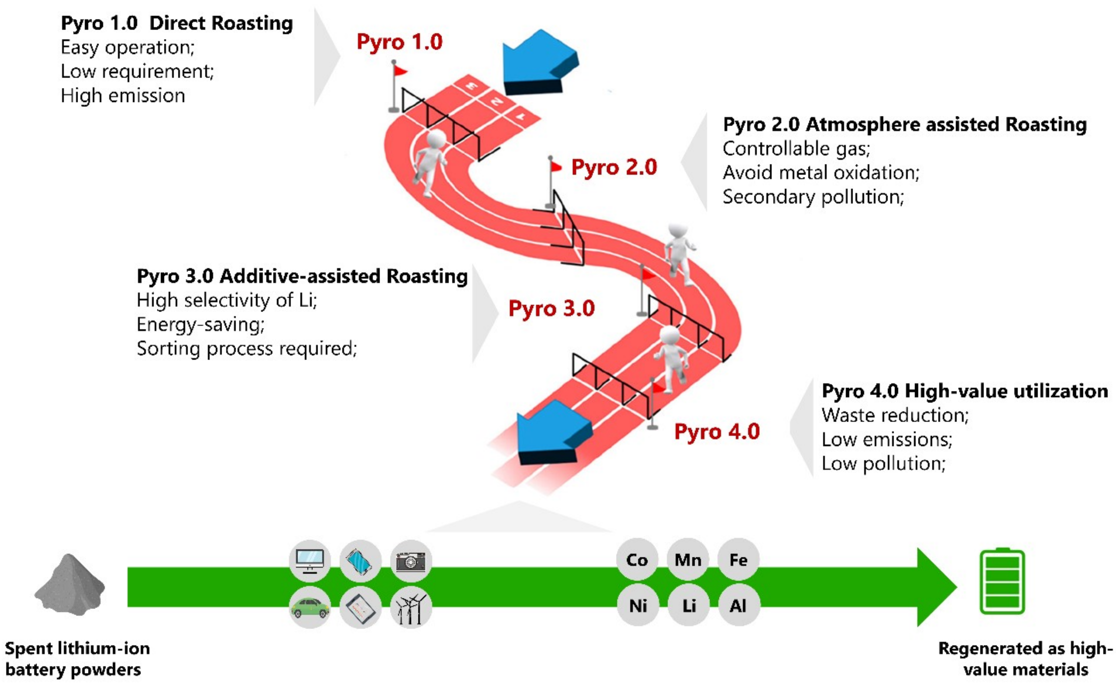


Fig. S4 Schematic diagram of the evolution of spent LIBs recycling from *Pyro 1.0* to *Pyro 4.0* by pyrometallurgical processes. Reproduced with permission from ref. [34]; Copyright 2021, American Chemical Society.

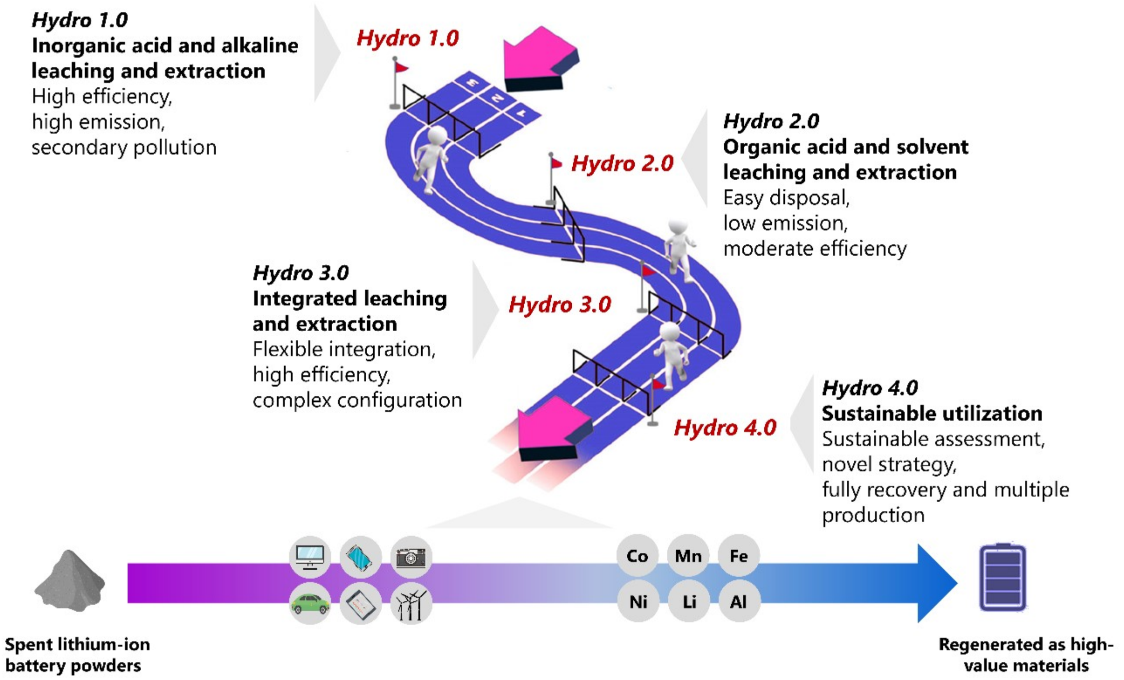


Fig. S5 Schematic diagram of the evolution of spent LIBs recycling from *hydro* 1.0 to *hydro* 4.0 by hydrometallurgical processes. Adapted and modified from ref. [35].

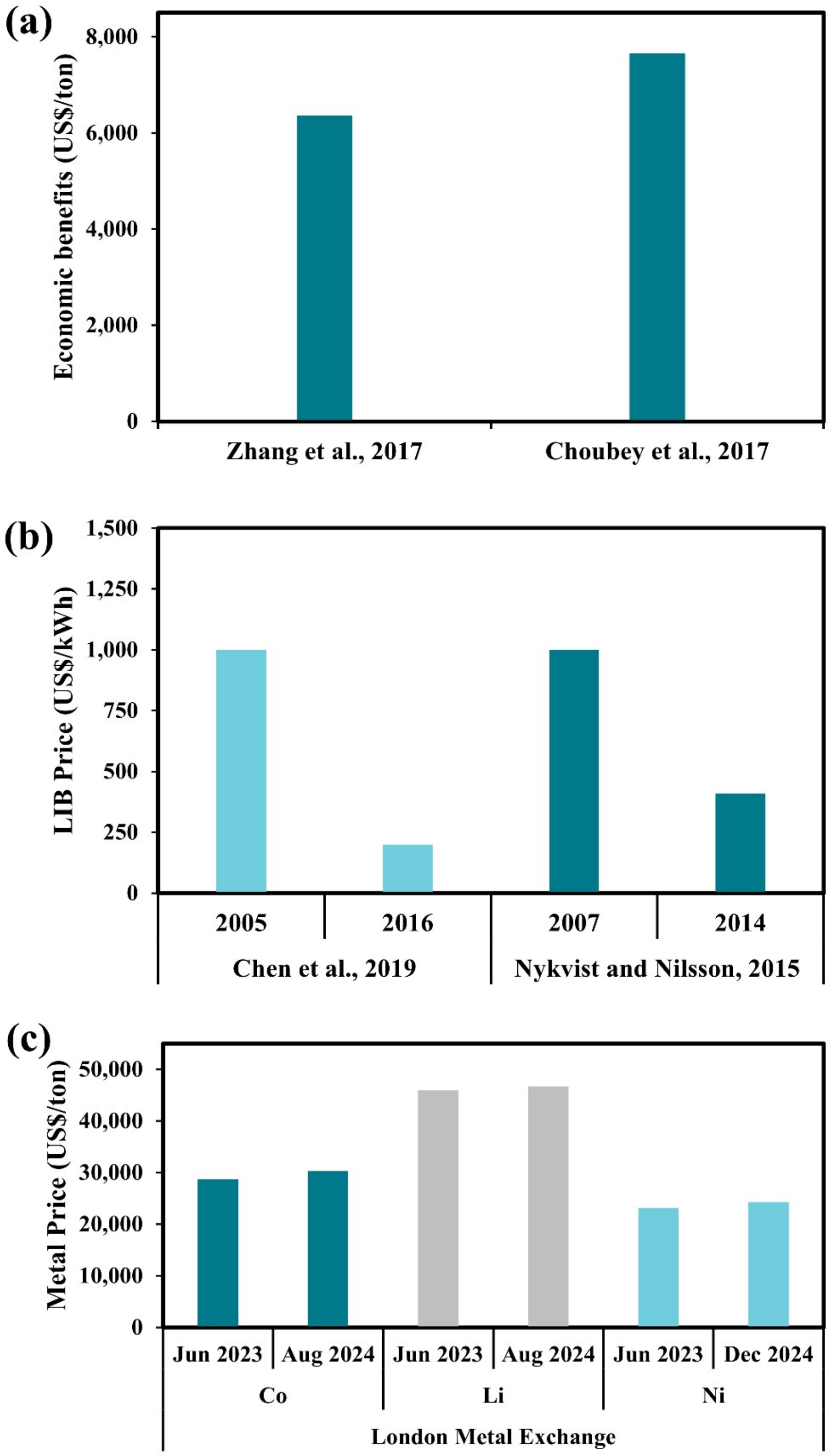


Fig. S6 Economic benefits for the recycling of spent LIBs[8,9] (a), changes of LIBs' price from 2005 – 2014[11,12] (b), and projection of the increase of price of key metals (Co, Li and Ni) used for the production of LIBs (c).

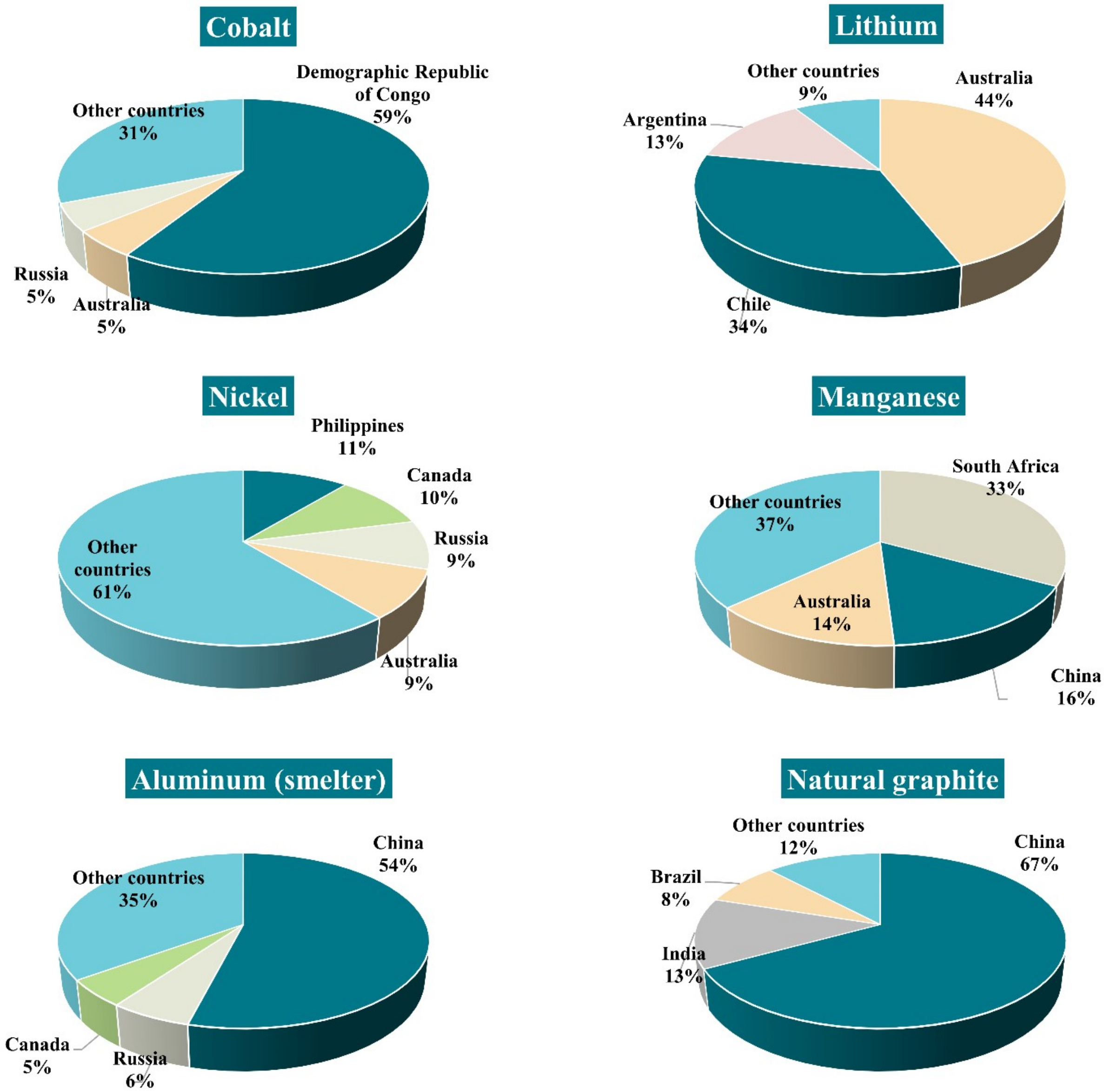


Fig. S7 Global production of key components of LIBs including metals (Co, Li, Ni, Mn and Al) and graphite. Date were collected from ref. [28].

Supplementary Tables

Table S1. Summary of advantages and disadvantages of different pre-treatment technologies. Reproduced (adapted and modified) with permission from ref..[27]; Copyright 2018, American Chemical Society.

Pre-treatment technology	Detail of methods	Advantages	Disadvantages
Mechanical separation	Separate materials according to different physical properties including density, conductivity, magnetic behavior, and so forth	Simple and convenient operation	Cannot recycle all kinds of components (e.g., fine structured organic and inorganic substances) in spent LIBs completely
Thermal process	Remove organic additives and binders via thermal treatment	Simple and convenient operation	Require high input of energy, cannot recover organic compounds, and would cause serious exhaust pollution if no exhaust purification device is equipped
Dissolution process	Dissolve electrolytes and binders using suitable solvents	Low energy consumption and almost no exhaust emission	High cost of organic solvent as well as device investment
Mechanochemical method	Discording the structure of the materials using grinding techniques	Enhancing the leaching efficiency of valuable metal and making the reaction conditions become mild	High energy consumption and noise problems

Table S2. Comparison of advantages and disadvantages of major spent LIBs recycling technologies. Adapted and modified from ref.[4,5,36]

Recycling technology	Advantages	Disadvantages
Direct recycling	Practically all battery materials can be recovered (anode, electrolyte and foils)	Complex mechanical pretreatment and separations are required
	Short recovery route	Mixing cathode materials could reduce the value of recycled product
	Energy efficient	Not scaled up to industrial level
	Environmentally friendly	
	Convenient for recycling manufacturing scraps	
Pyrometallurgy	Suitable for large-scale industrial production	High energy consumption
	Simple operation and short flow	High cost
	High adaptability for different raw material	Emission of hazardous gases
	High recovery of metals (e.g., Co, Ni and Cu)	Metals such as Li lost in the slag phase
	Acid and alkali free	
Hydrometallurgy	High metal recovery rates	High chemical reagents consumption
	High product purity	Secondary pollution of waste liquids
	Energy and capital-efficient	Little adaptability for different raw materials
	Less waste gas	Uncertain lithium recovery rate
Bioleaching	Low energy consumption	Long period for microorganism culture
	Environmentally friendly	Long reaction period
	Low operating cost	Low efficiency at higher pulp density
	Minimal use of chemicals	Microorganism toleration to toxic metals
Electrometallurgy	Simple, easy to control and scale up	Appropriate equipment required
	Clean and environmentally friendly	Low productivity and lengthy times required for impurity removal
	Cost effectiveness	
	Improved selectivity	
	Lower chemical consumption	

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