Italian National Agency for New Technologies,
Energy and Sustainable Economic Development

Ricerca e sviluppo nel settore delle batterie agli ioni di litio in ottica di Economia Circolare: criticità e prospettive

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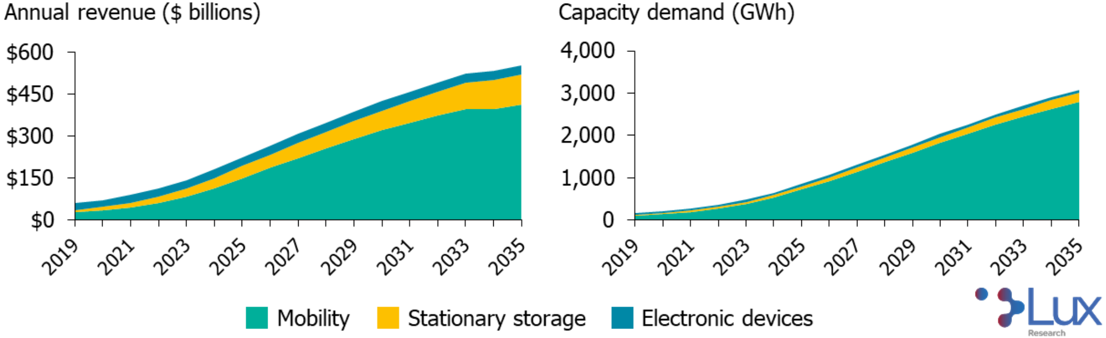
Li-ion batteries: a growing market

Global energy storage market forecast

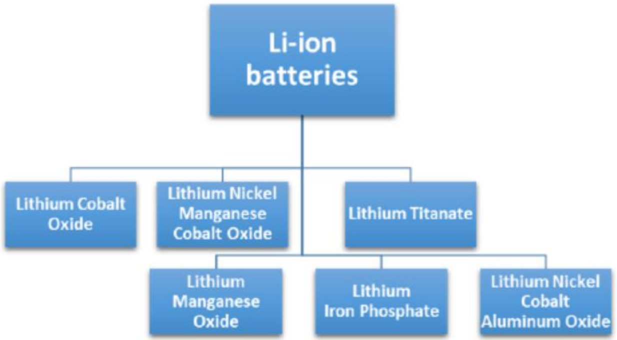
Total market size, 2019	$59 billion	164 GWh
Total market size, 2035	$554 billion	3,082 GWh
CAGR	15.0%	20.1%

Total energy storage market forecast



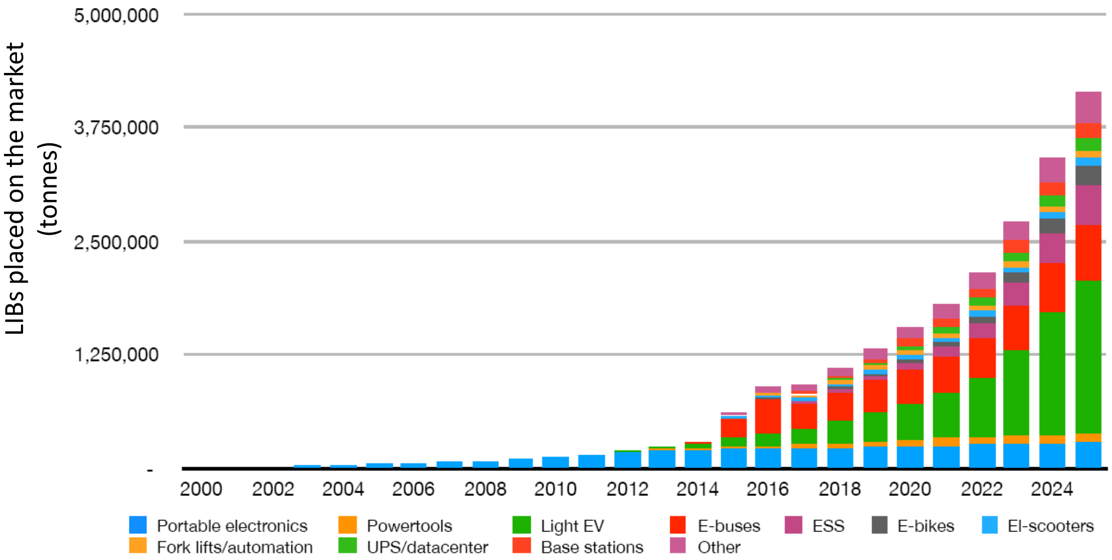
Source: Lux Research, Global Energy Storage Market 2019

The three main drivers of energy storage — ***mobility applications, electronic devices and stationary storage*** — will reach an annual deployment level of 3,082 GWh up from 164 GWh currently.



Li-ion batteries: a growing market

Lithium-ion batteries placed on the global market, by application 2000-2025 (tonnes)



Source: Circular Energy Storage

For Europe, LIBs production is a strategic imperative for the energy transition towards renewable sources and competitiveness in the automotive sector

necessity to adopt integrated systems to act on the entire value chain

Global LIB market is constantly growing and expects to multiply over the next 12 years from around 1,000,000 tons of LIBs placed on the market in 2018 to 7,500,000 tons in 2030.

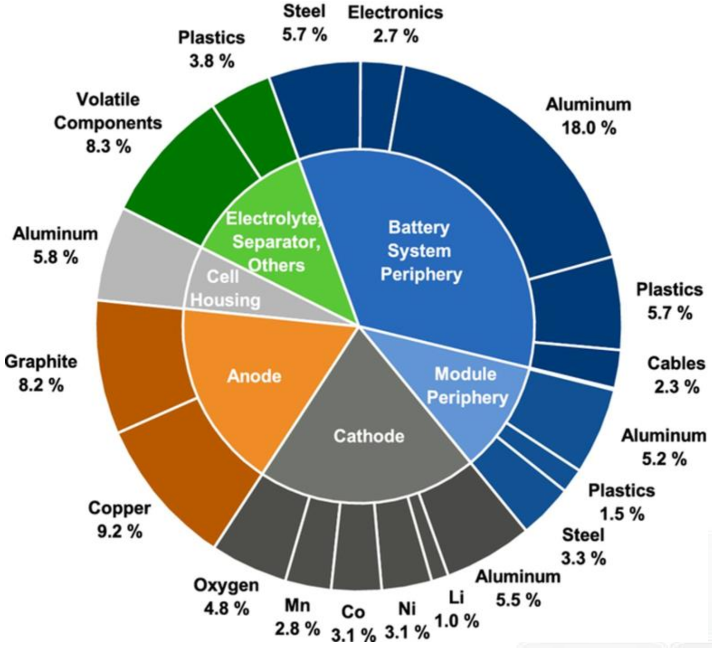
Li-ion batteries as an example of complex matrices

Complex matrices

«structures» in which materials of different types are present with different chemical species in different concentrations of natural or anthropic origin»

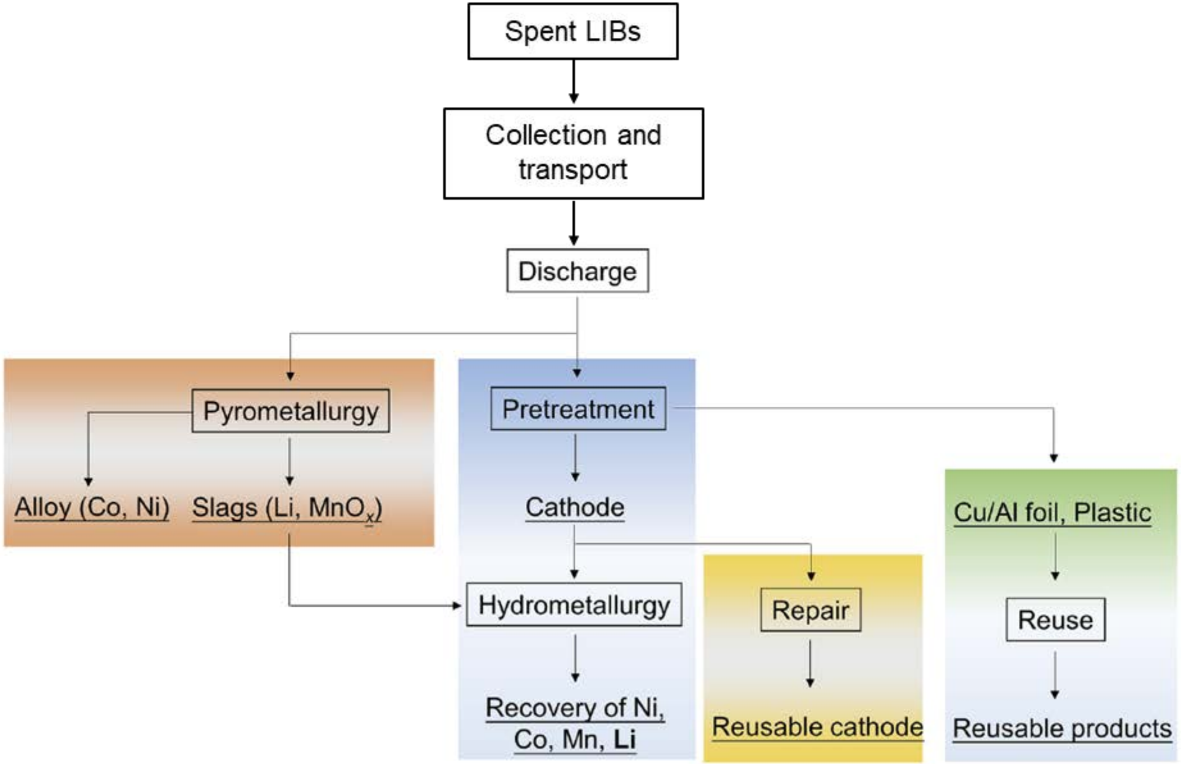
In these matrices, the sustainability of the treatment processes can be achieved by considering the entire waste as a resource:

PRODUCT-CENTRIC APPROACH



Source: J. Diekmann, C. Hanisch, L. Frobose, G. Schalicke, T. Loellhoeffel, A.S. Folster and A. Kwade. Ecological Recycling of Lithium-Ion Batteries from Electric Vehicles with Focus on Mechanical Processes. Journal of The Electrochemical Society 2017, 164, A6184-A6191.

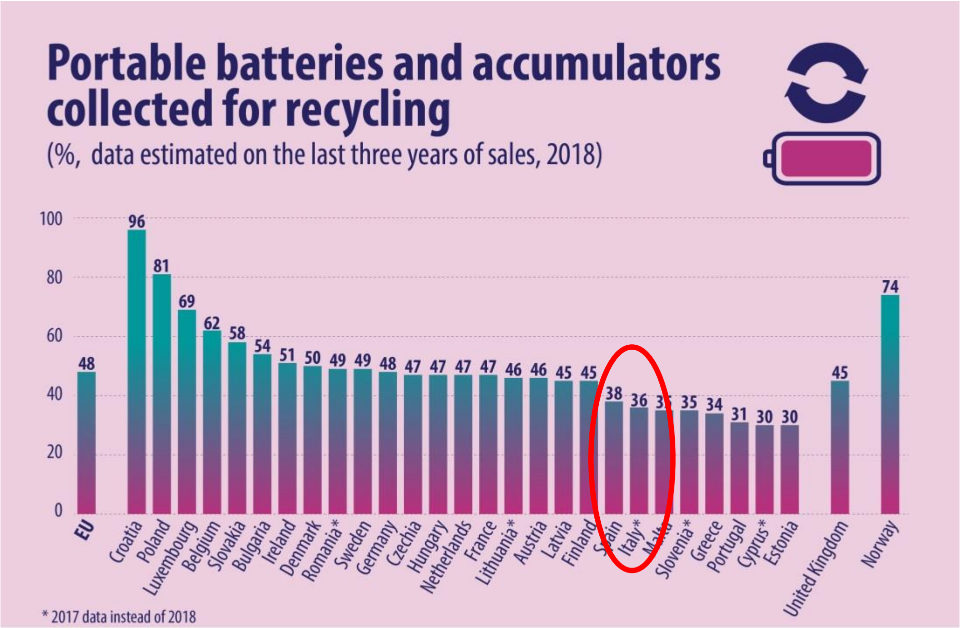
General flow sheet of EoL LIBs treatment processes



Source: adapted from C. Liu, J. Lin, H. Cao, Y. Zhang, Z. Sun. Recycling of spent lithium-ion batteries in view of lithium recovery: A critical review. Journal of Cleaner Production 228 (2019) 801-813.

Collection

In 2018, close to **48%** of portable batteries sold in the EU were collected for recycling.
191 000 tonnes of portable batteries were sold in the EU; 88 000 tonnes of used portable batteries were collected as waste to be recycled.



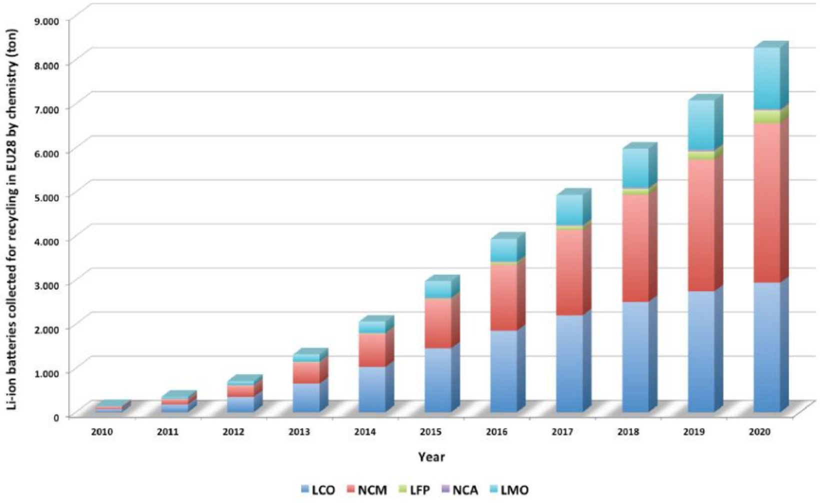
ec.europa.eu/**eurostat**

In 2018, most European member states have met or exceeded the 2016 target (set at 45%).*
However, **more efforts are still needed** to enhance the collection efficiency and reducing landfilling and/or incineration of spent LIBs.

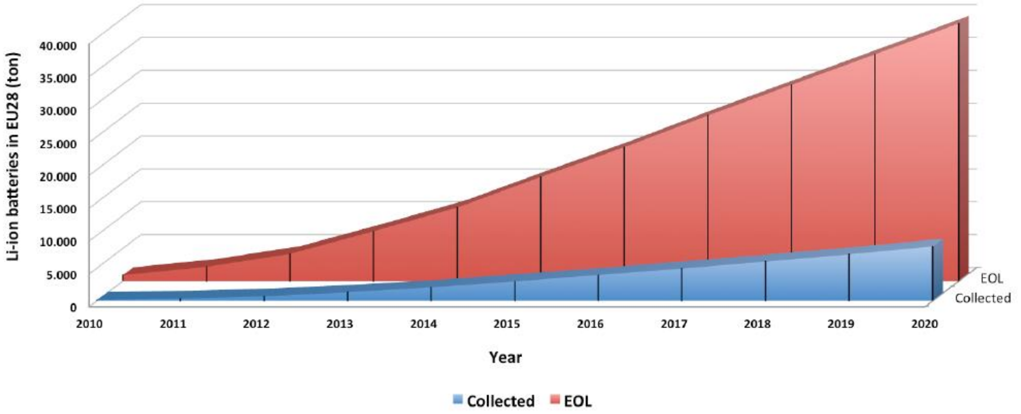
*Directive 2006/66/EC of the European Parliament and of the Council on batteries and accumulators and waste batteries and accumulators

Collection

Collected Li-ion batteries for recycling in EU28



Comparison of EOL versus collected Li-ion batteries for recycling in EU28



Source: Weyhe, R., Yang, X. Investigation about Lithium-Ion Battery Market Evolution and future Potential of Secondary Raw Material from Recycling, ACCUREC Recycling GmbH (Ed.), 2018.

Sorting

Collection centers place **LIBs**, **Pb-acid**, **NiCd** and **NiMH** batteries into designated drums, sacks or boxes. This sorting step can be otherwise performed directly at the treatment plant, normally by manual sorting by experienced personnel.

LIBs are then processed as ***mixed feed***. There are only few examples of industrial plants where LIBs are separated by sub-chemistry, however no information is available about the details of this sorting step.

The diversity of cathode chemistries is a challenge because they may require different conditions for an efficient recycling process. Treating them simultaneously **increase the required resources** (e.g. energy and time consumed by a sorting mechanism) or may have a **negative impact on the quality** of the outputs.

Discharging and disassembly

DISCHARGING

by immersing the batteries in salt water or by using charging/discharging equipment. Large-scale European processes, however, usually do not use these stabilization techniques and opt for opening the cells under an inert atmosphere.

DISASSEMBLY AND/OR MECHANICAL TREATMENT

- At industrial scale, discharging is normally followed by a **mechanical treatment** (crushing + magnetic and mechanical separation units). These pretreatment steps are sometimes performed in inert or cryogenic atmosphere to prevent violent reactions of Li and to minimize risks from the presence of organic solvents. This makes the separation of the components more difficult than if they were pre-sorted and considerably **reduces the economic value** of waste material streams.

- Most of the lab-scale processes relies on **manual disassembly** of the batteries components, which is **not applicable at industrial level**.

The **design** of LIBs varies significantly with different models and manufactures, which increases the difficulty of automated disassembly.

Furthermore LIBs design is **not optimized for easy disassembling**: use of adhesives, bonding methods and fixtures, products equipped with embedded rechargeable batteries (iPhone, tablets) do not allow easy dismantling either by hand or machines.

circular design, standardization of cells geometry and architecture, easy disassembly

development of **automatic** or semi-automatic pretreatment processes

Materials recovery - industrial technologies

Company/process	Location(s)	Details of technology	Main end products
Umicore	U.S.A.	combines pyrometallurgical and hydrometallurgical technologies; spent LIBs are fed to a single shaft furnace; alloy containing Co and Ni from furnace further processed through leaching; Li and Al mainly exist in the slag and need to be further treated through hydrometallurgical technologies	$CoCl_2$
SNAM	France	first stage is sortation techniques; rough crushed products then disposed by pyrolysis pretreatment, crushing, and sieving	
Batrec AG	Switzerland	spent LIBs stored and shredded under CO_2 atmosphere; scrap then neutralized by moist air and further treated with hydrometallurgical process	
Inmetco	U.S.A.	scrap processed in a rotary hearth furnace and further refined in an electric arc furnace	alloy (Co/Ni/Fe)
Sumitomo-Sony	Japan	electrolyte and plastics removed through calcination; pyrometallurgical process used to recover alloy containing Co-Ni-Fe; hydrometallurgical process conducted to recover Co	CoO
AkkuSer Ltd.	Finland	two-phase crushing line is designed; magnetic and other separation methods follow it; scrap then delivered to smelting plants and leaching	metal powder
Toxco	Canada	combines mechanical methods including shredding, milling, and screening and hydrometallurgical methods including leaching and precipitation	CoO, Li_2CO_3
Recupyl Valibat	France	mechanical methods used as first stage; hydrometallurgical methods then used to obtain $Co(OH)_2$ and Li_3PO_4	$Co(OH)_2$, Li_3PO_4
Accurec GmbH	Germany	vacuum furnace used first; mechanical methods then used to separate different materials; scrap then fed to an electric furnace; slag is disposed of through hydrometallurgical methods	Co alloy, Li_2CO_3
AEA	U.K.	first stage uses organic solvent to remove electrolyte, solvent, and binder; leaching of cathode carried by electrolyzing	LiOH, CoO
Glencore plc. (former Xstrata)	Canada/ Norway	combines pyro- and hydrometallurgical methods	alloy (Co/Ni/Cu)
Onto process	U.S.A.	preliminary step involves discharge, electrolyte recovery, refurbishing, and ball mill; supercritical fluid used to separate different materials	cathode powder
LithoRec process	Germany	combines similar mechanical and hydrometallurgical methods	CoO, Li salt
Green Ecomanufacture Hi-Tech Co	China	hydrometallurgical methods including leaching, purifying, and leaching-resynthesis used	Co powder
Bangpu Ni/Co High-Tech Co	China	hydrometallurgical methods including leaching, purifying, and leaching-resynthesis used	cathode material, Co_3O_4
American Manganese Inc., RecycLiCo Process	Canada	hydrometallurgical system including recycling of process water and reagents	Ni-Co Hydroxide, Ni-Mn-Co Hydroxide

Recycling of spent LIBs is relatively new compared to the recycling of NiCd and Pb-acid batteries.
Most of the commercial processes were not a LIB-dedicated recycling process in their original design: the core technology was based on **pyrometallurgical methods** typical of Co and Ni extractive metallurgy. Through this technology **only Co, Ni and Cu could be recovered** effectively, Li and Al being lost in the slag. Therefore, most of these companies established a process **combining pyro- & hydrometallurgical methods**.

Source: adapted from W. Lv, Z. Wang, H. Cao, Y. Sun, Y. Zhang and Z. Sun. A Critical Review and Analysis on the Recycling of Spent Lithium-Ion Batteries. ACS Sustainable Chem. Eng. 2018, 6, 1504–1521.

Materials recovery - lab-scale technologies

Raw Material	Reagent	T (° C)	t (min)	Leaching efficiency (%)	
				Co	Li
Inorganic Acid Leaching					
spent LIBs	1.75 mol/L HCl	50	90	99.0	100.0
spent LIBs ($LiCoO_2$)	4 mol/L HCl	80	30	90.6	93.1
$LiFePO_4$ and $LiMn_2O_4$	6.5 mol/LHCl + 5 vol % H_2O_2	30	60		74.1
LIB industry waste ($LiCoO_2$)	2 mol/L H_2SO_4+5 vol % H_2O_2	75	30	94.0	95.0
$LiNi_xMn_yCo_zO$ compounds	4 mol/L H_2SO_4 + 5 vol % H_2O_2	65−70	120	96.0	
spent LIBs (mixture)	1 mol/L H_2SO_4 + 0.075 M $NaHSO_3$	95	240	91.6	96.7
spent LIBs ($LiCoO_2$) (from laptop computers)	2 mol/L H_2SO_4 + 5 vol % H_2O_2	75	60	70.0	99.1
spent LIBs ($LiCoO_2$) (from mobile phones)	2% H_3PO_4 + 2 vol % H_2O_2	90	60	99.0	88.0
spent LIBs ($LiCoO_2$)	0.7 mol/L H_3PO_4 + 4 vol % H_2O_2	40	60	99.0	100.0
spent LIBs ($LiCoO_2$)	1 mol/L HNO_3 + 1.7 vol % H_2O_2	75	60	95.0	95.0
Alkaline Leaching					
spent LIBs ($Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$)	4 mol/L NH_3-1.5 mol/L $(NH_4)_2SO_4$ + 0.5 M Na_2SO_4	80	300	80.7	95.3
Organic Acid Leaching					
spent LIBs ($LiCoO_2$)	0.4 mol/L tartaric acid +0.02 mol/L ascorbic acid	80	60	93.0	95.0
spent $LiCoO_2$ and CoO	1 mol/L oxalate + 5 vol % H_2O_2	80	120	96.7	
spent LIBs ($LiCoO_2$)	2 mol/L citric acid + 0.6 g/g H_2O_2 (H_2O_2/spent LIBs)	70	80	96.0	98.0
spent LIBs ($LiCoO_2$)	1 mol/L oxalic acid	95	150	97.0	98.0
spent LIBs ($LiCoO_2$)	1 mol/L iminodiacetic acid + 0.02 M ascorbic acid	80	120	99.0	90.0
spent LIBs ($LiCoO_2$)	1 mol/L maleic acid +0.02 M ascorbic acid	80	120	99.0	96.0
spent LIBs ($LiCoO_2$)	0.5 mol/L glycine +0.02 M ascorbic acid	80	120	91.0	
spent LIBs ($LiCoO_2$)	1.5 mol/L succinic acid + 4 vol % H_2O_2	70	40	100.0	96.0
spent LIBs ($LiCoO_2$ and $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$)	2 mol/L L-tartaric acid + 4 vol % H_2O_2	70	30	98.6	99.1

Research trends

- Hydro/iono/solvometallurgical techniques: leaching with ***organic acids*** (citric, oxalic, tartaric, maleic acid) and ***ionic liquids***, which potentially have a smaller environmental impact that mineral acids
- ***Mechanochemical treatment*** (MC)
  It can decrease the particle size and break the crystal structure, thus facilitating the leaching process. Examples of acid-free mechanochemical process which eliminates the need for acid and alkali materials and the discharge of wastewater
- ***Direct regeneration*** of the active materials (such as solid-state regeneration methods): the obtained products have good electrochemical properties which meet the reuse requirement for LIBs, thus suggesting the applicability of such methods on a higher scale

Source: adapted from W. Lv, Z. Wang, H. Cao, Y. Sun, Y. Zhang and Z. Sun. A Critical Review and Analysis on the Recycling of Spent Lithium-Ion Batteries. ACS Sustainable Chem. Eng. 2018, 6, 1504−1521.

Recycling technologies

An **all-component integrated strategy** aimed at the valorization of the whole waste fractions is **missing**:

- Industrial processes: mixed feed with focus Co, Ni and Cu recovery; Li Al and Mn are lost in the slag and are not recovered
- Some companies (such as Accurec) utilises vacuum pyrolysis to remove the electrolyte, which is then condensed and destined for thermal use; the only recycler to report to reclaim the electrolyte is Duesenfeld: the electrolyte is evaporated in a vacuum and recovered in condensate form
- Lab scale-processes: single cathode feed; Li recovery

In order to be cost-effective, a recycling chain needs to be oriented to the valorization of the whole waste: not only the ***cathode*** materials, but also the ***anode*** (graphite) and the ***electrolyte*** should be valorized, according to the principles of Circular Economy:

PRODUCT-CENTRIC APPROACH

Our research line: materials recovery from EoL LIBs

Discharging → Dismantling

Other materials:
- casing
- metallic fraction
- plastic fraction
- etc.

→ Characterisation

Battery packs

Electrolyte removal → Characterisation of the cathodic material → Leaching → Separation/ purification → Characterisation of the outputs

By-products and waste streams valorisation

Conclusions

Improvements to make LIB recycling processes more sustainable include:

- circular design
- manufacturer standardization of batteries
- labelling system
- improved collection system
- smart sorting and characterization
- automated disassembly techniques
- integrated, product-centric, closed-loop recycling processes

✓ increased sustainability (environmental and economic)
✓ higher value of recovered material streams
✓ reduction of the risks for workers

Thank you for your attention!

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