Extraction of Lithium and Cobalt from Spent Lithium-Ion Batteries (LIBs) and Waste Prevention

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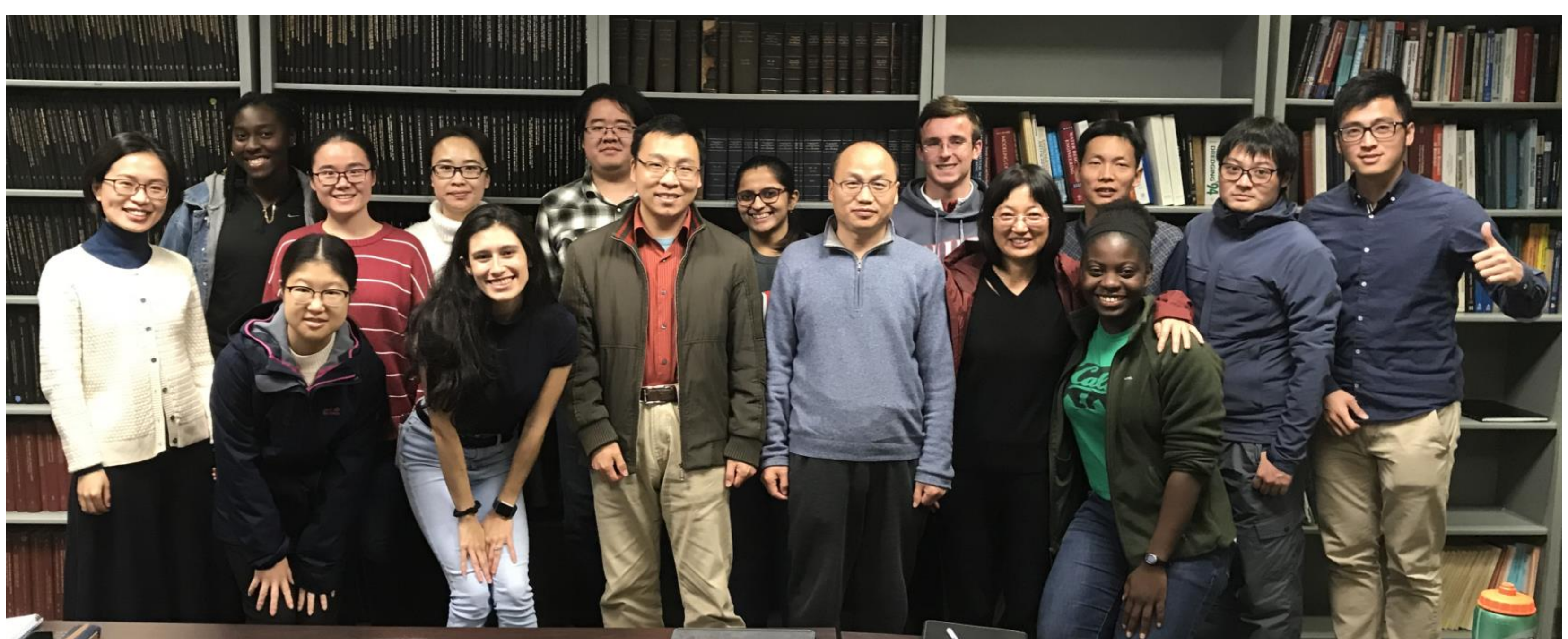
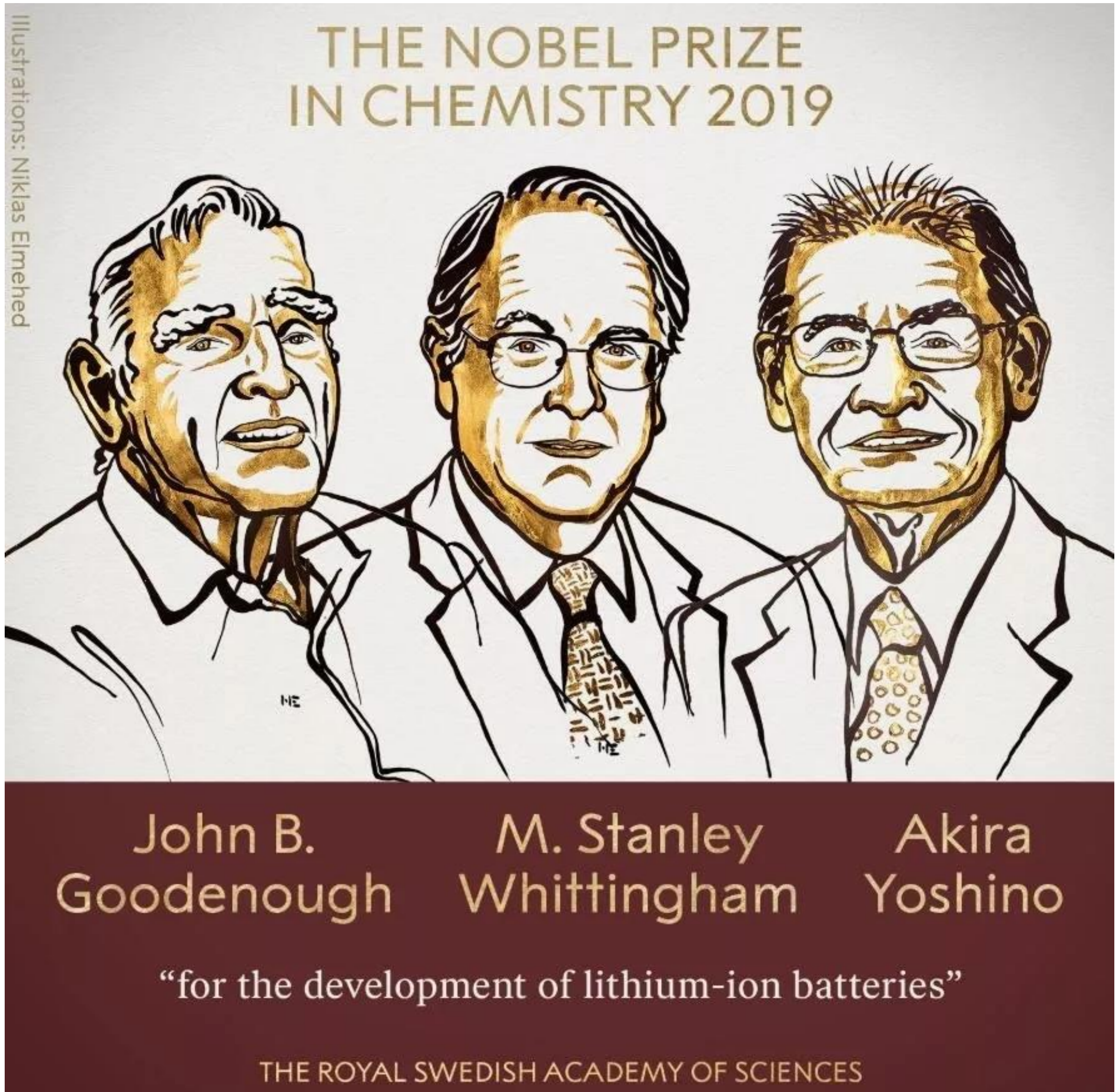
- High School Interns: Saachi Kuthari (Millburn High School), Hari Ramesh (Morris Hills High School) and Bijou Choi (Bergen County Technical High Schools)

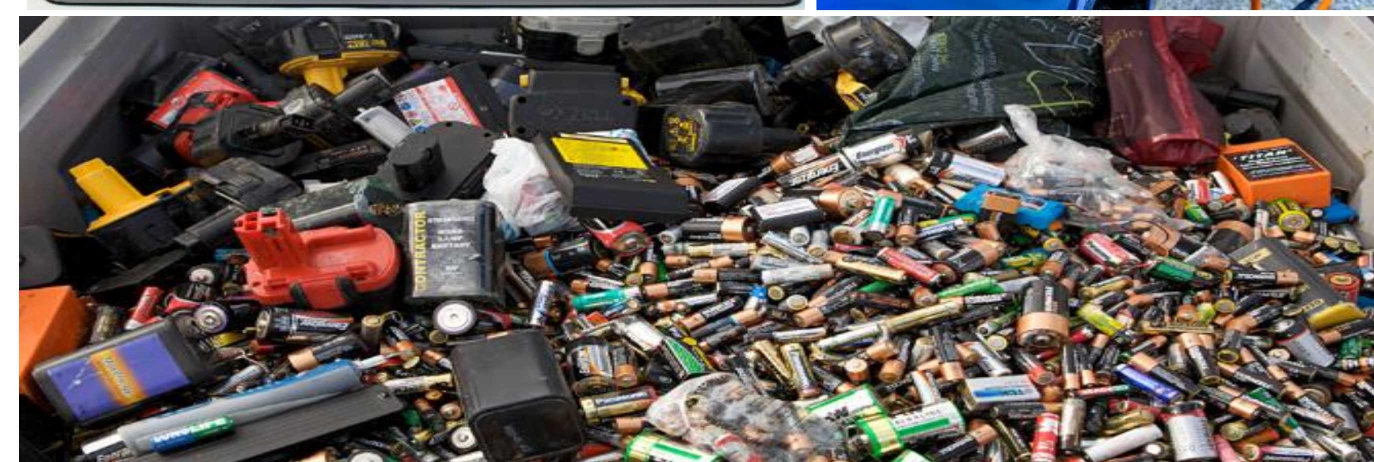


Outline

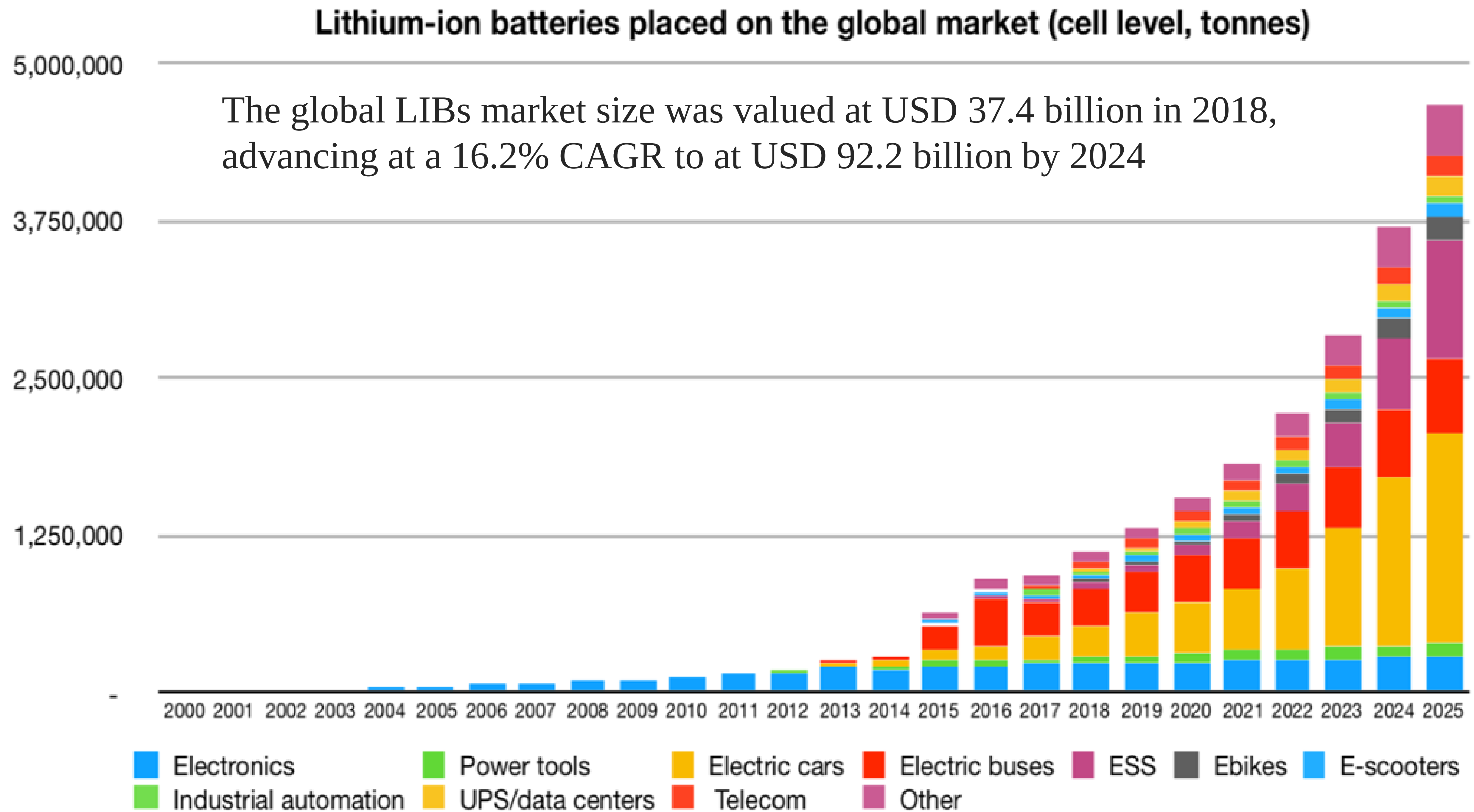
- Introduction to the basics of LIBs
  - Soaring applications and demand of LIBs
  - Principles, current status and future directions
  - Pollution release and prevention
- The rationale for recovery and reuse of LIBs
- Pretreatment and chemical extraction from spent-LIBs and their potential risks and environment pollution/mitigation
- Comparison of two major technologies: hydrometallurgy and pyrometallurgy
- Conclusions

Diverse spent Lithium-ion batteries from gigantic applications



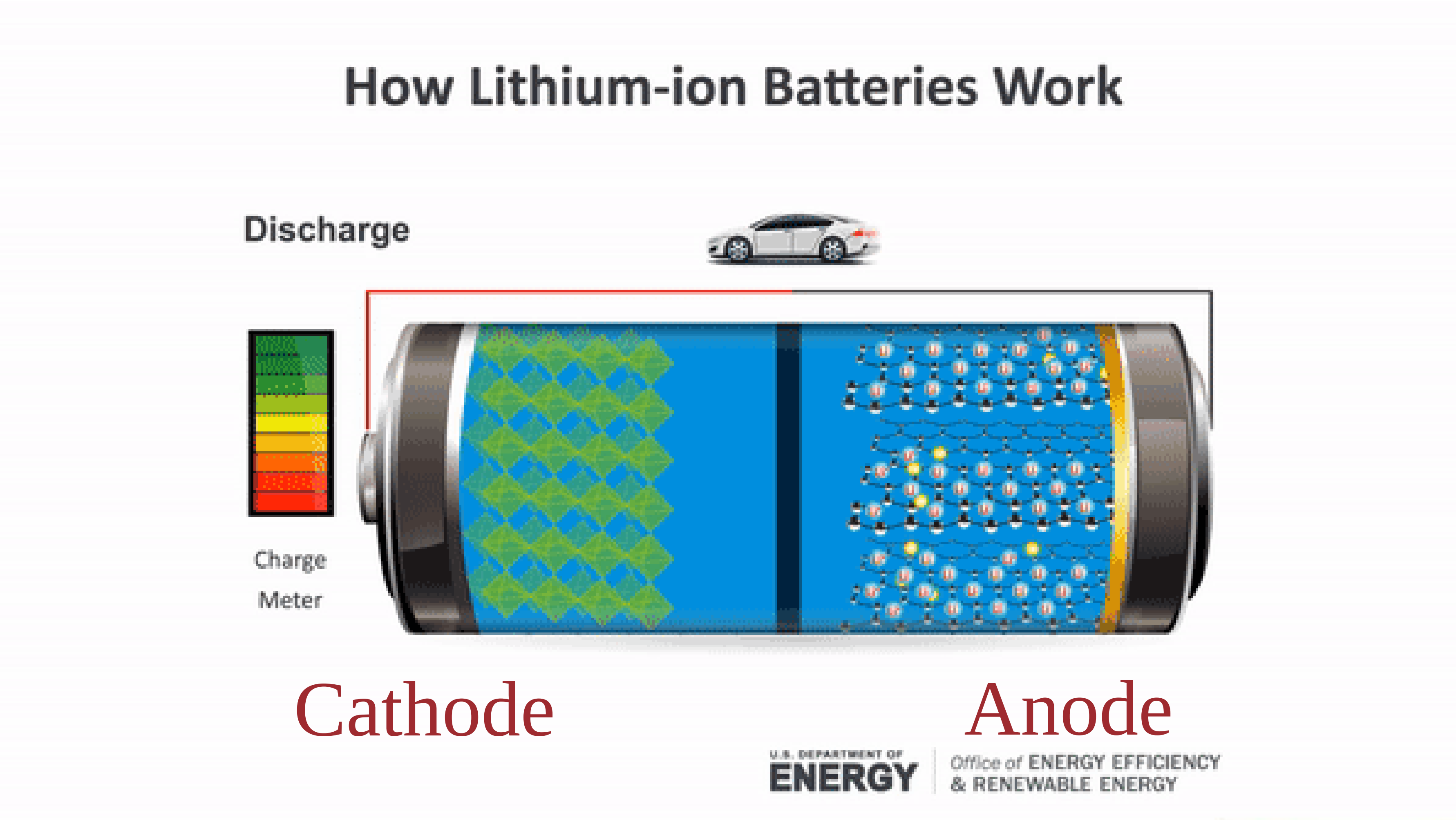


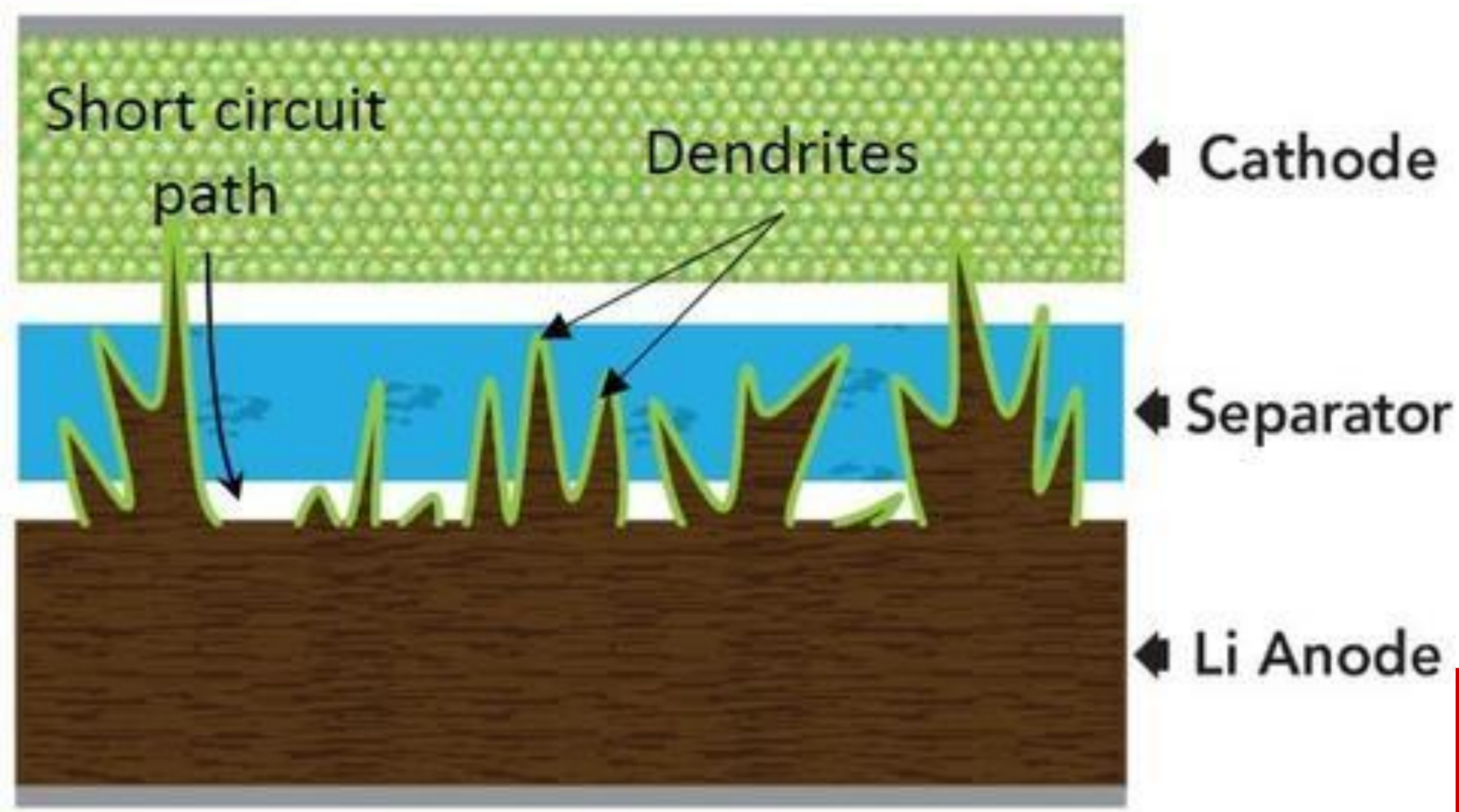
Market and Industrial Applications



The global LIBs market size was valued at USD 37.4 billion in 2018, advancing at a 16.2% CAGR to at USD 92.2 billion by 2024

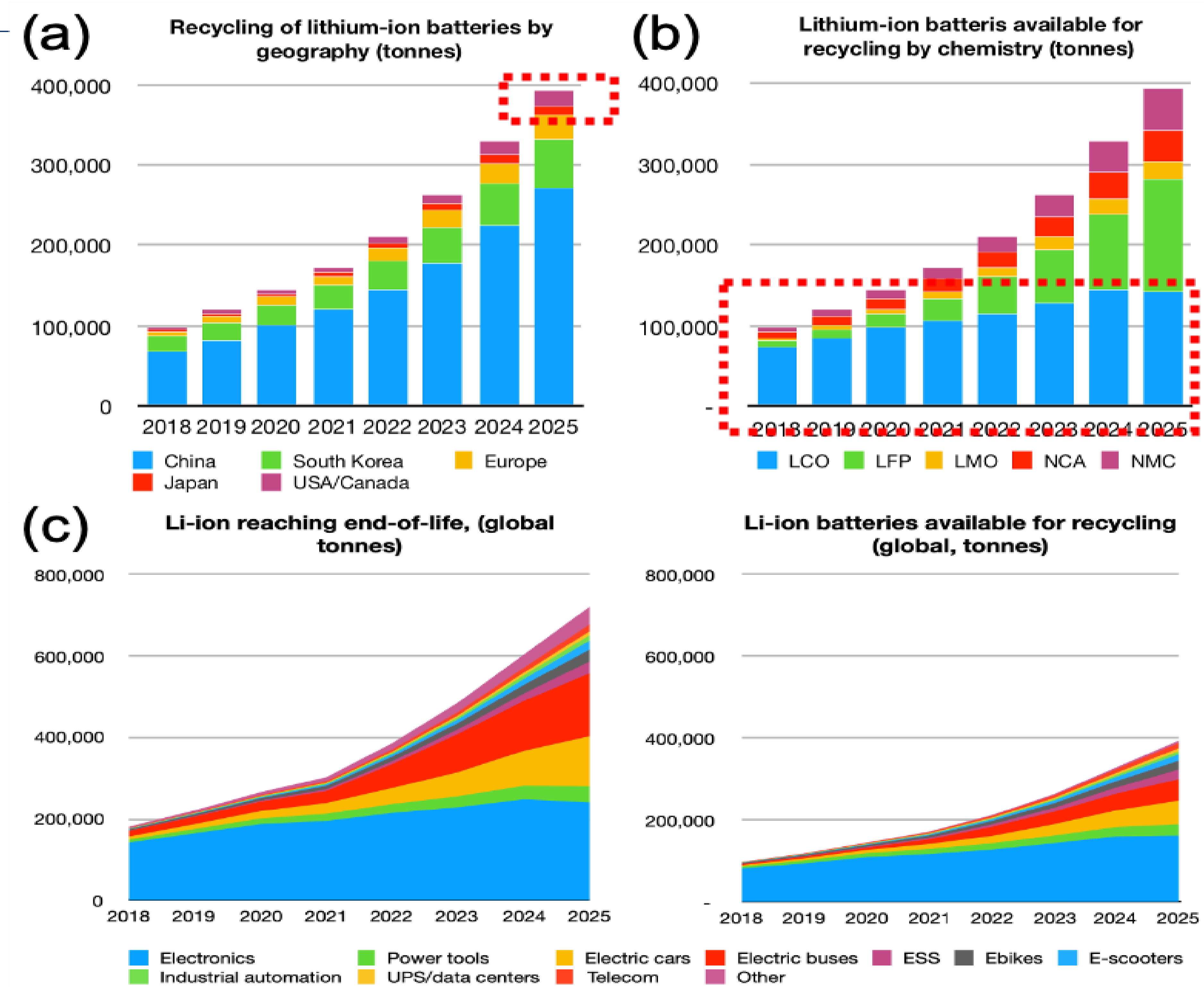
Resource: Melin, H. E. *The lithium-ion battery end-of-life market-A baseline study*; 2018.


How Lithium-ion Batteries Work
Discharge
Charge
Meter
Cathode
Anode
U.S. DEPARTMENT OF
ENERGY
Office of ENERGY EFFICIENCY
& RENEWABLE ENERGY


Short circuit
path
Dendrites
Cathode
Separator
Li Anode

Projections of amounts, types and sources of spent LIBs

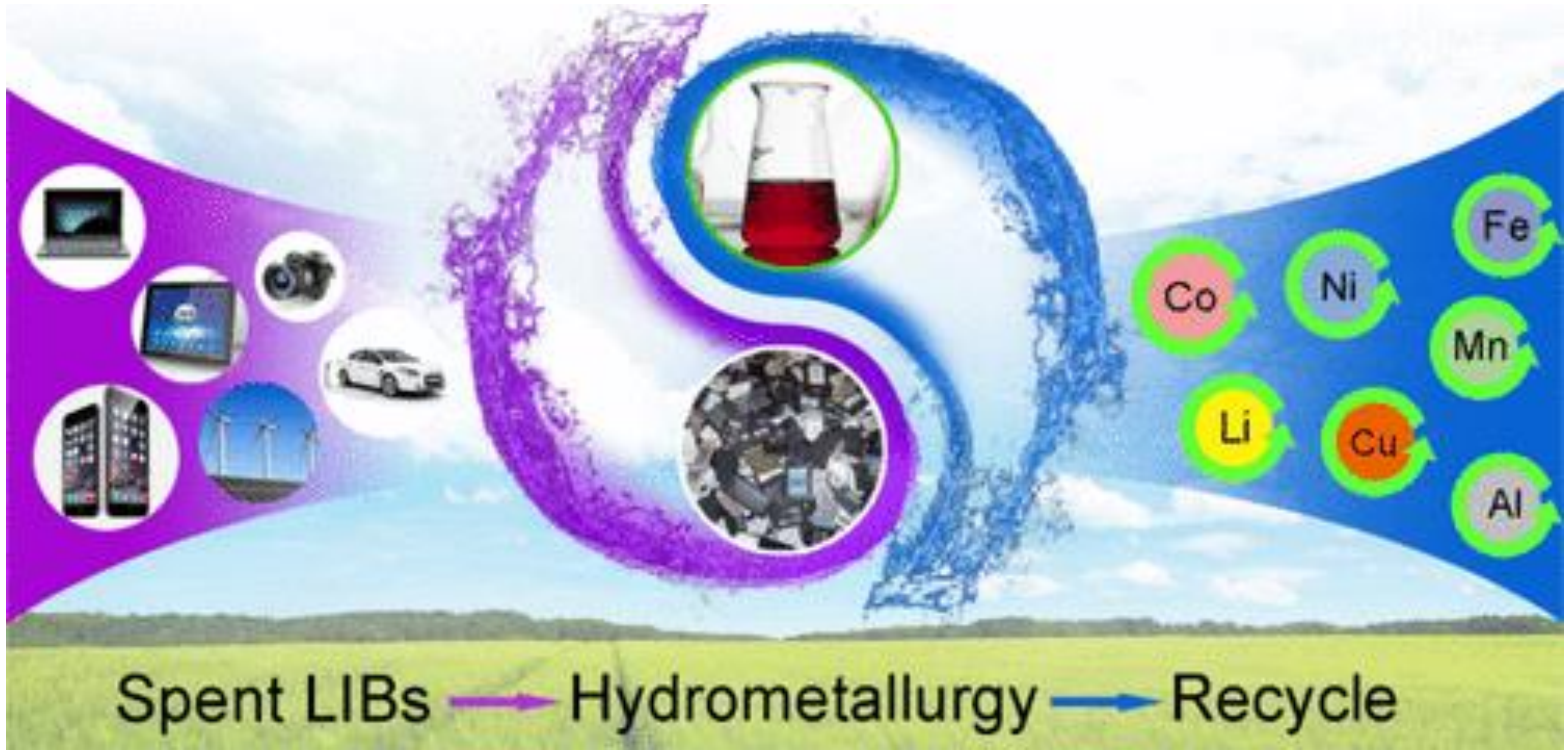
- Recycling business varies with countries
- LCO and LFP are dominant LIBs for recycling
- Electronics and EV dump increasing LIBs
- Total available LIBs for recycling: 400,000 tons globally



Melin, H. E. *The lithium-ion battery end-of-life market-A baseline study*; 2018.

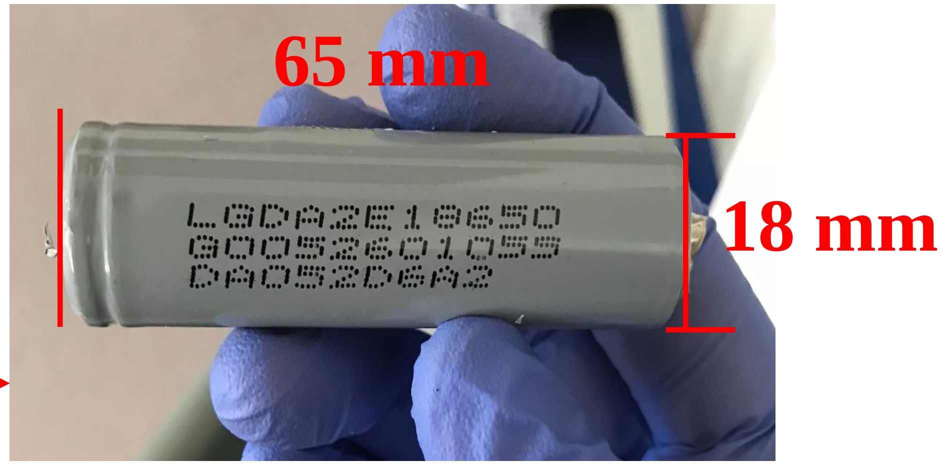
Rationale for recycle, reuse and recovery

- Pollution from excessive or increasing levels of Li, Co, and other solvents/plastics
- Water/air/soil contamination and water/energy consumption from natural mining
- Limited natural mines and supply chain



Yao, Yonglin, et al. "Hydrometallurgical processes for recycling spent lithium-ion batteries: a critical review." *ACS Sustainable Chemistry & Engineering* 6.11 (2018): 13611-13627.

18650 LCO LIBs used in our research at NJIT



- Widely used
- High value metals

Average Material Content of spent LCO Type LIBs

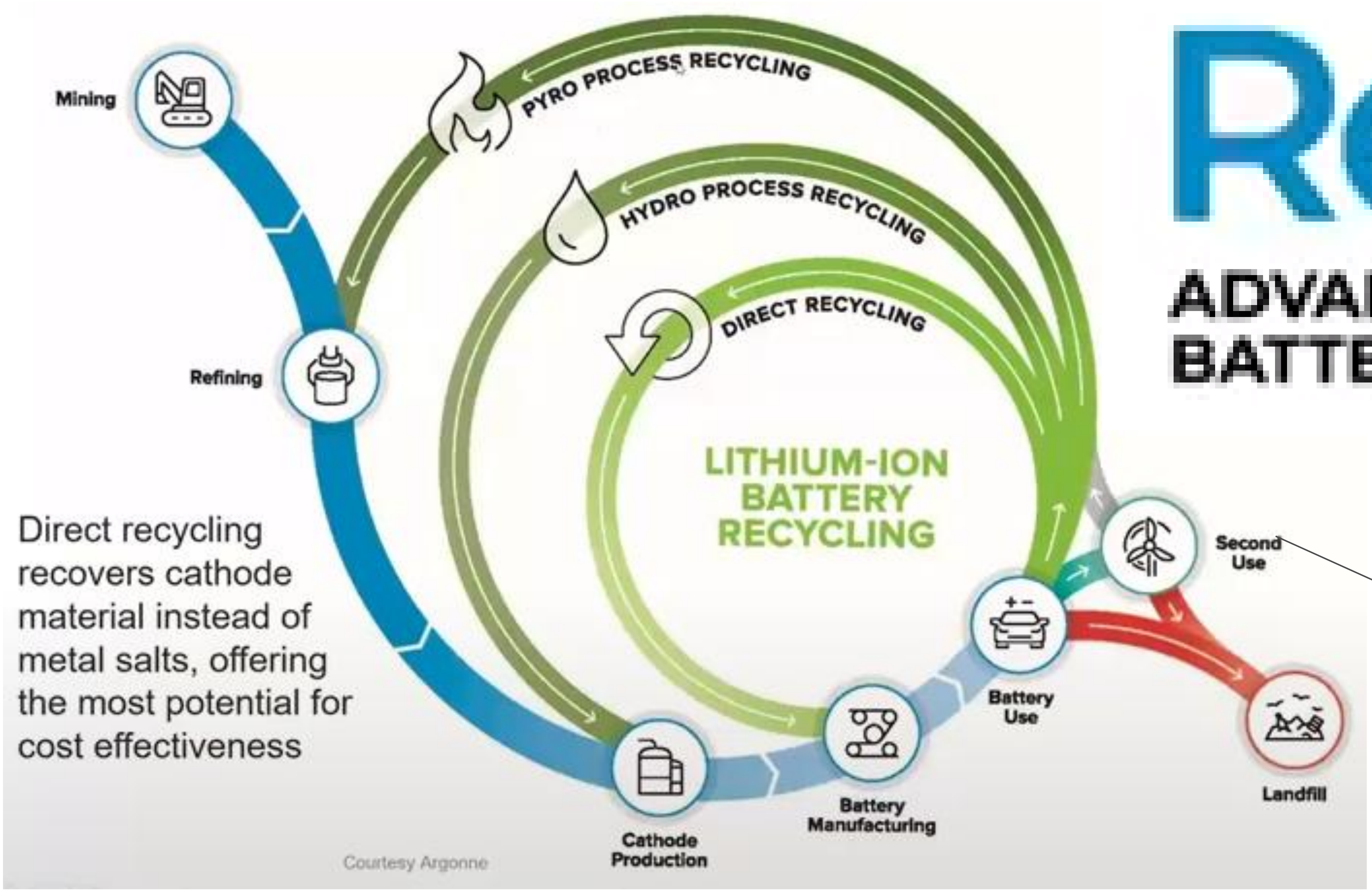
Battery component	Product data sheet in mass-%
Casing (nickel plated steel)	20-25
Cathode material ($LiCoO_2$)	25-30
Anode (graphite or lithium alloy anodes **)**	14-19
Electrolyte such as $LiPF_6$ with propylene carbonate (PC) and dimethoxyethane (DME); LiBF4, $LiCF_3SO_3$ and $LiN(SO_2CF_3)_2$	10-15
Copper foil	5-9
Aluminum	5-7
Separator (e.g., Polyolefin and ceramic-filled polyolefin PE, PP, and PP/PE/PP)	-

Lin, Leqi. "Recovery of valuable metals from spent lithium-ion batteries using organic acids: assessment of technoeconomic feasibility." (2020). Master Thesis defended in May 2020 at NJIT

NJIT New Jersey Institute of Technology

Reuse and recycling of LIB's materials

The recovered chemicals (e.g., Li and Co) can be utilized for re-synthesis of cathode materials via the sol–gel method, re-lithiation or co-precipitation



ReCell
ADVANCED BATTERY RECYCLING

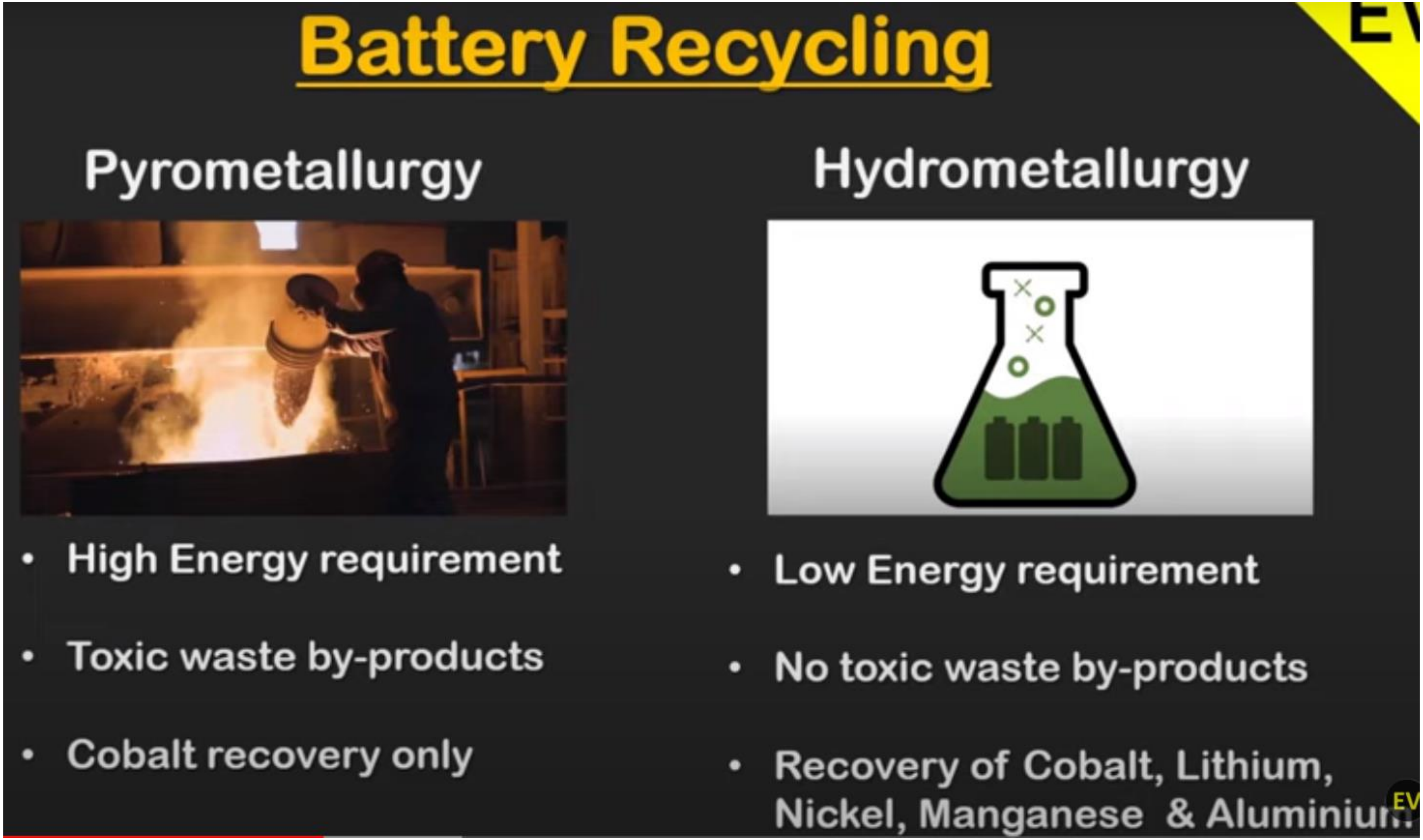
- Batteries on site for lighting energy storage, refrigerators
- Can last 7-10 years of life.

Direct recycling of LIB's materials

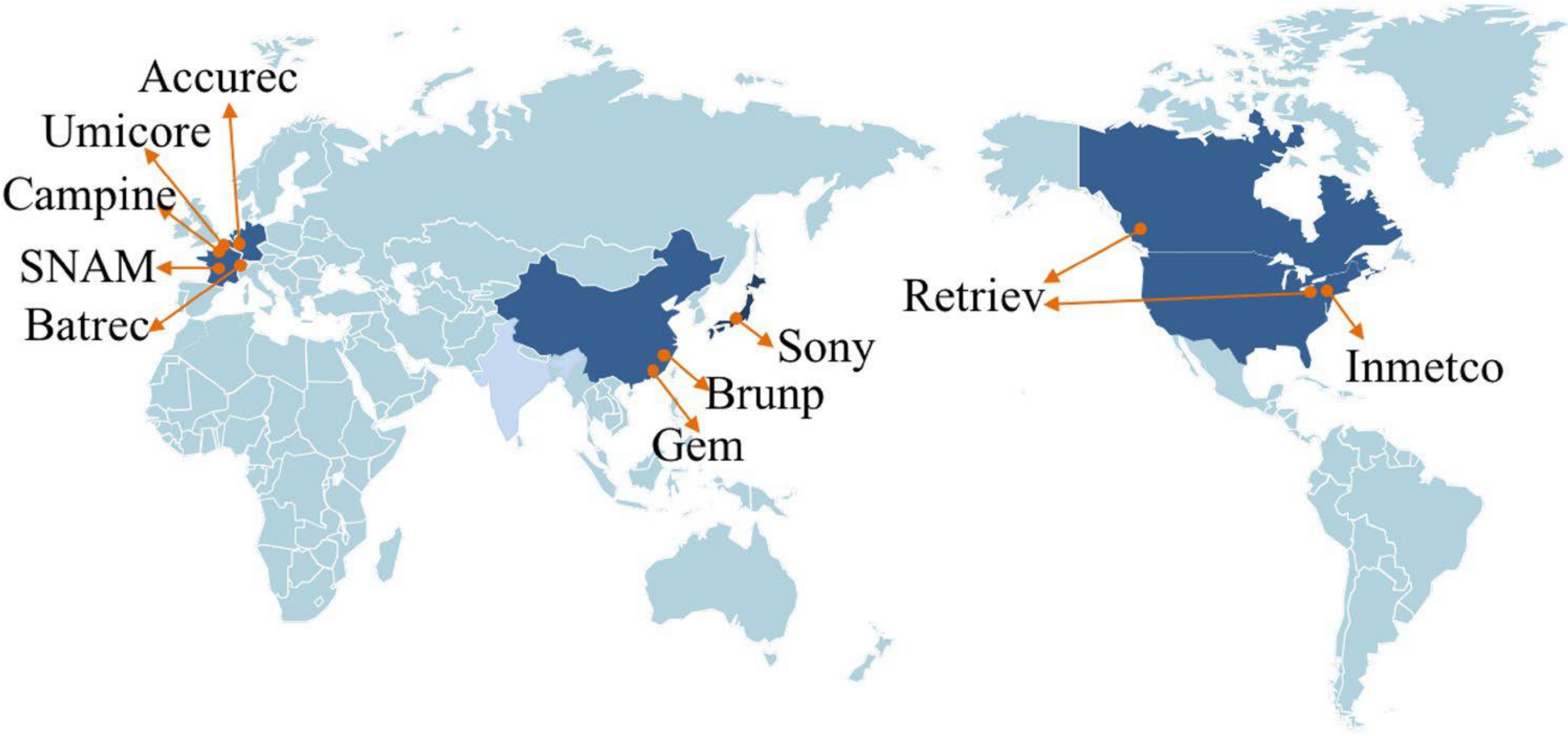
Unit Operations

Shredding
Delamination
Binder Removal
Relithiation

Hydrometallurgy and Pyrometallurgy



Major LIB recycling companies



Li, Li, et al. "The recycling of spent lithium-ion batteries: a review of current processes and technologies." *Electrochemical Energy Reviews* 1.4 (2018): 461-482.

Major LIB recycling companies and their approaches

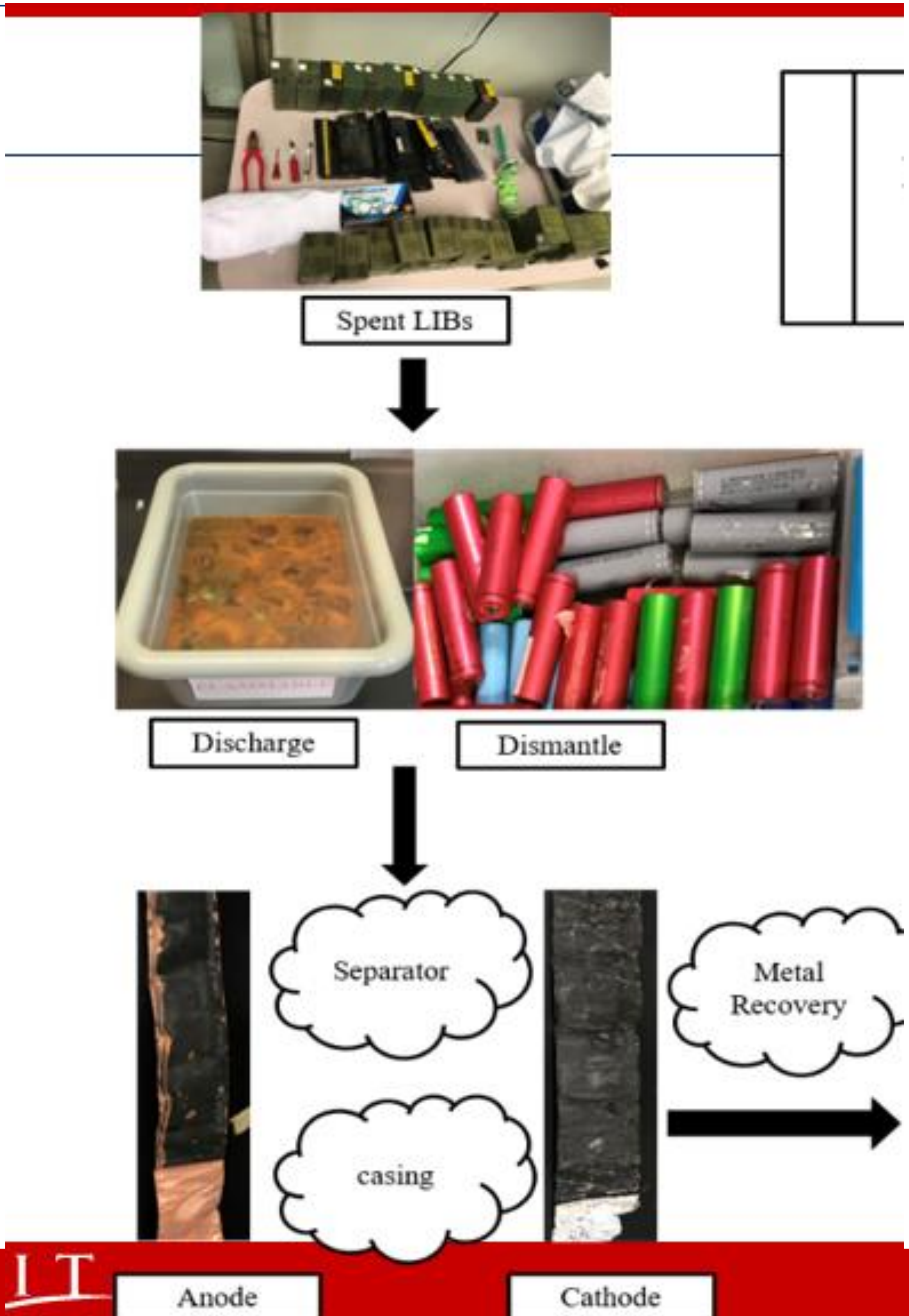
Table 2 Summary of industrial LIB recycling processes

Company	Battery type	Methods
Umicore	Li-, Ni-based	Pyrometallurgy and hydrometallurgy
Retriev **(EPA certified)**	All	Pyrometallurgy (Ni-based) Hydrometallurgy (Li-based) Mechanical process (Pb-acid)
Batrec	Li-, Hg-based	Pyrometallurgy
Accurec	All (except Pb and Hg)	Pyrometallurgy
SNAM	Li-, Ni-based	Pyrometallurgy
Inmetco	Li-, Ni-based	Pyrometallurgy
Recupyl	Li-, Zn-based	Hydrometallurgy
Sony & Sumitomo	All	Pyrometallurgy
Xstrata	Li-, Ni-based	Pyrometallurgy and hydrometallurgy
GEM	Li-, Ni-based	Hydrometallurgy
Brunp	Li-, Ni-based	Hydrometallurgy

Li, Li, et al. "The recycling of spent lithium-ion batteries: a review of current processes and technologies." *Electrochemical Energy Reviews* 1.4 (2018): 461-482.

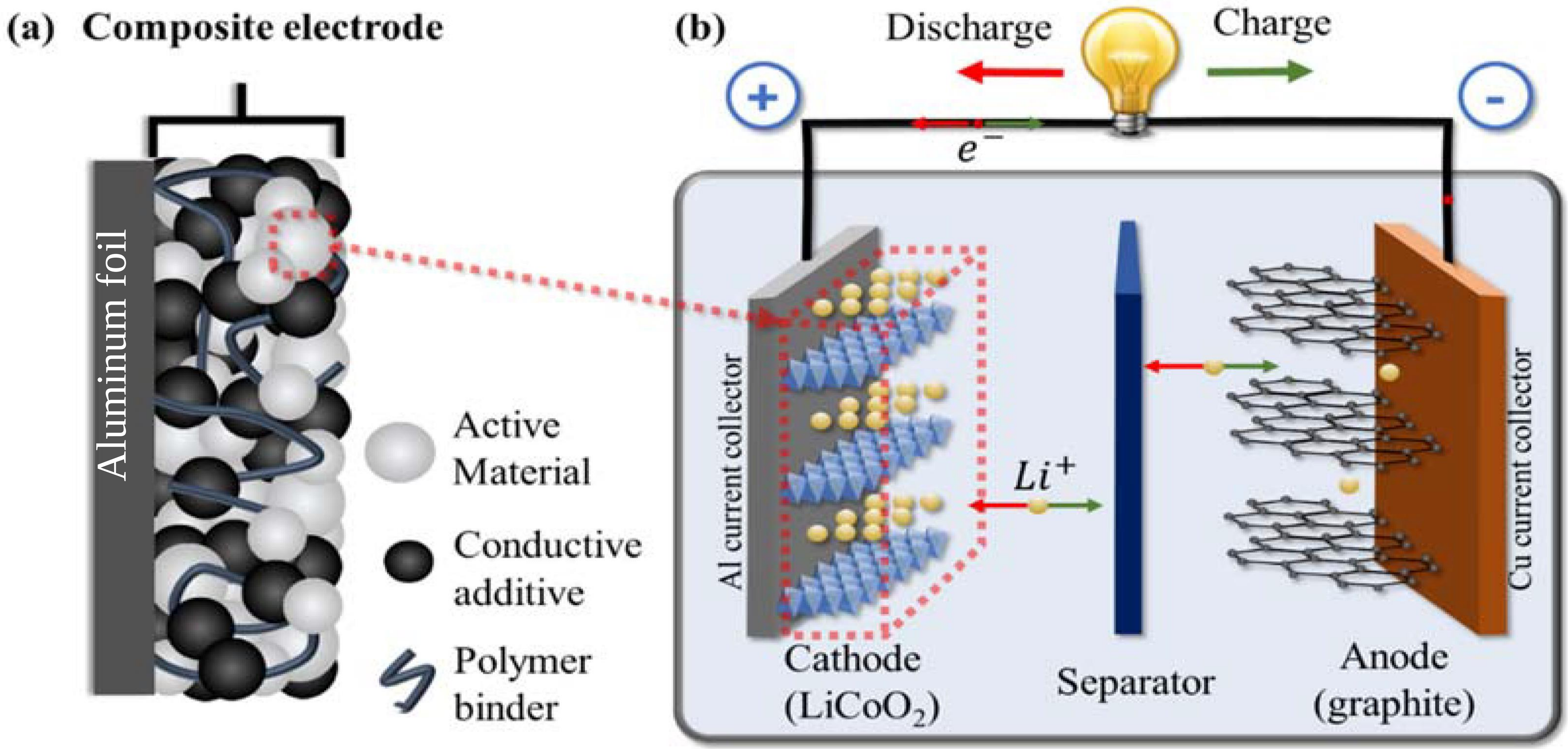
Potential risks and environmental pollution

- Battery combustion or explosion if not fully discharged.
- Volatile electrolyte emission: harmful to human health
- Sharps and skin cut when unfolding the casing/separator materials



Potential risks and environmental pollution for the cathode recovery

Organic solvents such as N-methyl pyrrolidone (NMP), trifluoroacetate (TFA) or dimethylformamide (DMF) are usually chosen to dissolve the polyvinylidene fluoride (PVDF) or Polytetrafluoroethylene (PTFE) binders at the temperature below 100 ^oC for 1 h.

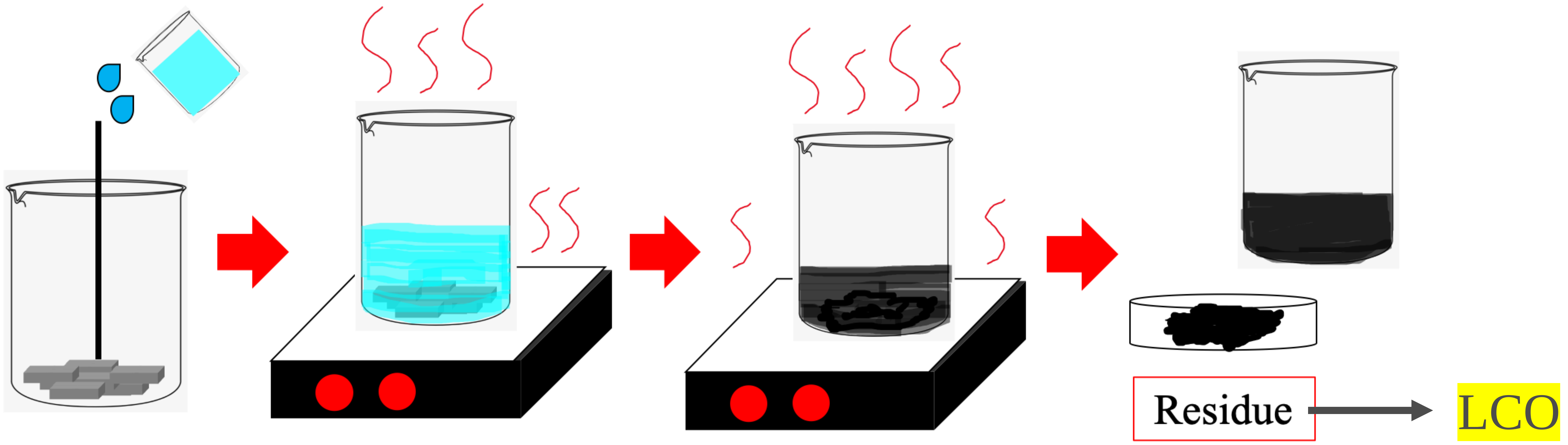


Potential risks and environmental pollution for cathode treatment

Sodium hydroxide (NaOH) is commonly used to separate the cathode materials from the aluminum foil, which produces sodium aluminum oxide waste.

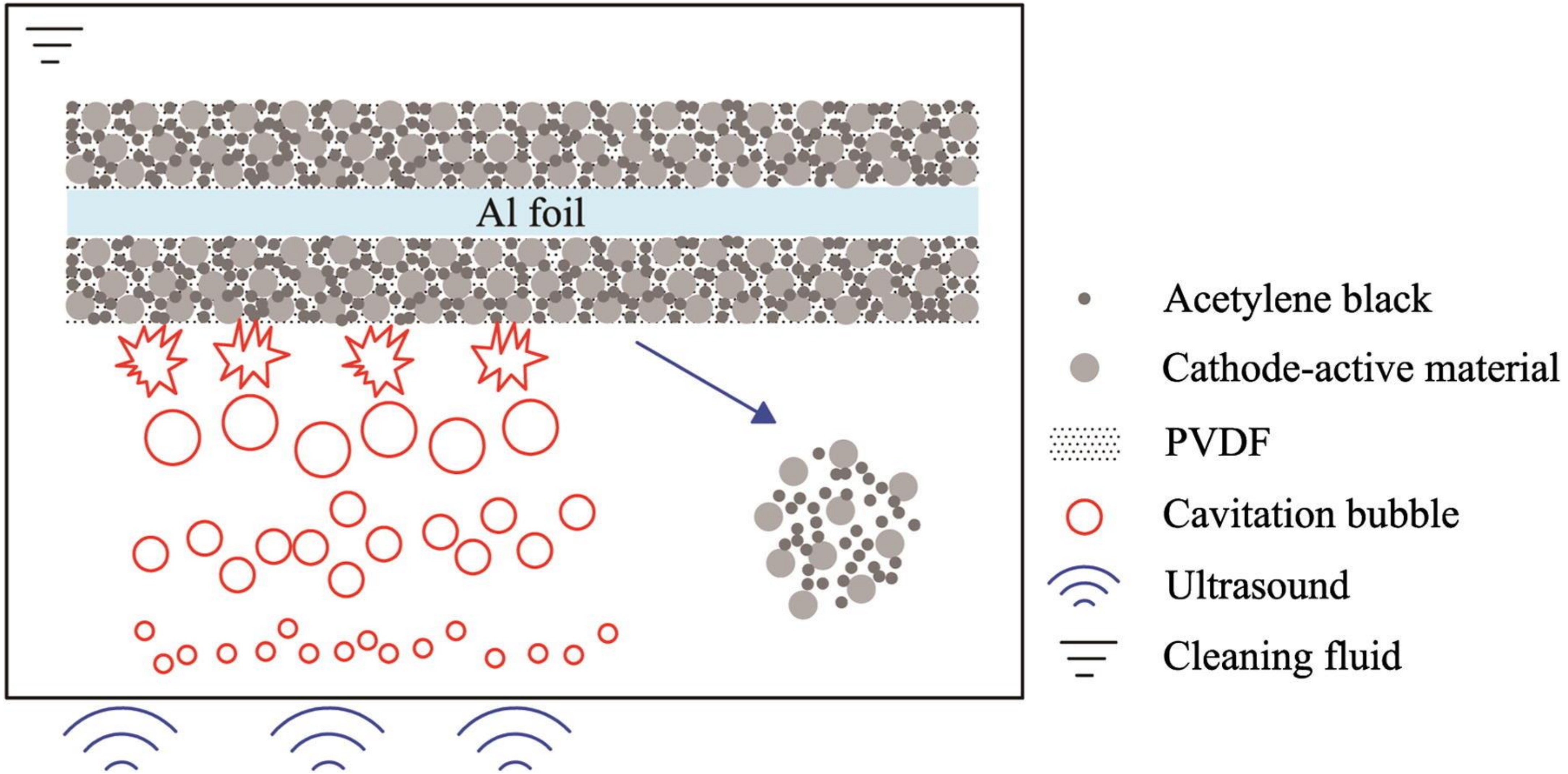
$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]$$

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



Environmental pollution abatement in hydrometallurgy or pyrometallurgy

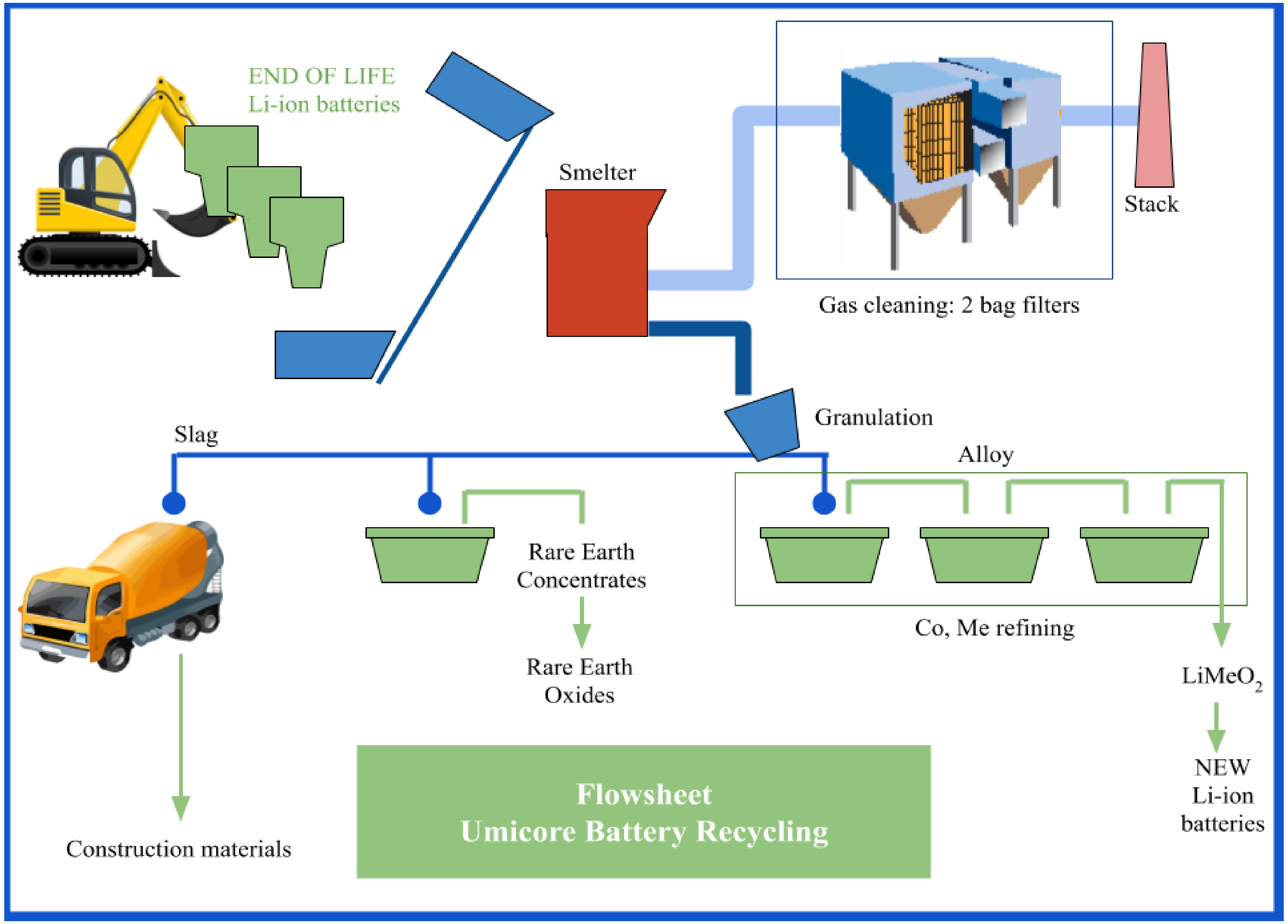
- Ultrasonication: agitation detaches cathode particles from aluminum foil but thermal treatment of the collected cathode is often needed to eliminate remaining carbon (i.e., graphene) and PVDF binder.
- Direct thermal treatment at 350-800 °C in furnace to decompose most organic binders. However, toxic vapor gases such as hydrofluoric acid (HF) are released and must be treated by air scrubber.



Pyrometallurgy Method

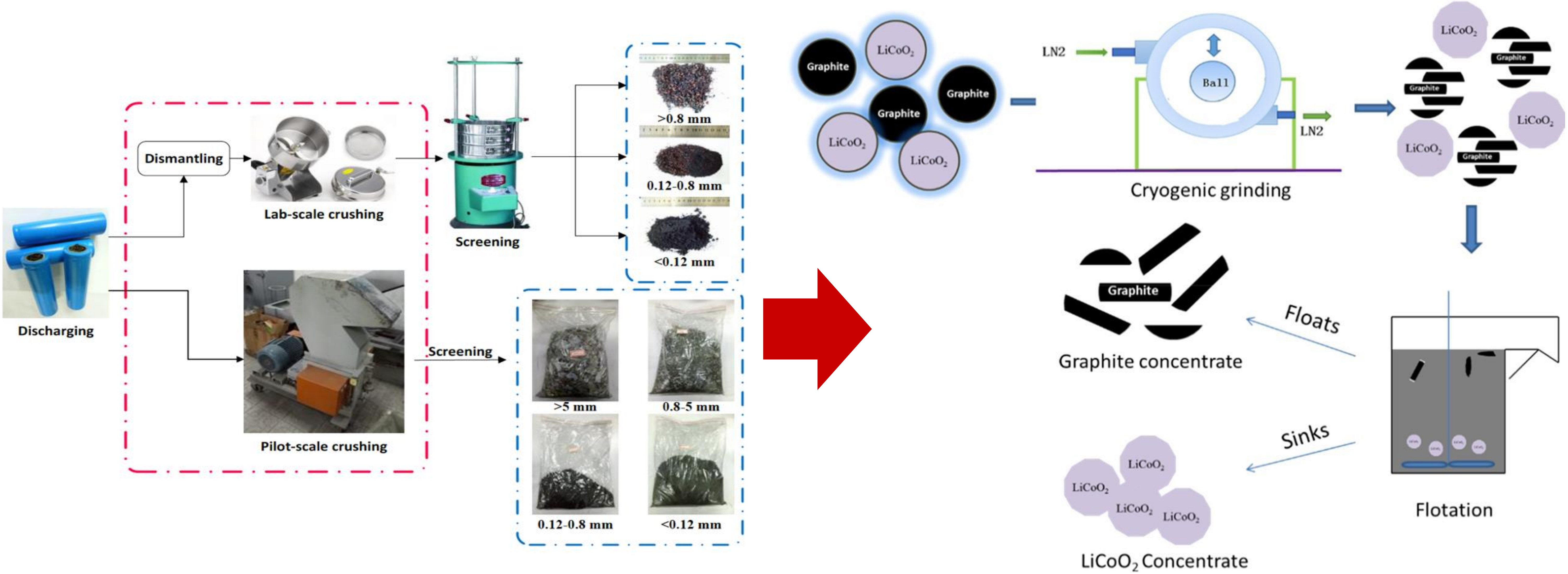
Pyrometallurgy, widely used by industries such as Umicore, Accurec, Sony, Onto and Inmetco,[106] involves the combustion of organic materials at high temperatures to reduce and smelt metals.

1. pyrolyzed in a furnace at 300-500 ºC to evaporate the electrolyte and plastic housing
2. 1400-1700 ºC where they are transformed to metal alloys
3. Li is usually lost in the form of slag residue and gaseous Li_2O or Li_2CO_3 due to the high temperature (over 500 ºC).
4. Low efficiency, high energy consumption, and pollution ar.



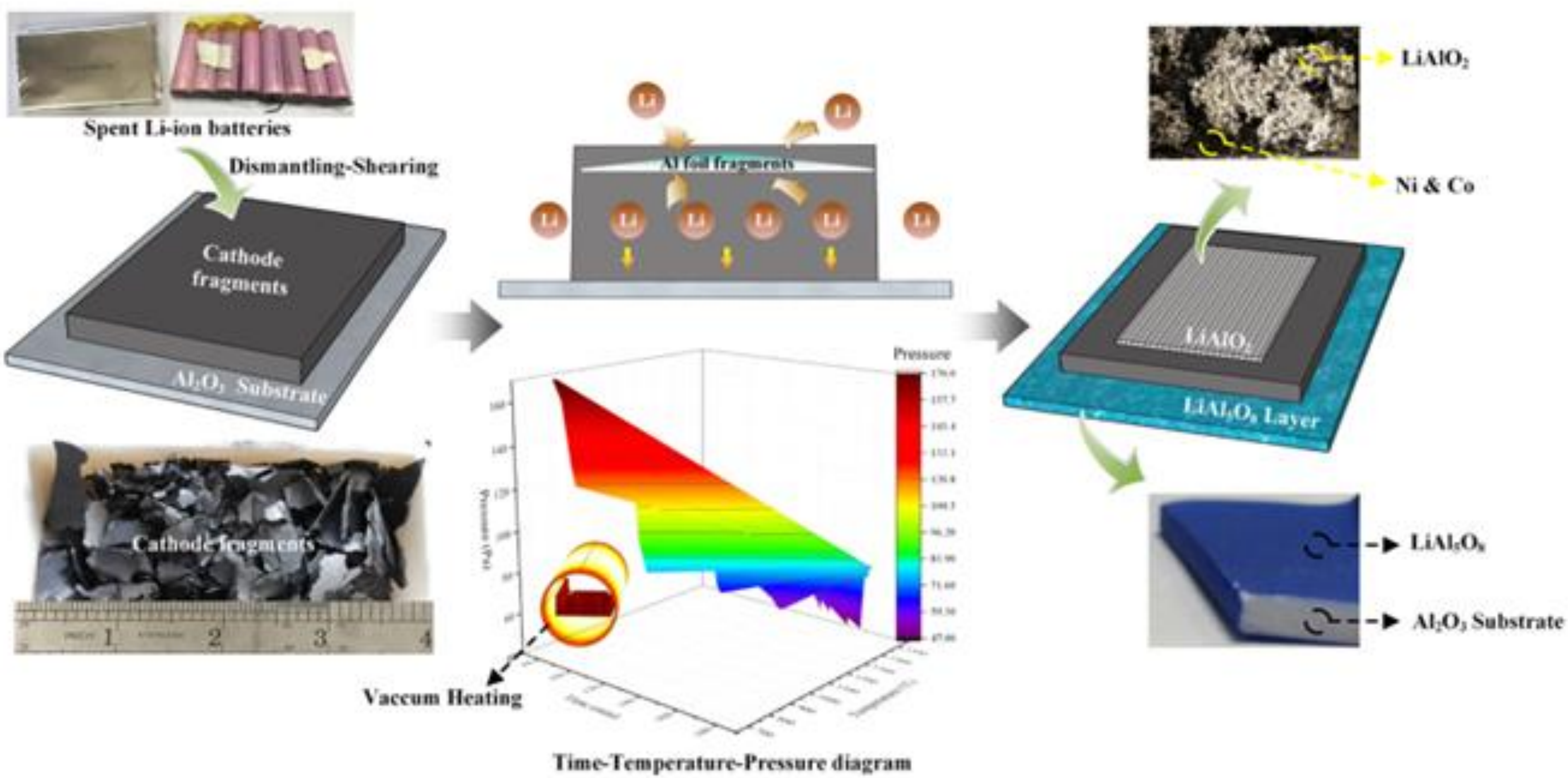
Environmental pollution abatement

Novel approaches in mechanical separation processes of crushing, removing, housing, skinning, shredding, shearing and sieving.



Vacuum Heating Method in **Pyrometallurgy**

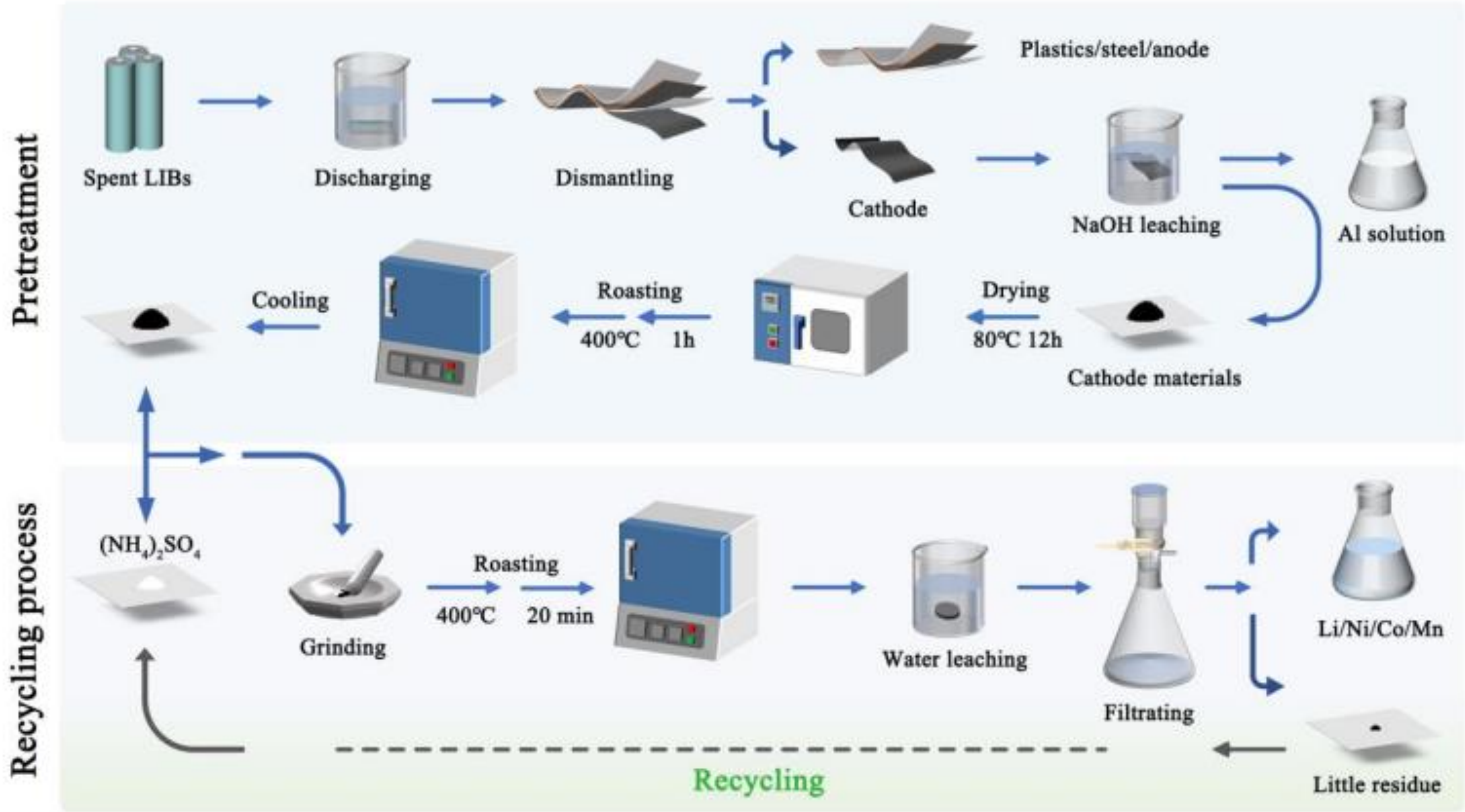
Vacuum heating is an environment-friendly technology to recover high value γ – $LiAlO_2$ and $LiAl_5O_8$ under vacuum and high temperature (1723 K) conditions. Ni−Co alloy particles were removed from the sample by magnetic separation.



doi.org/10.1021/acs.est.1c00694.

Low-Temperature Roasting Approach

A low-temperature and acid-free leaching method to recycle spent $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$(NMC111) via ammonium sulfate roasting and water leaching.



doi:10.1021/acssuschemeng.0c01205.s001.

Conclusions

1. Li/Ni/Co/Mn, and more specifically Li and Co, are commodities in high demand because of their high values and demand for electronics and battery manufacturing
2. Most lithium batteries end up in a landfill so far in the US with less than 5 percent of lithium batteries are recycled at the end of their lives.
3. Recycling spent LIBs can reduce the material demand from foreign countries, potentially leading to sustainable material management and national security of key materials for economy.
4. Currently recycling processes are energy-intensive, produce toxic byproducts, and only recover some of the metals present, like cobalt and nickel.
5. Many obstacles for conventional recovery of cathodic materials through pyro-metallurgy (operations at elevated temperatures) and hydrometallurgy (leaching of elements from solid matrix and their subsequent precipitation)

Backup/supplementary slides in the following

Industrial Recycling Processes

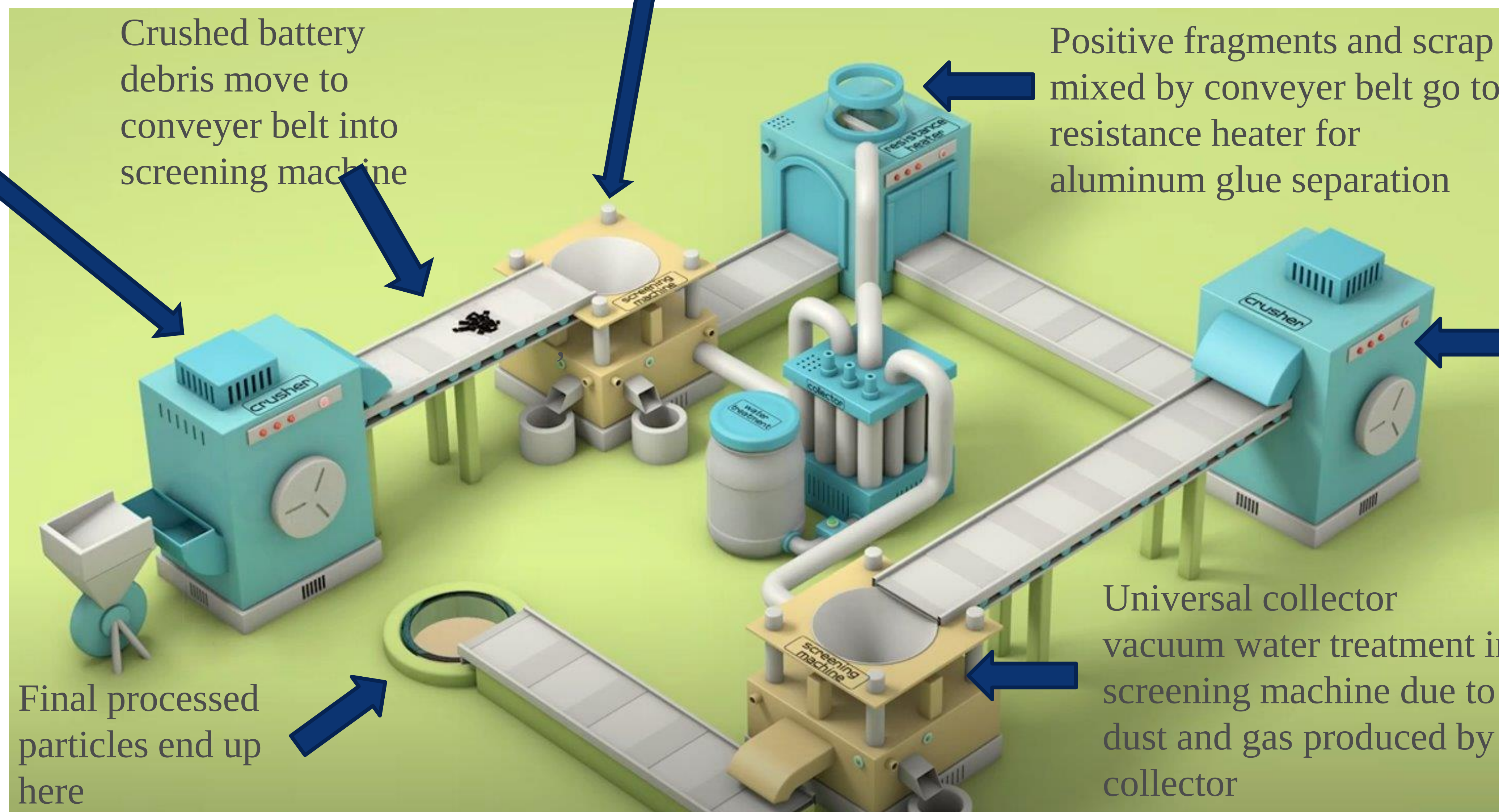
Waste batteries mixed into broken crusher

Crushed battery debris move to conveyer belt into screening machine

Screening machine separates iron filings, aluminum scrap

Positive fragments and scrap mixed by conveyer belt go to resistance heater for aluminum glue separation

Scrap crushed and sieved for battery cathode powder and aluminum power

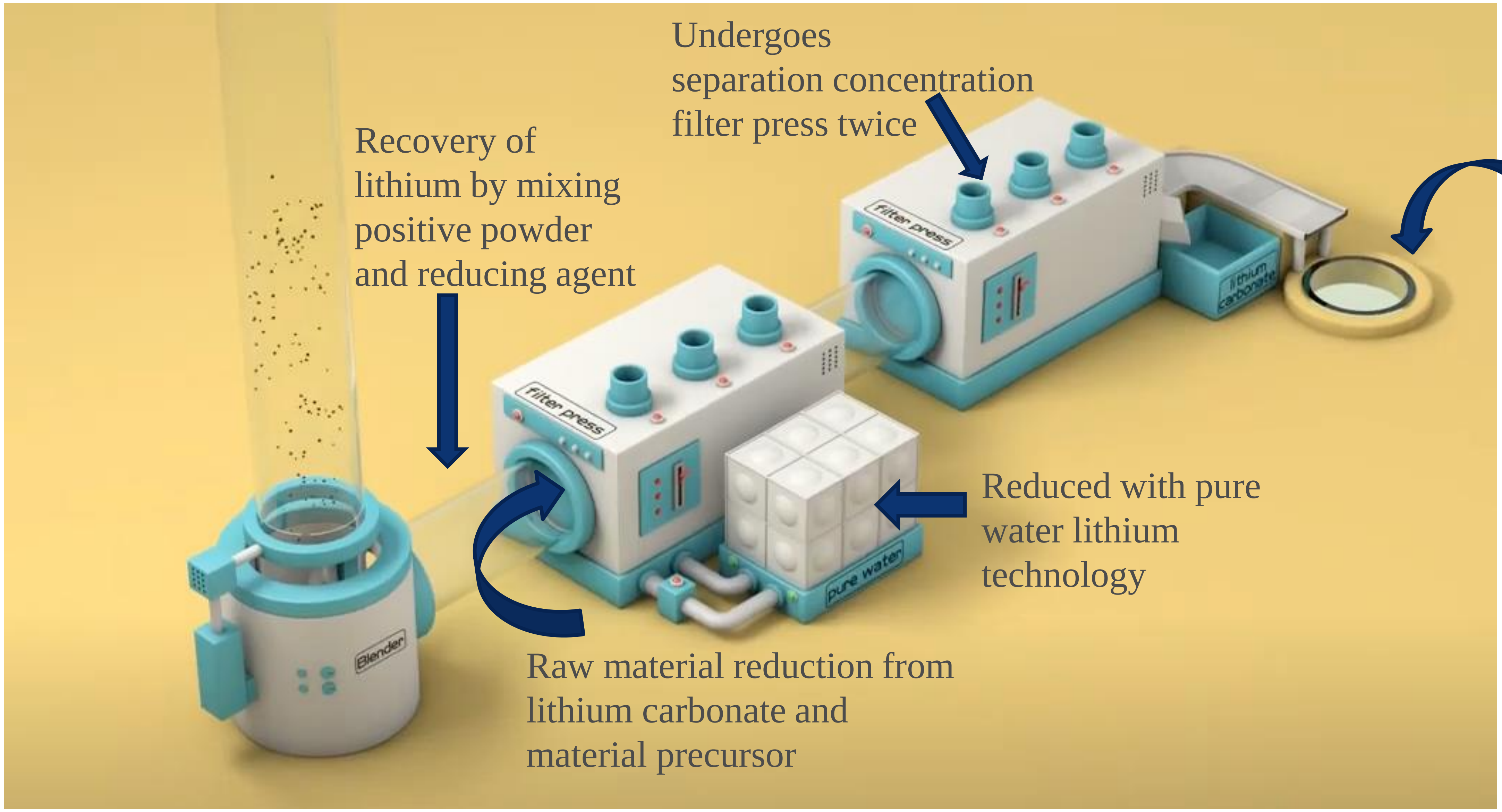


Universal collector vacuum water treatment in screening machine due to dust and gas produced by collector

Final processed particles end up here

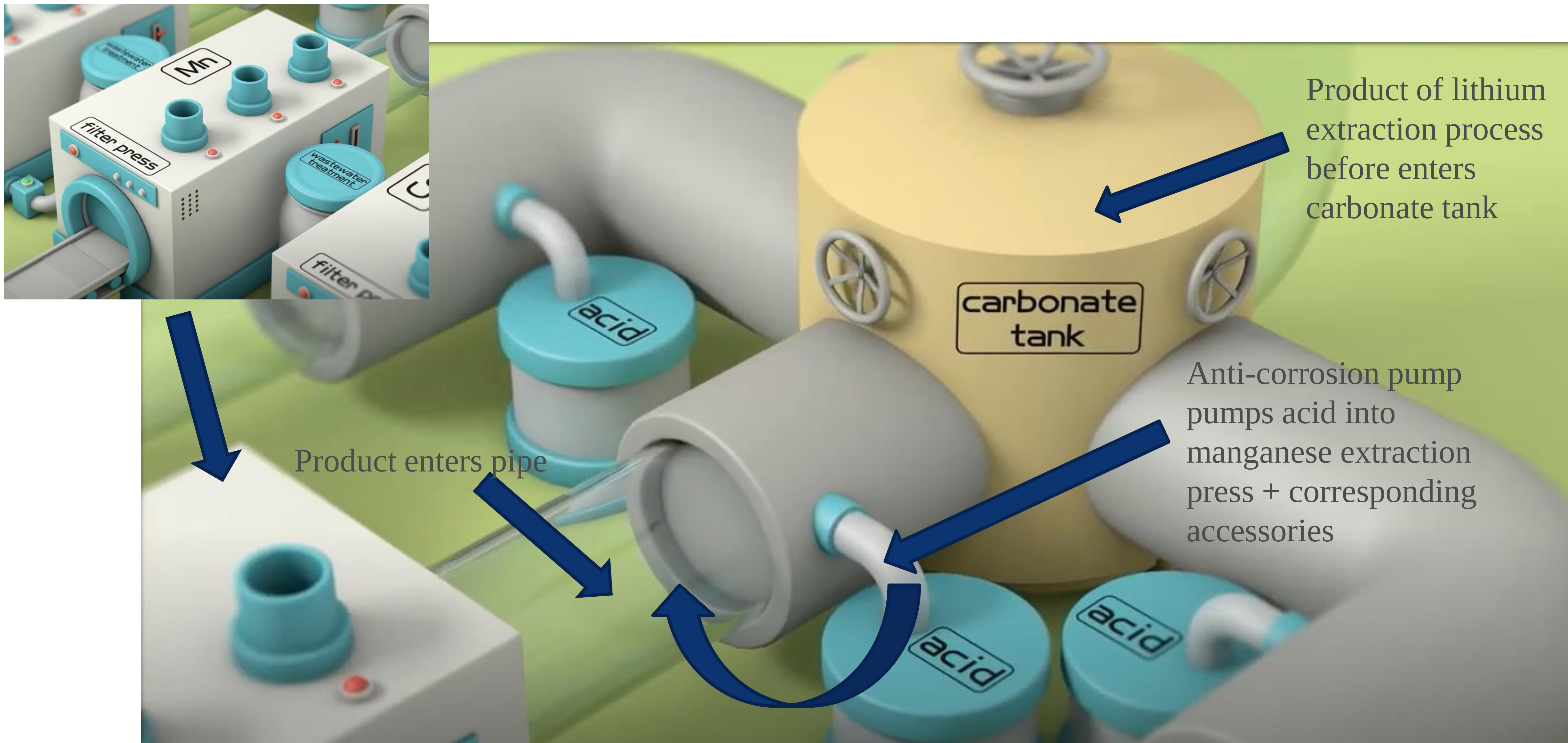
(Anhua Taisen Recycling Technology Co. Ltd., 2018)

Industrial Recycling Processes



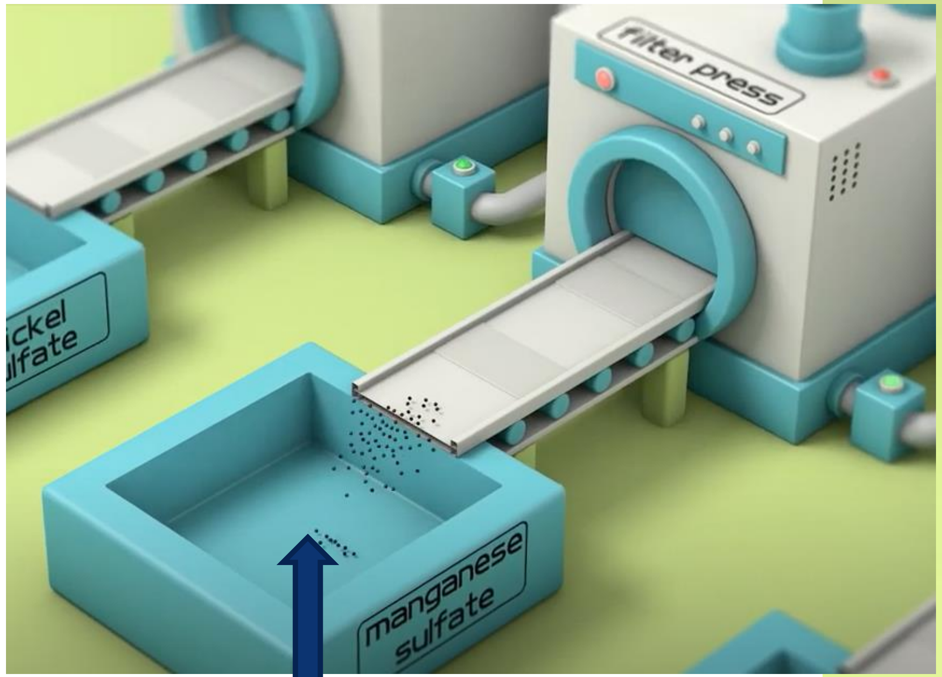
(Anhua Taisen Recycling Technology Co. Ltd., 2018)

Industrial Recycling Processes

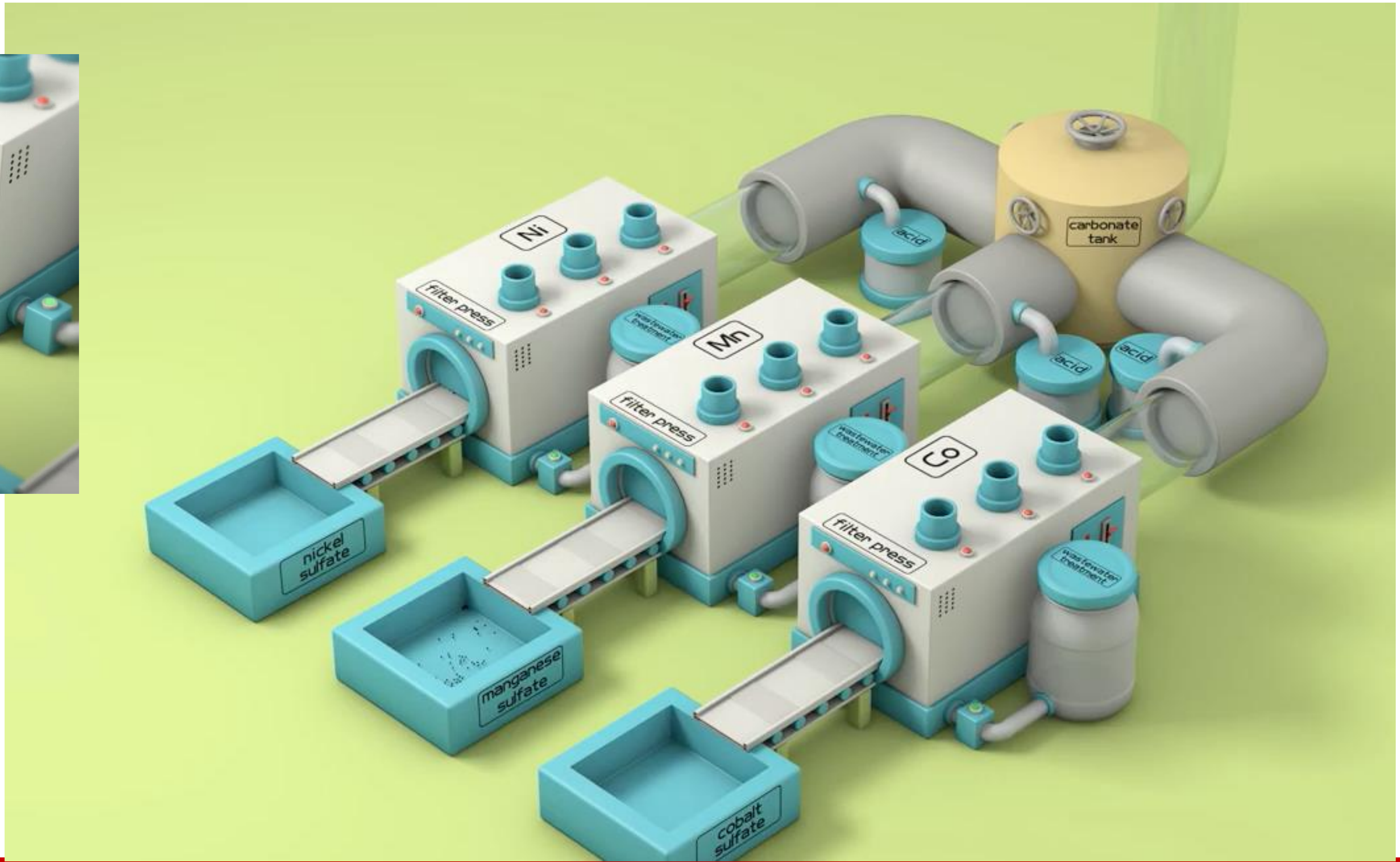


(Anhua Taisen Recycling Technology Co. Ltd., 2018)

Industrial Recycling Processes



Manganese filter press from before releases manganese sulfate



(Anhua Taisen Recycling Technology Co. Ltd., 2018)