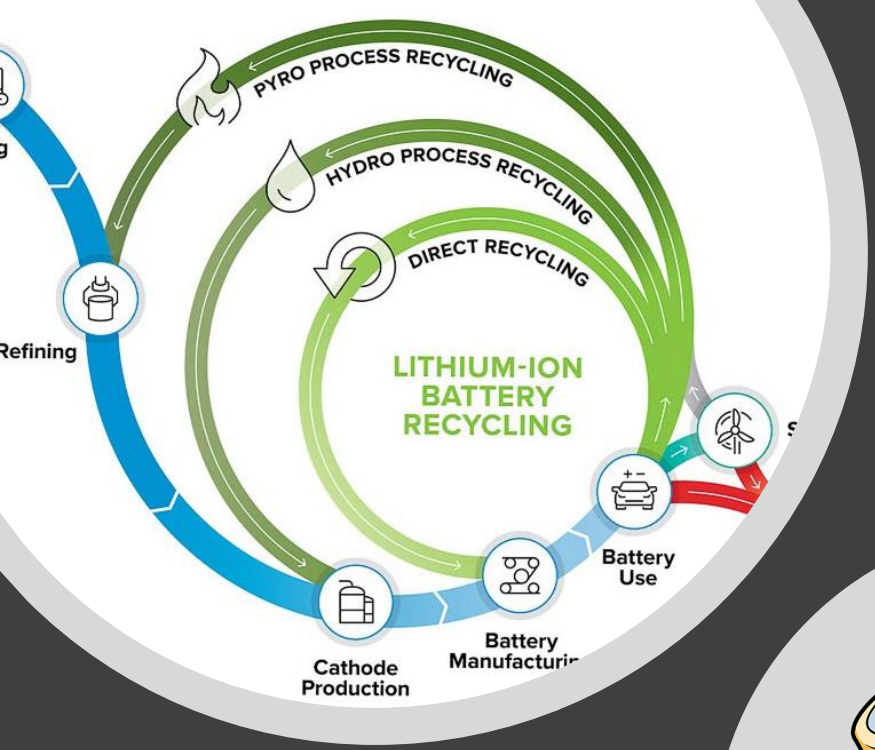

Az akkumulátorok és azok újrahasznosításának fontossága a fenntartható elektromobilitás tükrében

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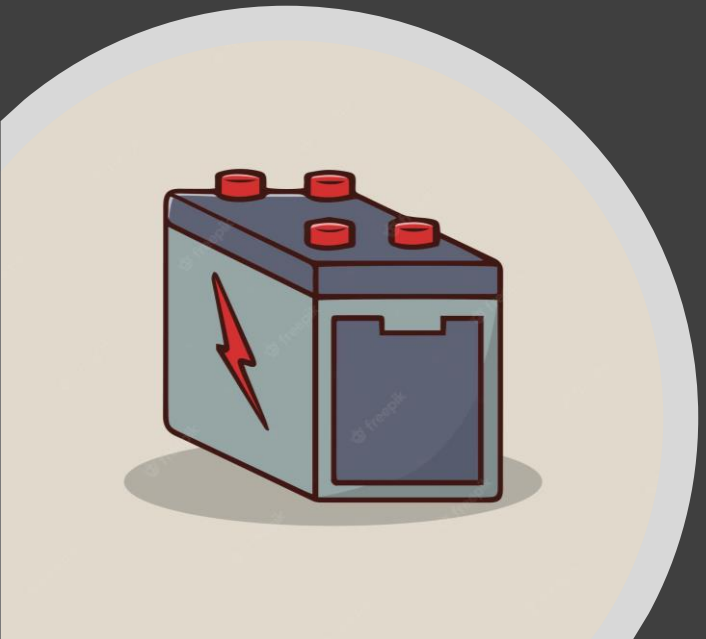
tudományos főmunkatárs, kutatócsoport vezető
Természettudományi Kutatóközpont (TTK), Anyag- és Környezetkémiai Intézet



V. Magyar Közlekedési Konferencia - 46. Útügyi Napok
Heves Megyei Területi Szervezet, Közlekedésépítési Tagozat, Közúti Szakosztály,
2022. október 11-13.

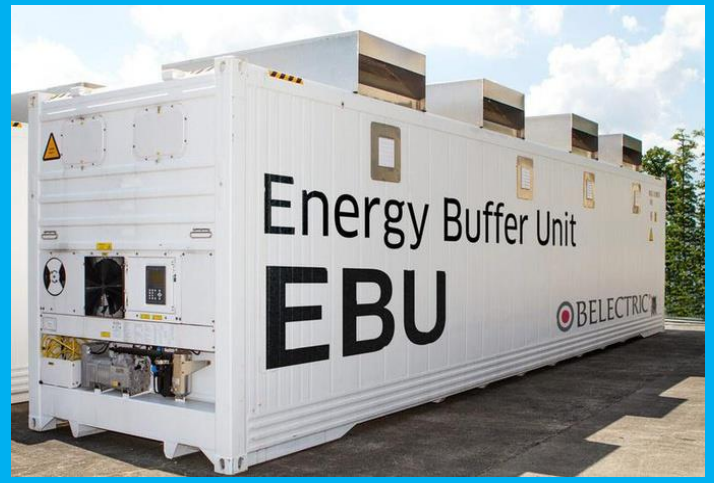
Importance of the electrochemical energy storage

Stationary applications

solar

wind

wave



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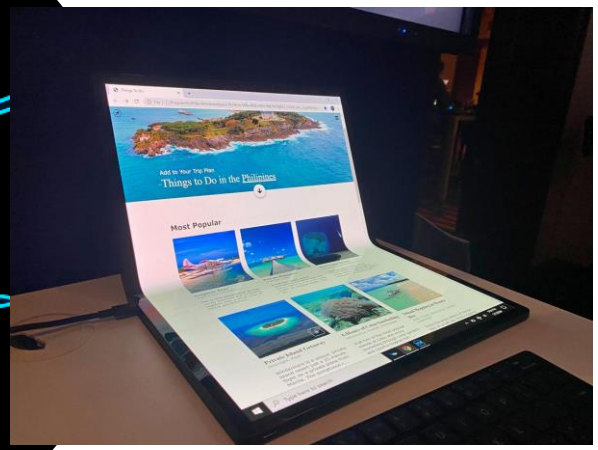
Importance of the electrochemical energy storage

Mobile applications

electric bikes

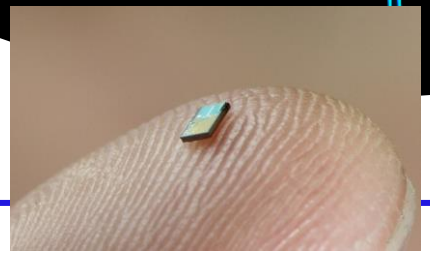
power tools

battery electric coach

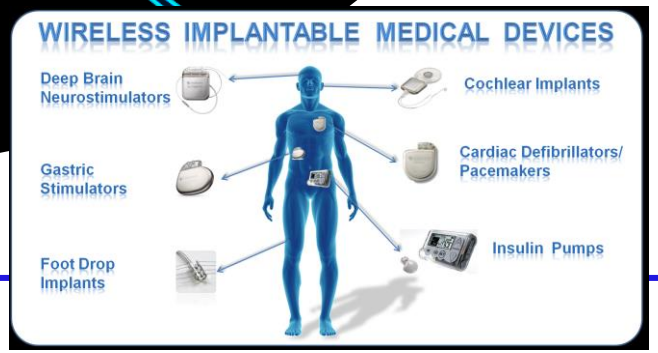


flexible electronics

battery electric vehicle



„smart dust”



digital implants

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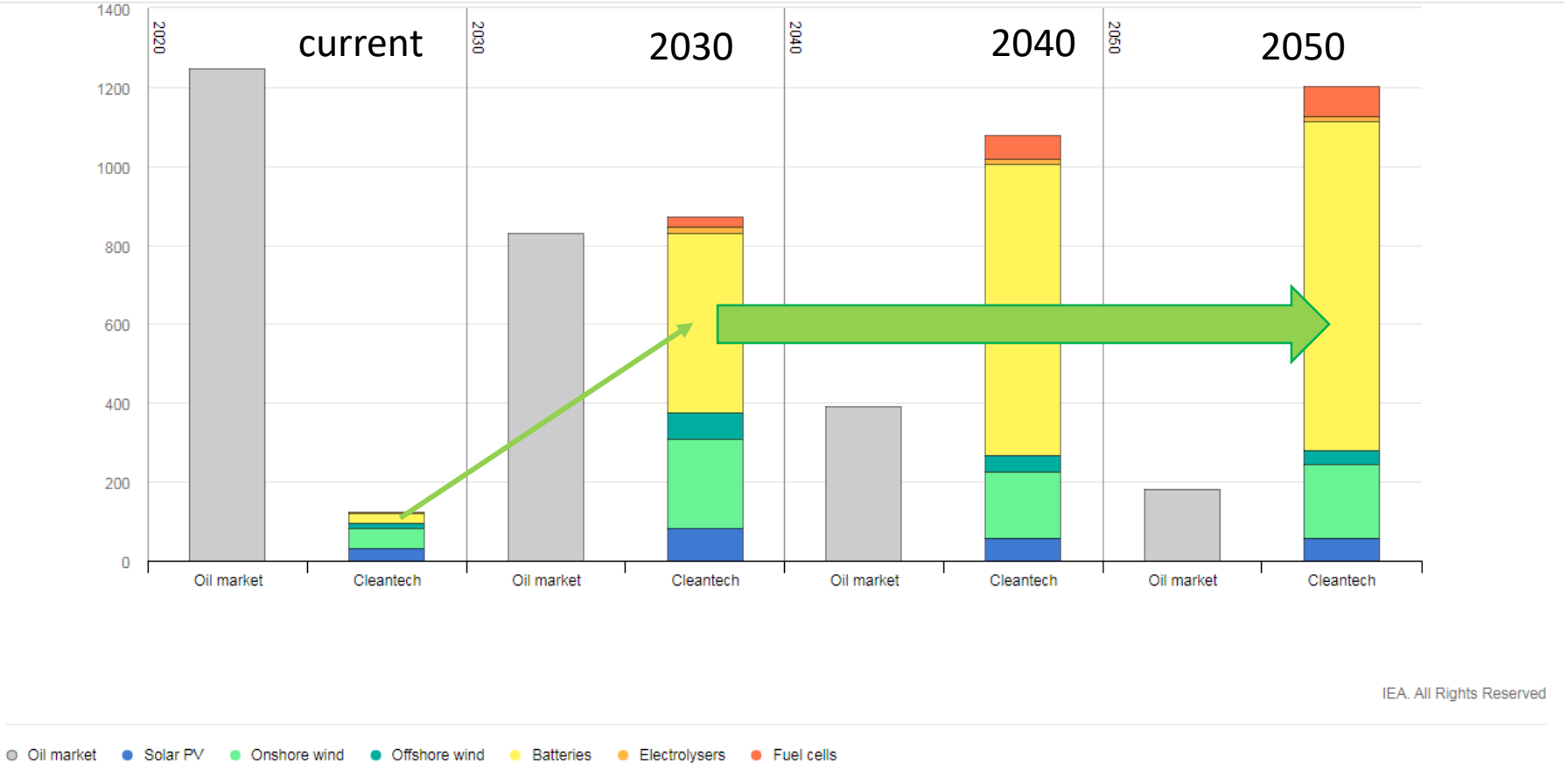
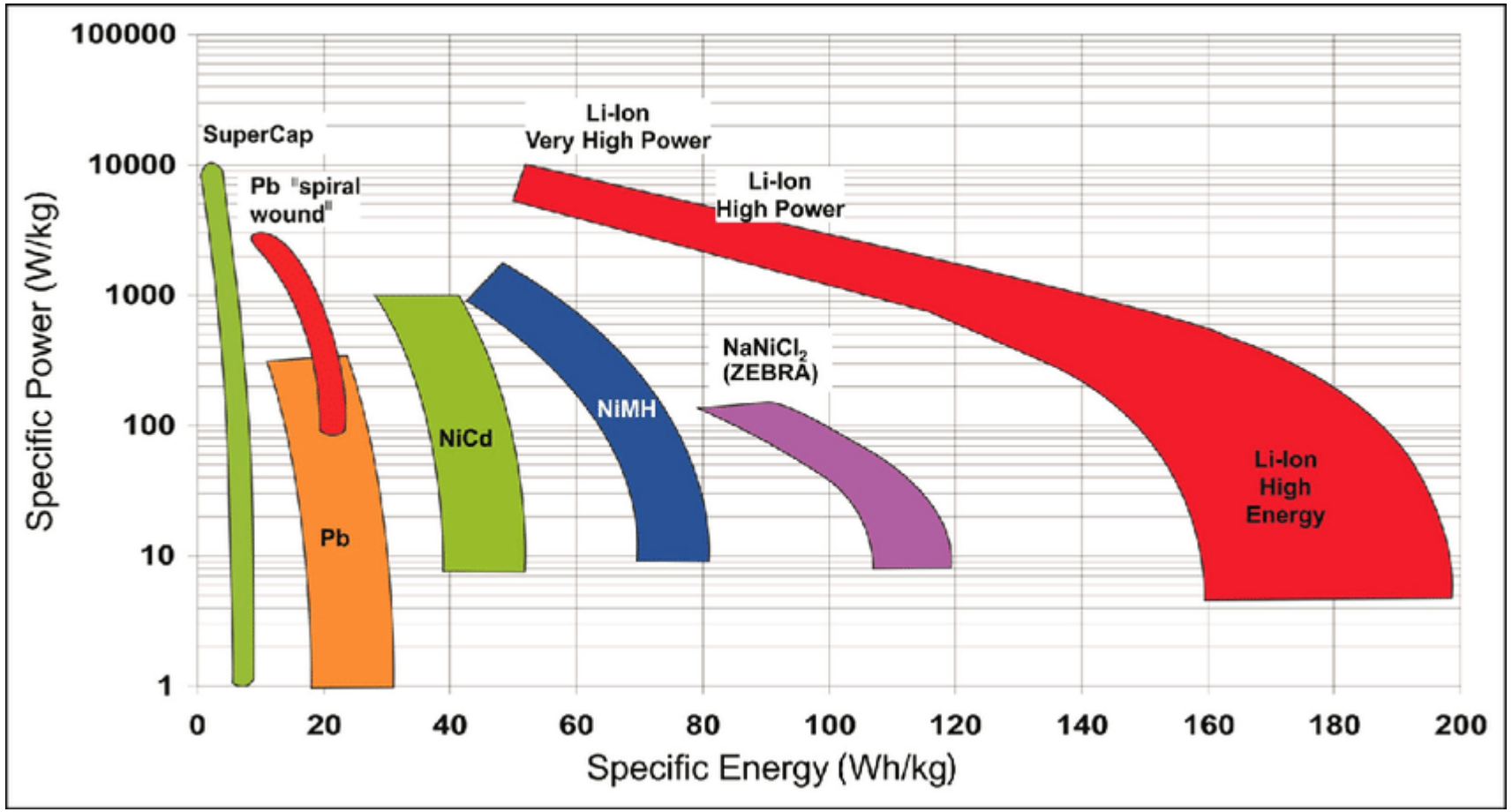
Battery industry is the key component of the green-energy transition

Estimated market sizes and related investments of oil-based-, and selected clean energy technology equipment in the Net Zero Scenario, 2020-2050 (USD billion, 2020)



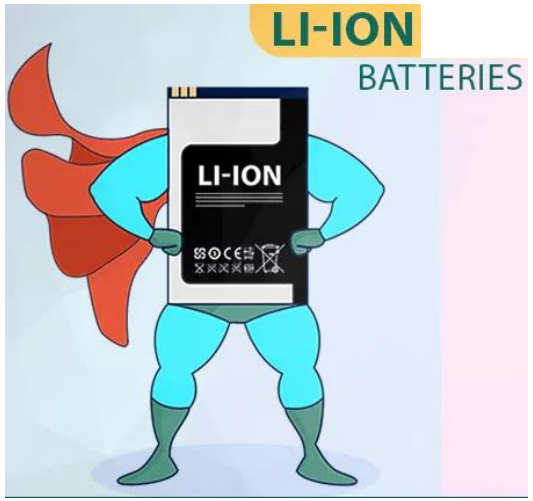
source: IEA World Energy Outlook 2021

The Ragone-plot



Why Li-ion?

Highest possible cell voltage →
→ highest energy density



Construction and functioning principle of the Li-ion batteries

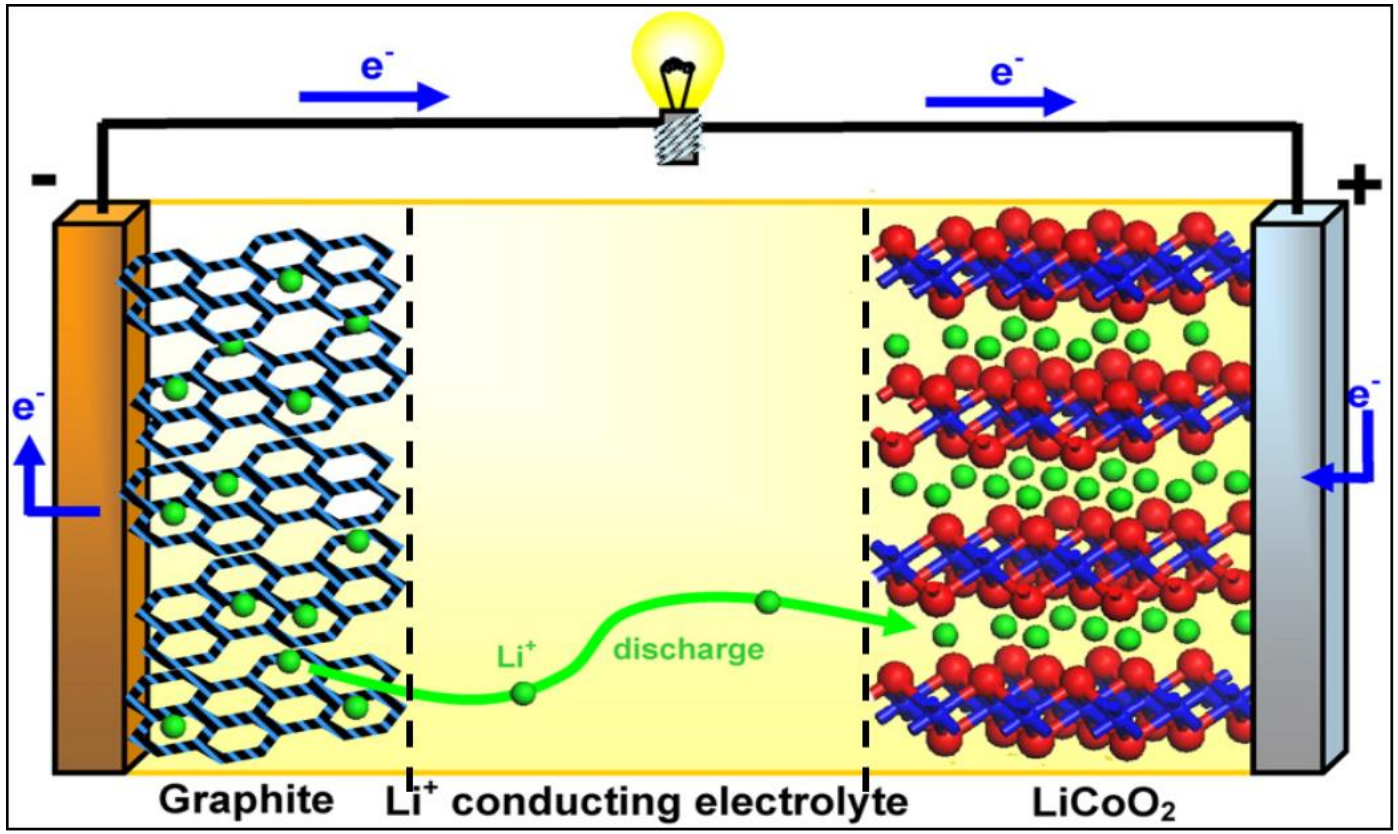
Electrochemically active components:

- **anode active host**
- **cathode active host**

Electrochemically inactive components :

- electrode additives
  - conductive carbon
  - binder (PVdF, CMC)
- electrolyte (organic carbonate, $LiPF_6$)
- separator (polyolefin foil)
- current collector (Cu, Al)
- housing (pouch, hard case steel ABS)
- safety elements (CID, PTC)

„The rocking-chair principle"



Quelle: Bruce, Solid State Ionics 179 (2008) 752–760

Different material combinations are possible.

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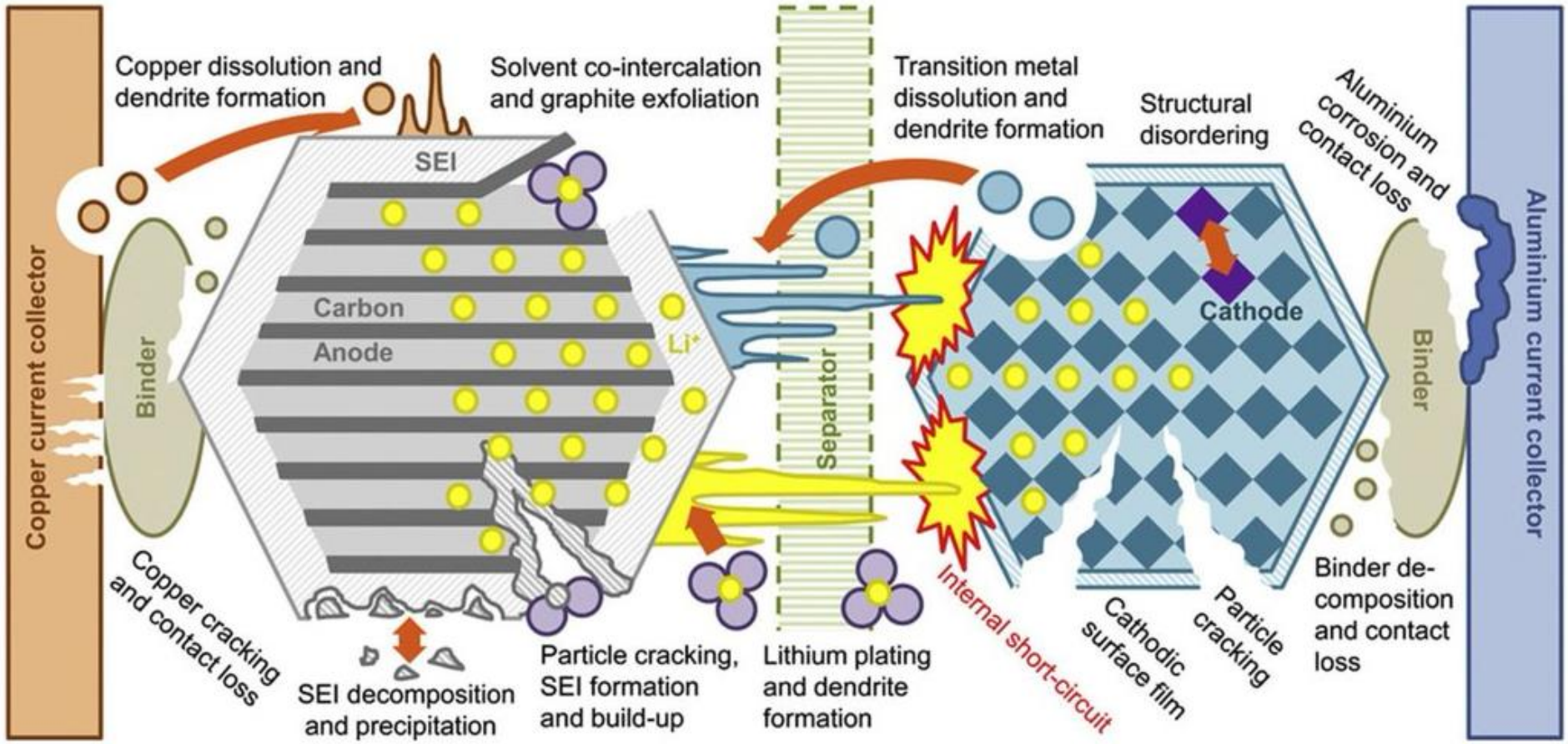
Degradation mechanisms in conventional Li-ion batteries



C. R. Birkl, M. R. Roberts, E. McTurk, P. G. Bruce, and D. A. Howey, "Degradation diagnostics for lithium ion cells," *J. Power Sources*, vol. 341, pp. 373–386, Feb. 2017.

Li-ion battery R + D + I → *Materials & battery cell concepts*

Abbreviations:
- **LFP:** $LiFePO_4$
- **NCA:** $Li(NiCoAl)O_2$
- **NMC:** $Li(NiMnCo)O_2$
- **NMC111:** Ni:Mn:Co = 1:1:1
- **HE:** high-energy
- **HV:** high-voltage

Cell generation	Cell chemistry	
Generation 5	▪ Li/O_2 (lithium-air)	beyond 2025
Generation 4	▪ All solid-state battery with lithium anode ▪ conversion cathodes (primarily Li-S)	beyond 2025
Generation 3b	▪ Cathode: HE-NMC, HV-spinel ▪ Anode: silicon/carbon	~2025
Generation 3a	▪ Cathode: NMC622 to NMC811 ▪ Anode: carbon (graphite - silicon blend (5-10%))	2020-2022
Generation 2b	▪ Cathode: NMC523 to NMC622 ▪ Anode: 100% carbon	current
Generation 2a	▪ Cathode: NMC111 ▪ Anode: 100% carbon	current
Generation 1	▪ Cathode: LFP, NCA ▪ Anode: 100% carbon	current

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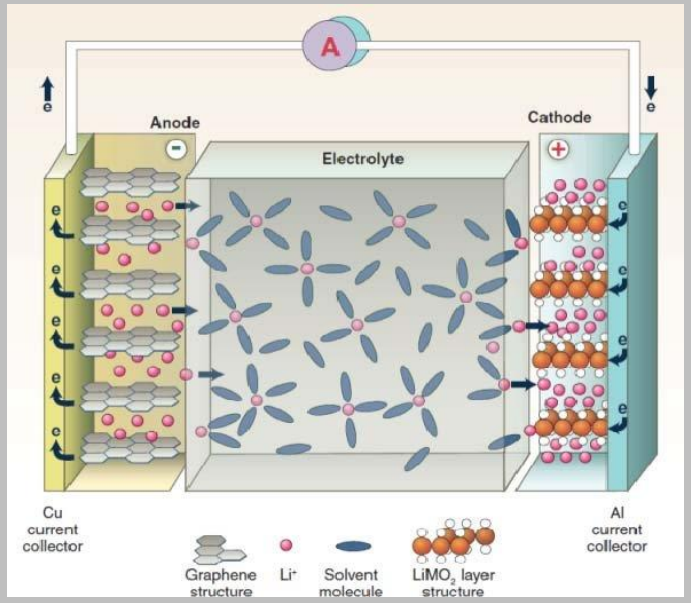
Generation 1/2a/2b →

→ Intercalation electrodes

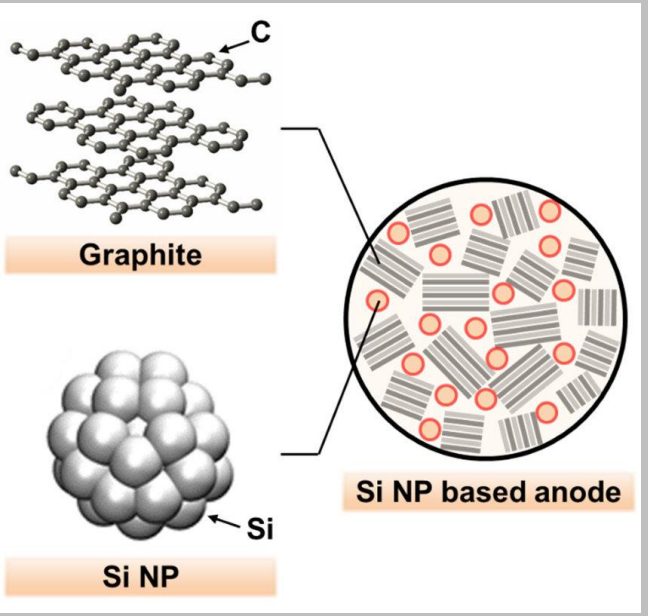
(pl. $LiCoO_2$/C, $LiFePO_4$/C, NMCxyz/C, etc.)



Generation 3a/3b →

→ Alloying-type electrodes

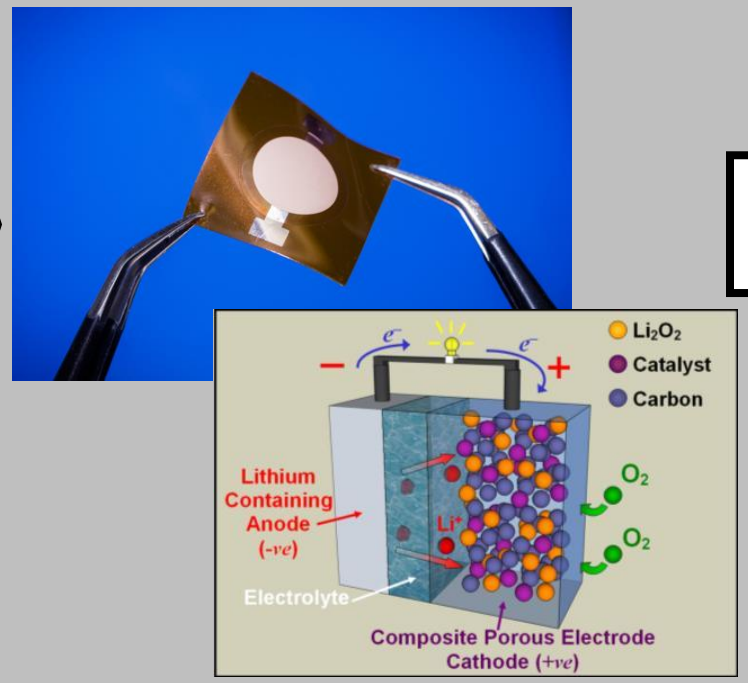
(e.g. Si/C and Si anode)



Generation 4/5 →

→ Conversion-type electrodes

(e.g. Li-SSB, Li-S, Li-O_2 systems)



***(theoretical)* specific energy increases**

(practical) cycle life performance declines

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Contemporary Li-ion batteries and their components

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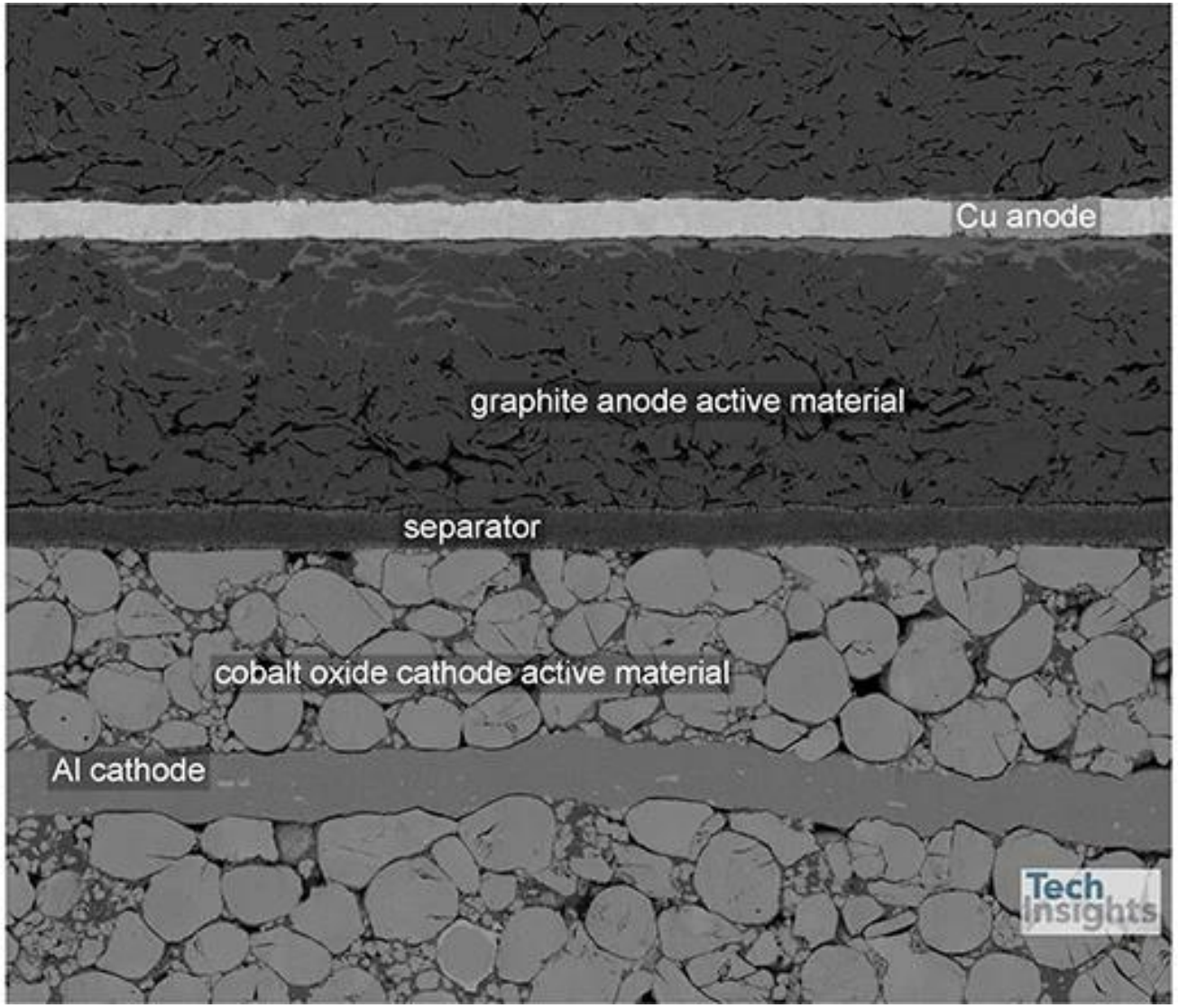

EB-BG977ABU Cross-Sectional Detail SEM

(source: The World of Lithium Ion Batteries; May 13, 2020 by Sinjin Dixon-Warren, retrieved in May/2022)

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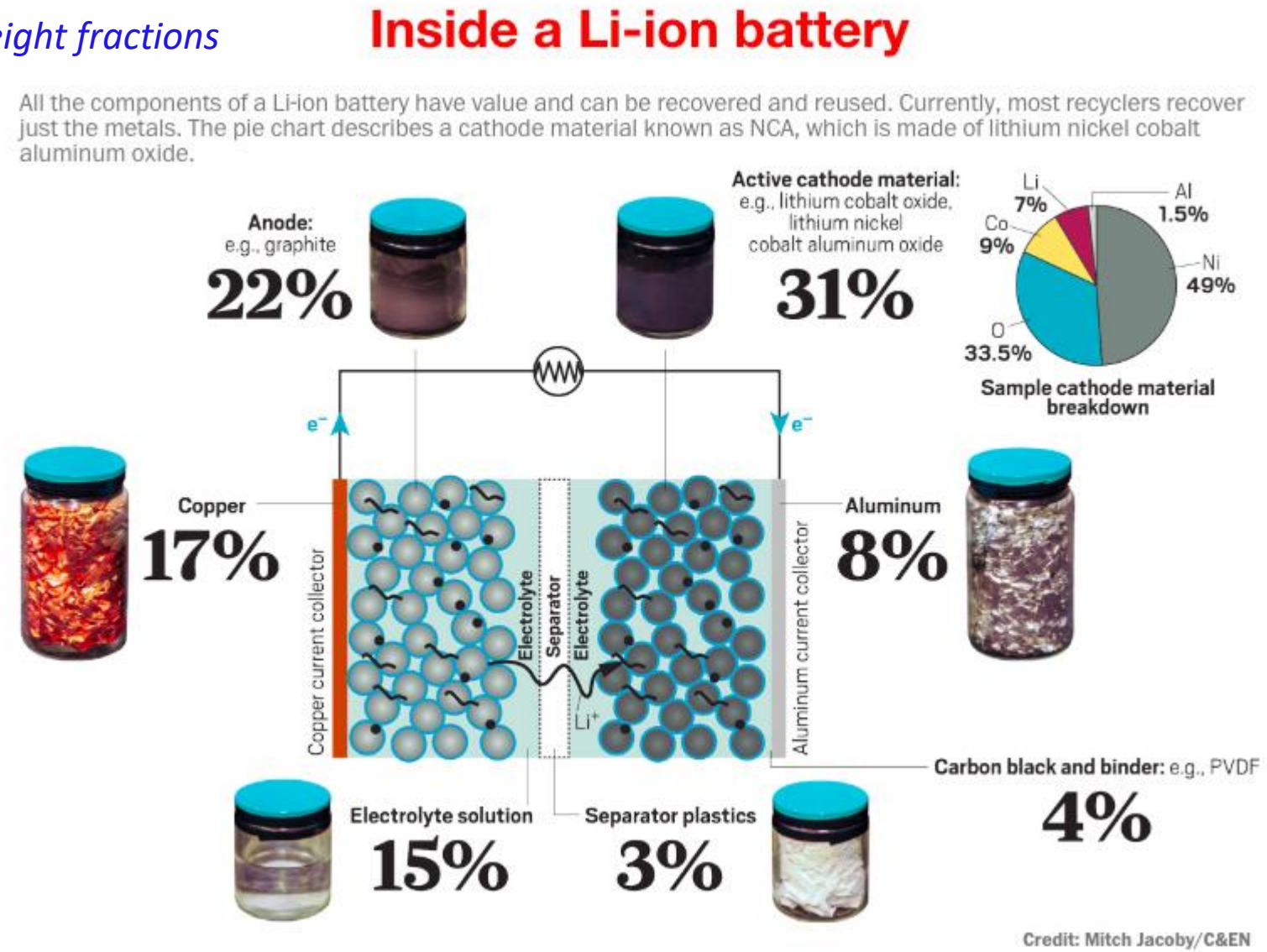
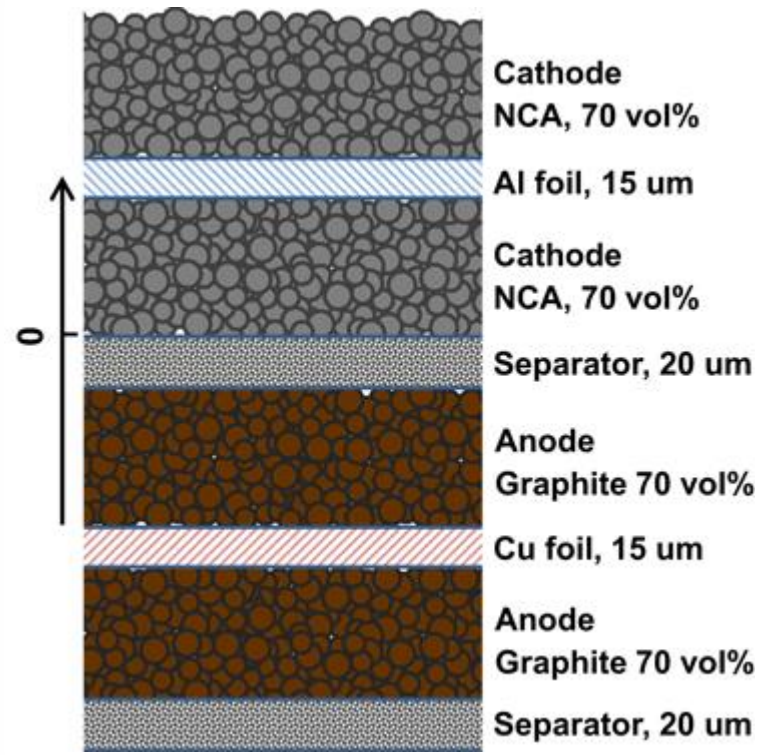
Main components of the Li-ion batteries

weight fractions





Du, Z., Wood, D.L., Daniel, C. et al. Understanding limiting factors in thick electrode performance as applied to high energy density Li-ion batteries. J Appl Electrochem 47, 405–415 (2017). https://doi.org/10.1007/s10800-017-1047-4

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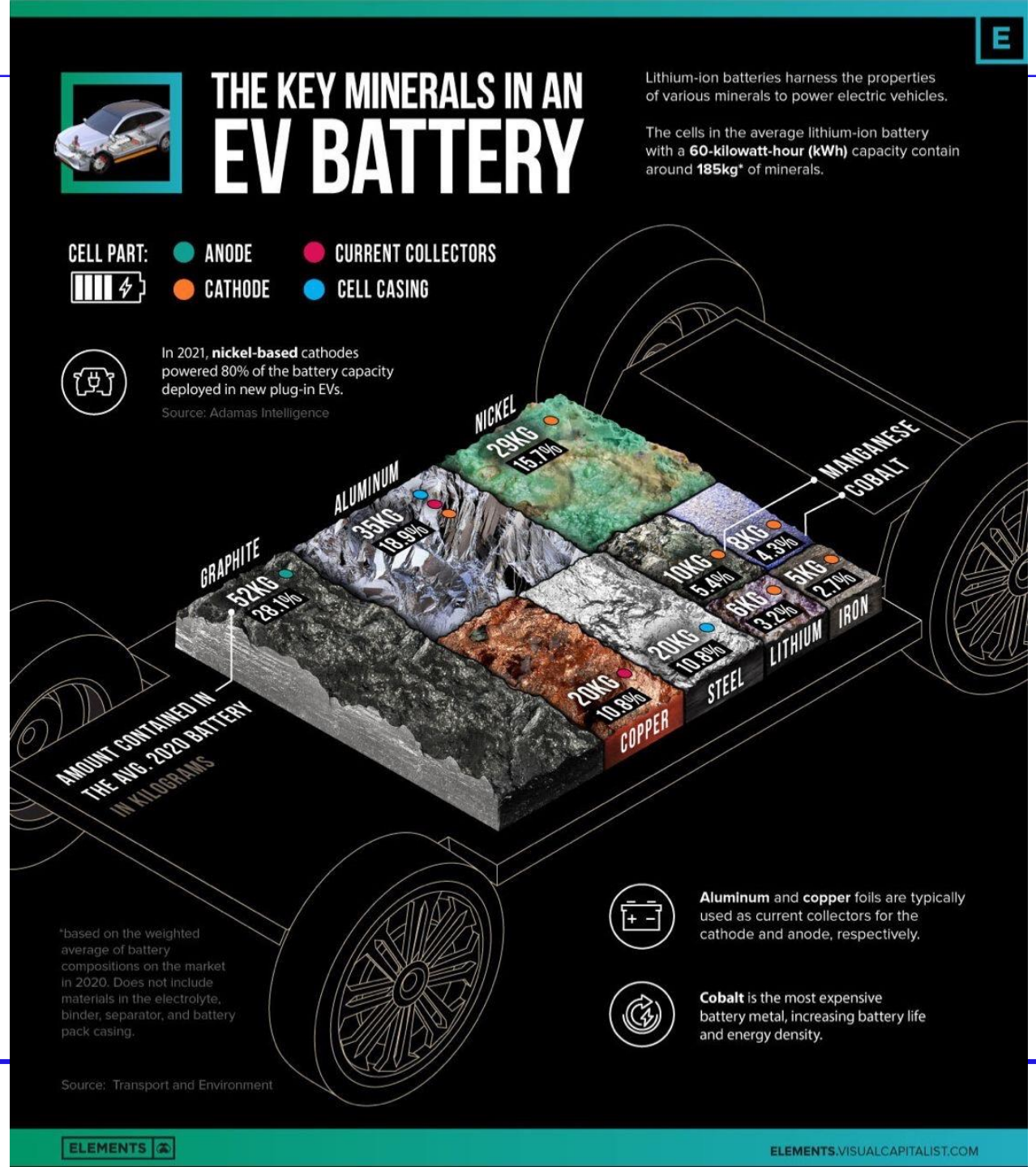
Minerals in an EV battery pack

An average 60 kWh EV car pack;

ca. 185 kg minerals

Graphite – 52 kg	(28.1%)
Aluminum – 35 kg	(18.9%)
Copper – 20 kg	(10.8%)
Steel – 20 kg	(10,8%)
Nickel – 29 kg	(15.7%)
Manganese – 10 kg	(5.4%)
Cobalt – 8 kg	(4.3%)
Iron – 5 kg	(2.7%)
Lithium – 6 kg	(3.2%)



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The global supply chain of Li-ion battery materials

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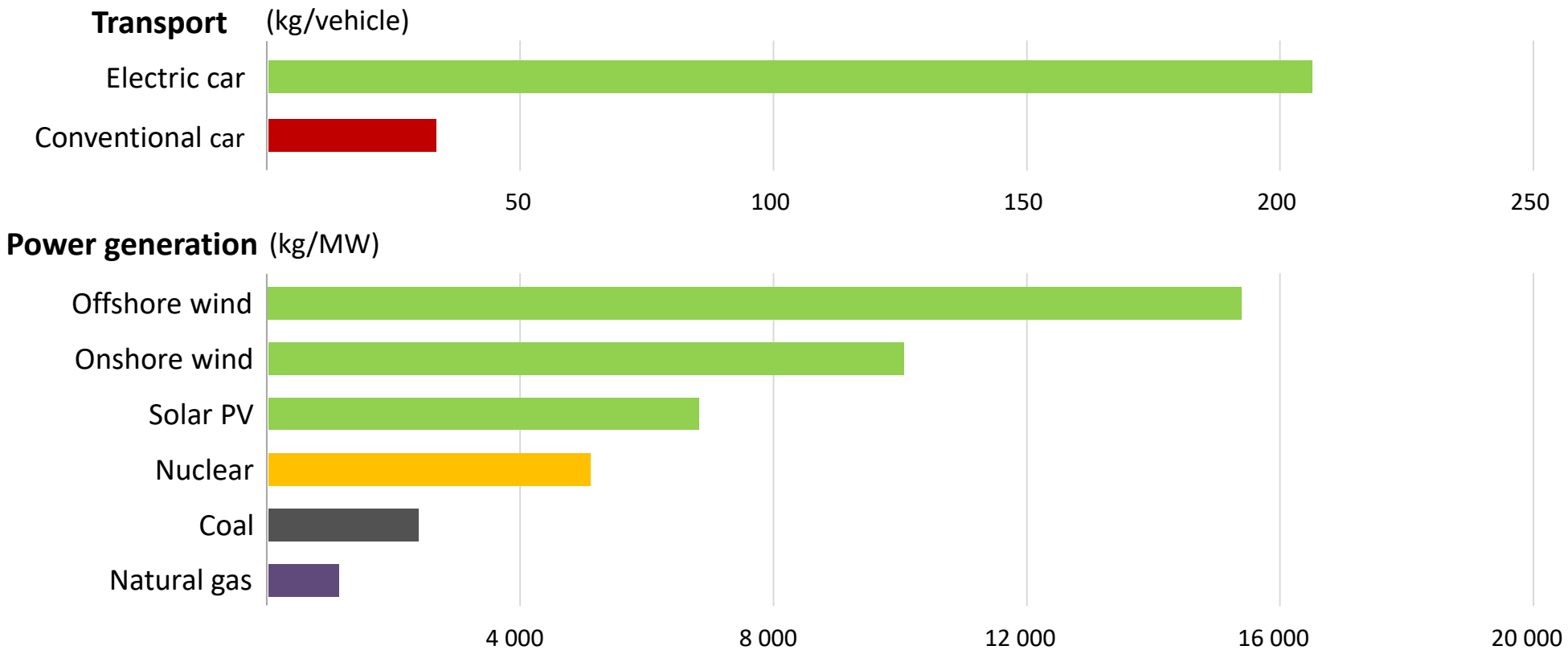
Minerals used in selected energy technologies



source: IEA (2022) World Energy Outlook Special Report.

A typical **electric car requires six times** the mineral inputs of a conventional car.
An **offshore wind plant requires thirteen times more** mineral resources than a similarly sized gas-fired power plant.

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The shift to a more mineral-intensive energy system

- Green-energy transition needs very high amount of minerals.
- Shift to a „**inorganic mineral dependence**" from the „**fossil fuels dependence**"
- The green energy system powered by *clean energy technologies (PV, wind, BEVs, BESS, etc.)* needs significantly more minerals:
  - Lithium (Li), nickel (Ni), cobalt (Co), manganese (Mn) and natural graphite (C) for **batteries**
  - Rare earth elements for wind turbines and **electric vehicles motors**
  - Copper (Cu), silicon (Si) and silver (Ag) for **solar photovoltaic panels**
  - Copper (Cu) and aluminum (Al) for **electricity grids**

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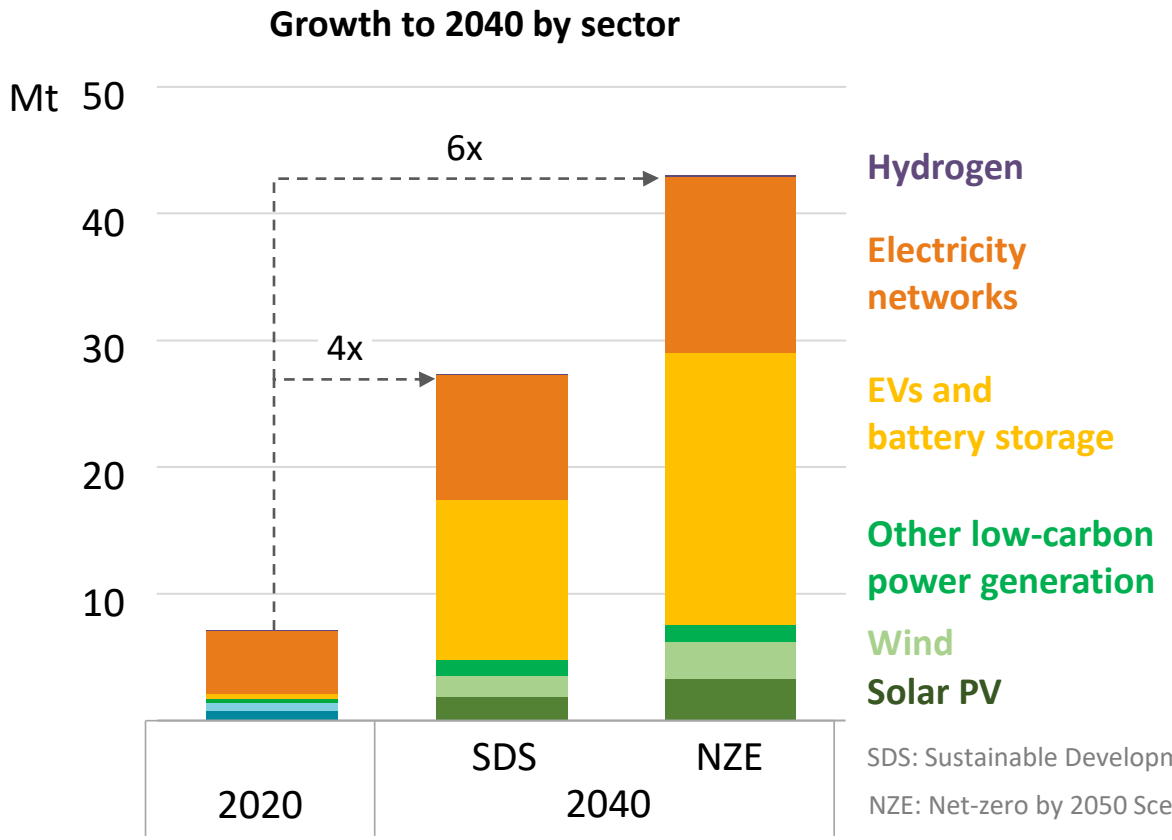
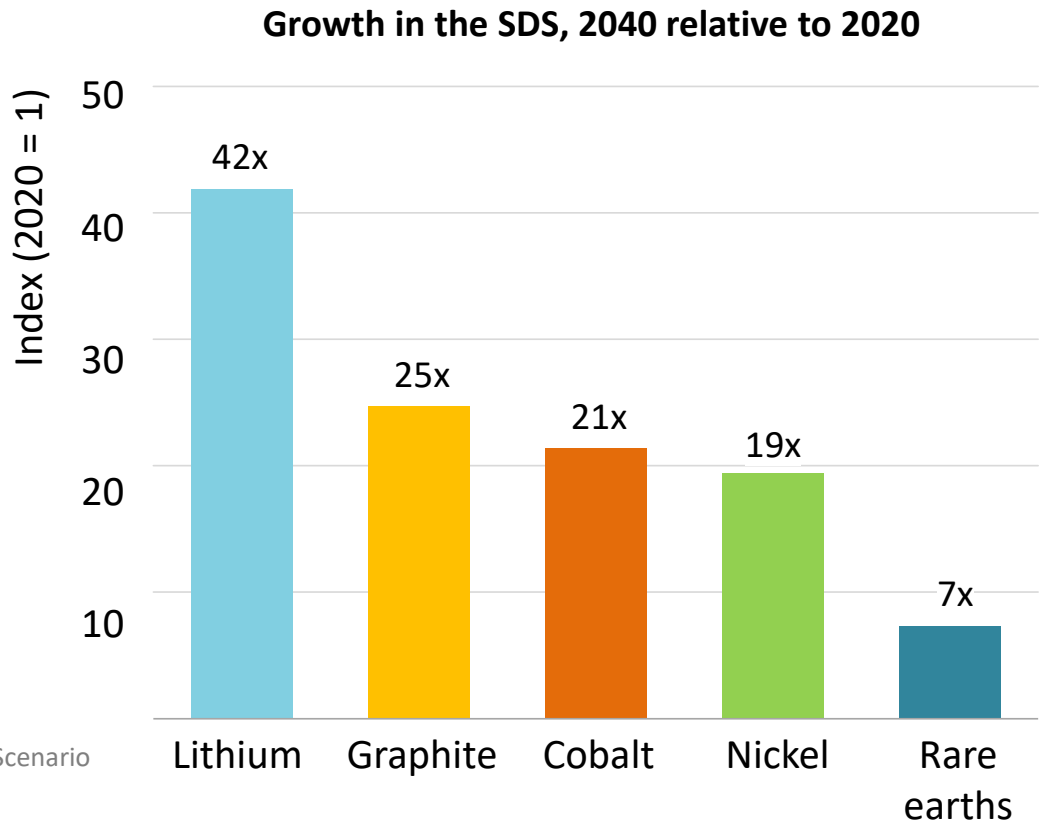
The shift to a more mineral-intensive energy system

Mineral demand for clean energy technologies by scenario (SDS and NZE)





Demand for critical minerals is set to soar over the next two decades as the world pursues net zero goals; overall requirements rise by as much as 6 times, but individual minerals, led by lithium, rise even faster

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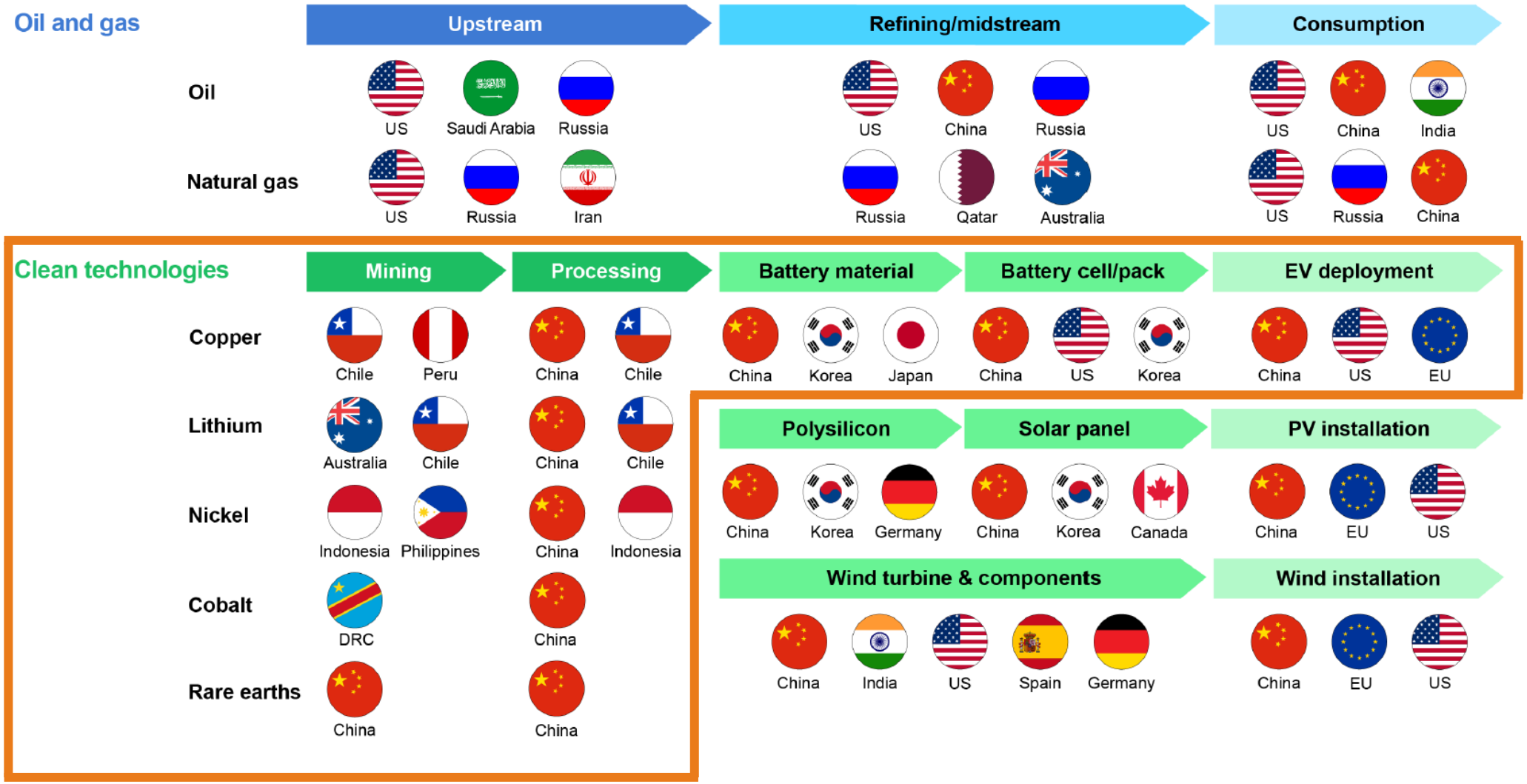
source: IEA (2022) World Energy Outlook Special Report.

The shift from a „fuel-intensive” to a „mineral-intensive” energy system

Indicative supply chains of oil and gas and selected clean energy technologies



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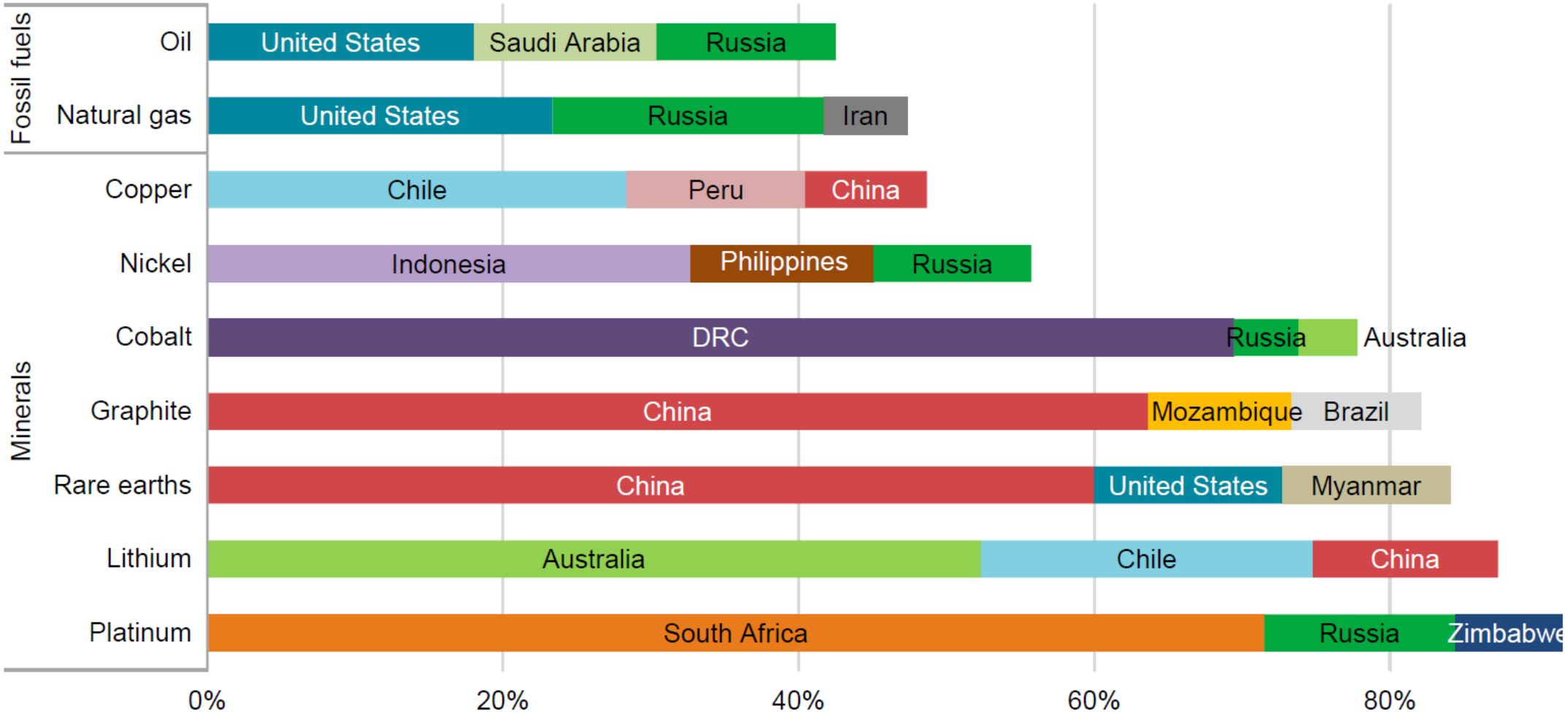
source: IEA (2022) World Energy Outlook Special Report.

The shift from a „fuel-intensive” to a „mineral-intensive” energy system

Share of top three producing countries in total production for selected minerals and fossil fuels, 2019



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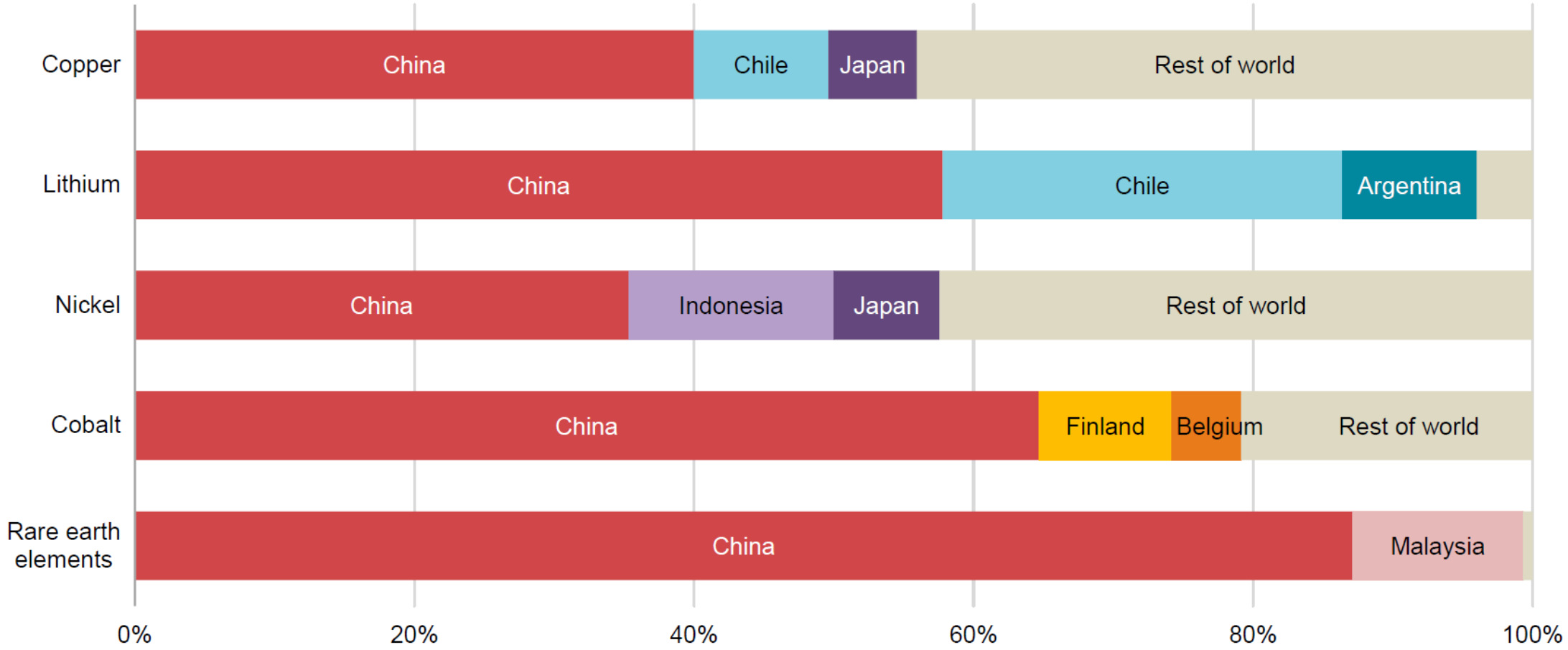
sources: IEA (2020b); USGS (2021). IEA (2022) World Energy Outlook Special Report.

The shift from a „fuel-intensive” to a „material-intensive” energy system

Share of processing volume by country for selected minerals, 2019



source: World Bureau of Metal Statistics (2020); Adamas Intelligence (2020) for rare earth elements; IEA (2022) World Energy Outlook Special Report.

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Critical raw materials (CRMs) list of the European Commission

2020 critical raw materials (new as compared to 2017 in bold)		
Antimony	Hafnium	Phosphorus
Baryte	Heavy Rare Earth Elements	Scandium
Beryllium	Light Rare Earth Elements	Silicon metal
Bismuth	Indium	Tantalum
Borate	Magnesium	Tungsten
Cobalt	Natural graphite	Vanadium
Coking coal	Natural rubber	**Bauxite**
Fluorspar	Niobium	**Lithium**
Gallium	Platinum Group Metals	**Titanium**
Germanium	Phosphate rock	**Strontium**

The CRMs list has been updated in 2020.
The 2020 EU list contains 30 materials as compared to 14 materials in 2011, 20 materials in 2014 and 27 materials in 2017. 26 materials stay on the list. Bauxite, lithium, titanium and strontium are added to the list for the first time.

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Source: https://ec.europa.eu/growth/sectors/raw-materials/areas-specific-interest/critical-raw-materials_en

The Li-ion battery recycling

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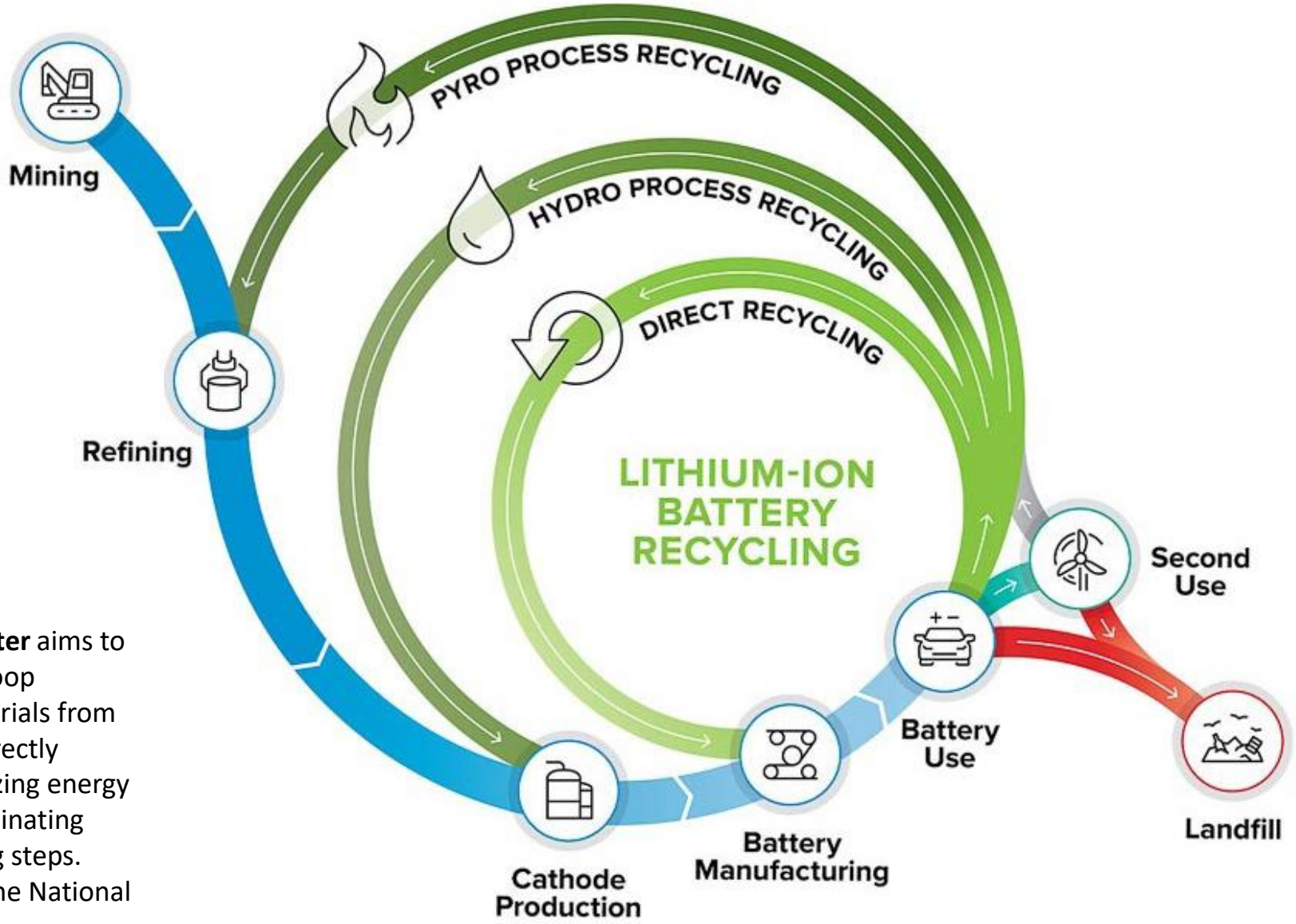
Strategies on Li-ion battery recycling

sustainability
profitability
development
pretreatment



The **DOE's ReCell Center** aims to drive toward closed-loop recycling, where materials from spent batteries are directly recycled, thus minimizing energy use and waste by eliminating mining and processing steps. (Image source: Argonne National Laboratory, ANL)

source: https://www.designnews.com/electronics-test/volkswagen-doe-want-ev-battery-recycling-fun-and-profit

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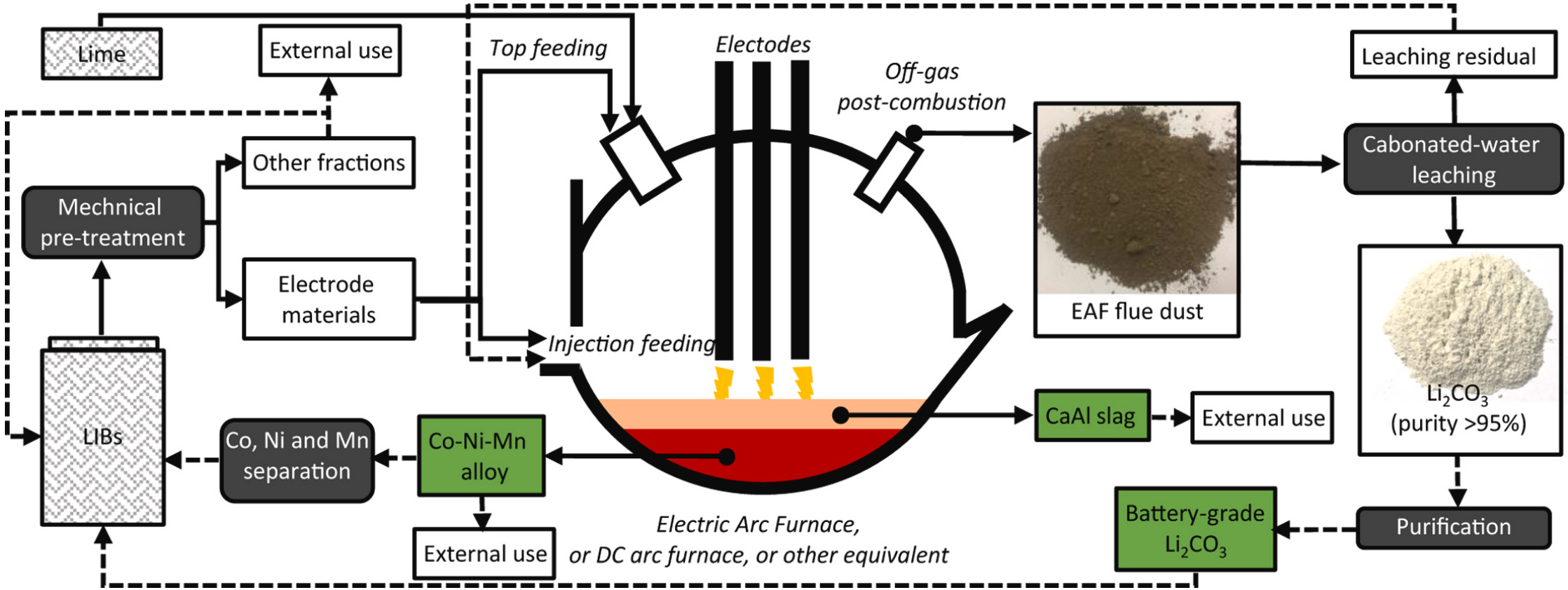
Note: The US Department of Energy (DOE) has created its first advanced battery recycling research and development initiative—the ReCell Center. It is a collaboration between Argonne National Laboratory (ANL), the National Renewable Energy Laboratory (NREL), Oak Ridge National Laboratory (ORNL), and several universities including Worcester Polytechnic Institute, University of California at San Diego, and Michigan Technological University. In addition, collaborators from the battery supply chain, including battery manufacturers, automotive original equipment manufacturers (OEMs), recycling centers, battery lifecycle management services, and material suppliers, will be working with the center.

Pyrometallurgy-based process on Li-ion battery recycling



source: https://doi.org/10.1016/j.jpowsour.2020.229089

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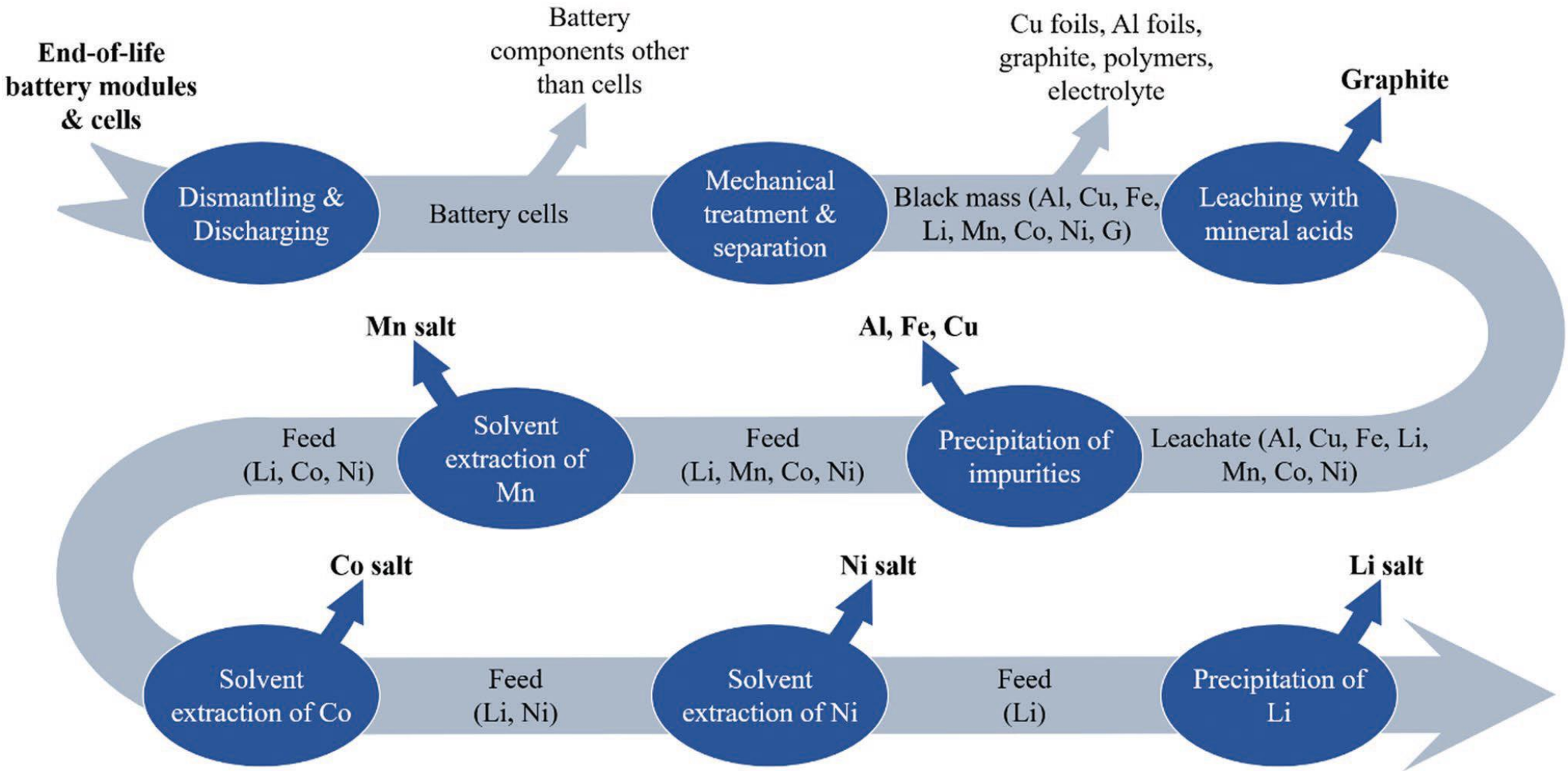
Hydrometallurgy-based process on Li-ion battery recycling

Overview about traditional hydrometallurgical processing



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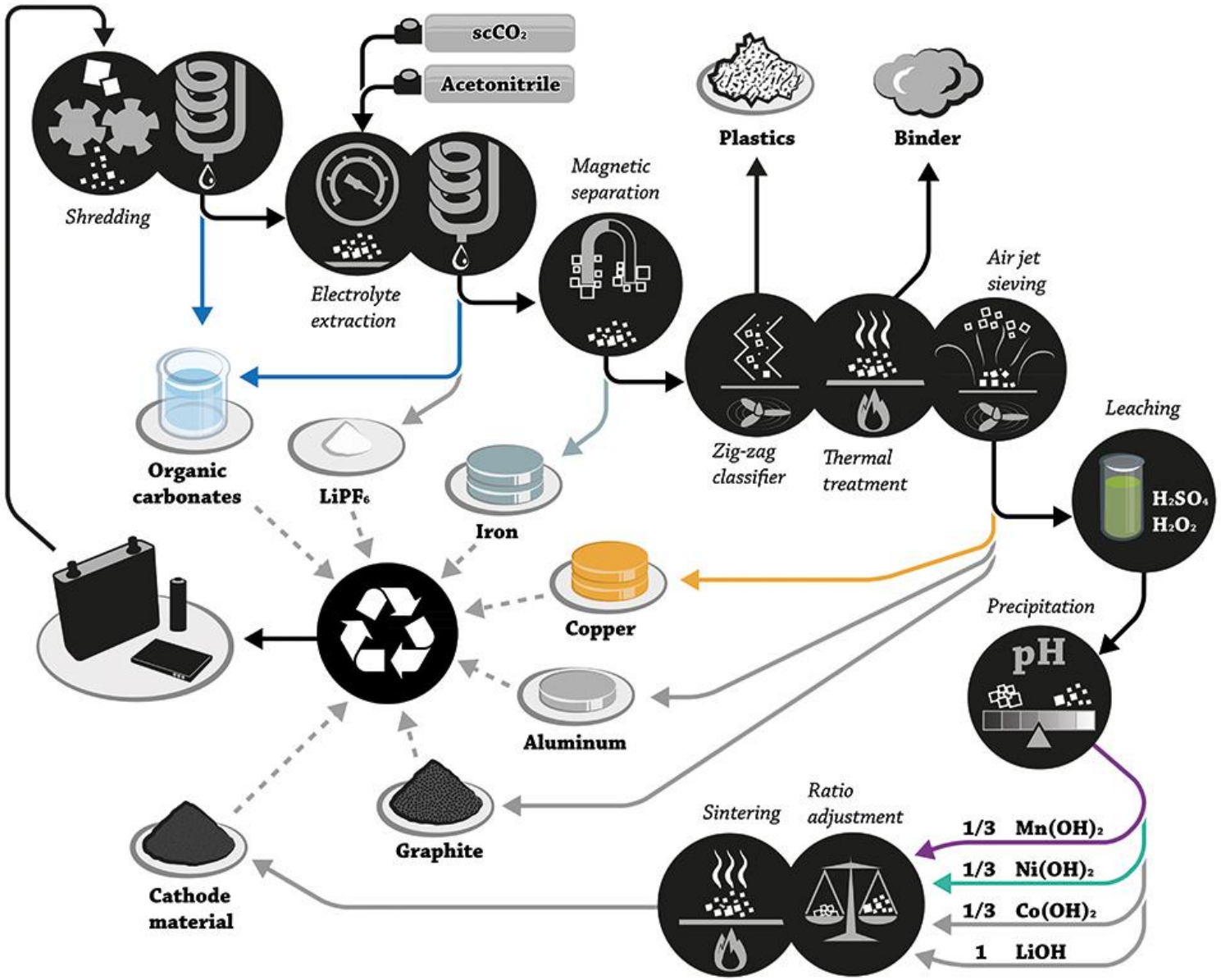
source: DOI: 10.1002/aenm.202102917

Hydrometallurgy-based process on Li-ion battery recycling



LithoRec process, which is a **mechanical-hydrometallurgical process** aims to meet the demands of the EU directive by the utilization of most materials from a LIB which is a central key of this process.

source: https://analyticalscience.wiley.com/do/10.1002/gitlab.15680/full/

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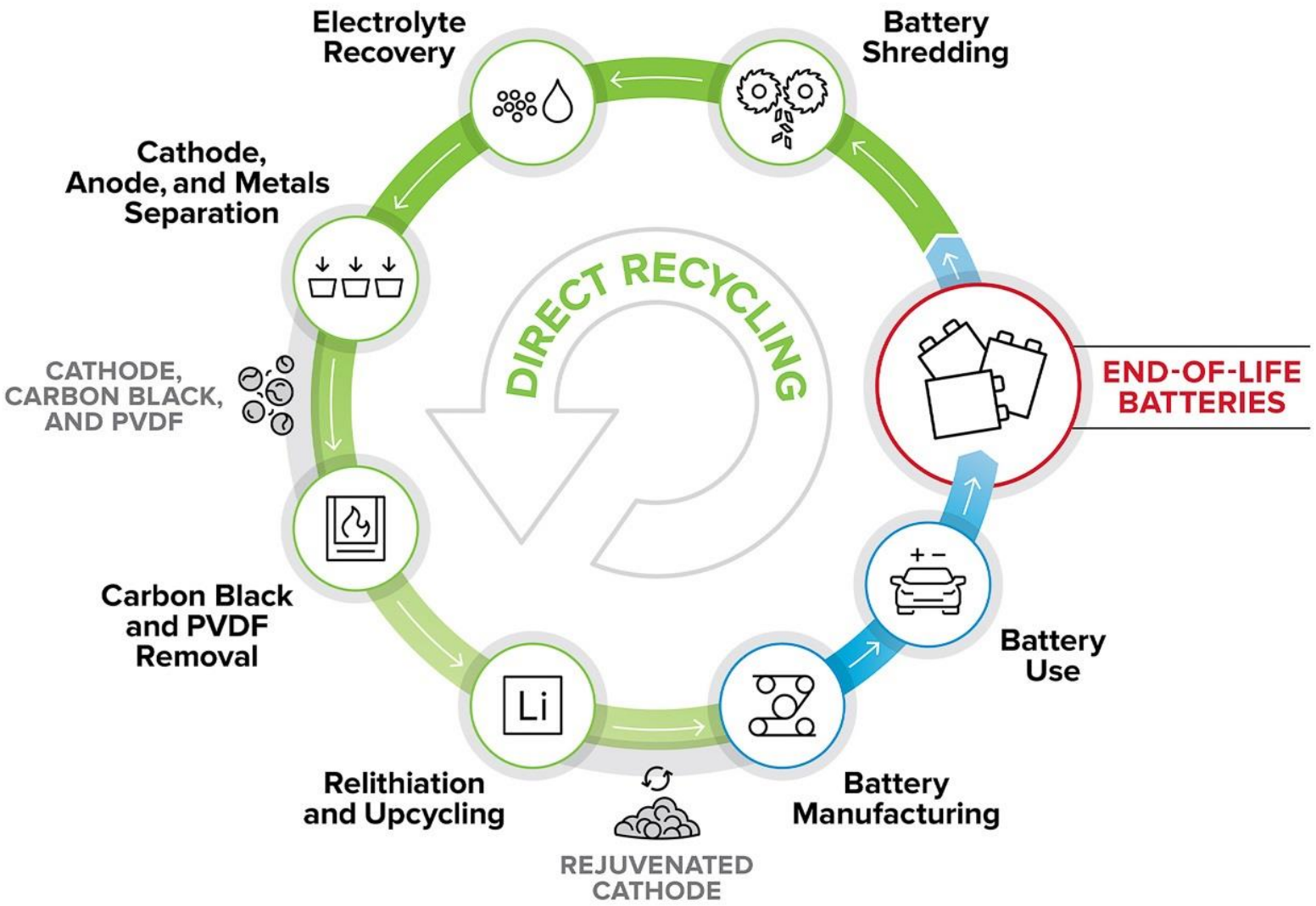
Direct recycling of EoL Li-ion batteries



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Comparison of the three main existing battery recycling routes

CIC energiGUNE
MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

	# HYDROMETALLURGY	# PYROMETALLURGY	# DIRECTRECYCLING
ADVANTAGES	High recovery of several components (including graphite) Achievement of products with the quality required by the battery industry. Avoidance of toxic off-gassing Flexible; Can be applied to any battery chemistry Low energy consumption Proven and implementable technology	Simple process Easy control of fire and explosion risk No mechanical pretreatment required High metal recovery Proven and implementable technology	Low energy cost Suitable for LFP batteries (does not depend on the price of the recyclable elements to be feasible) Suitable for recycling manufacturing scrap
DISADVANTAGES	Wastewater generation No electrolyte recovery Requires pretreatment for safe battery handling Operational complexity	High costs High emission generation Metallic yield losses (diffusion of lithium to slag) No electrolyte and graphite recovery Complicated to obtain "battery grade" products (sufficient quality for new batteries) Profitability dependent on batteries containing cobalt	Requires mechanical pretreatment Low quality; the recovered material does not have the same performance. Must be performed for each type of battery (does not work with mixed chemistries) Has not been verified at industrial level

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Li-ion battery recycling – The emerging big industry on the horizon

* Note: Non-exhaustive list (includes those agents with recent announcements associated with the sector or participants in large alliances).

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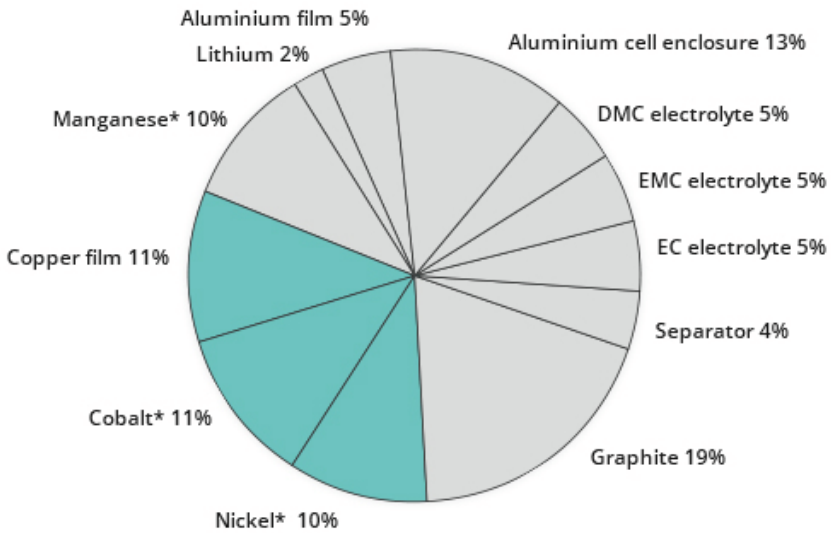
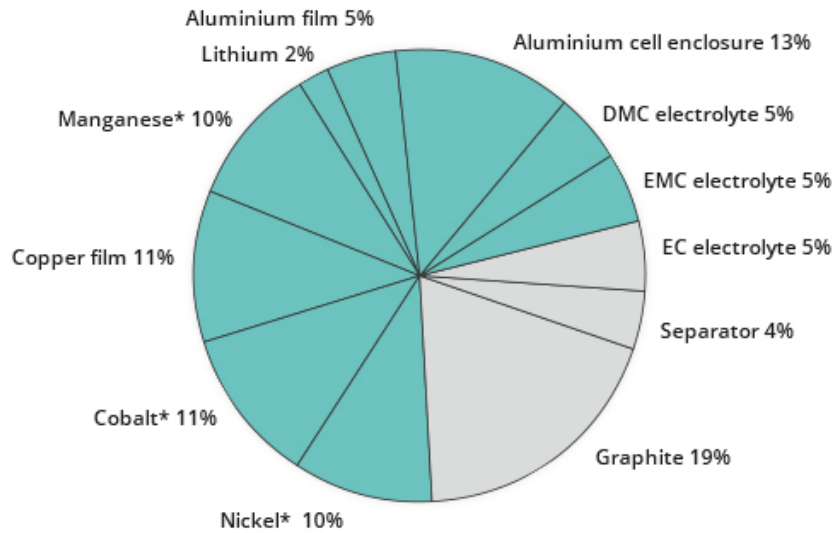
Li-ion battery recycling – The recovery rate

Recycling efficiency of a lithium-ion battery cell

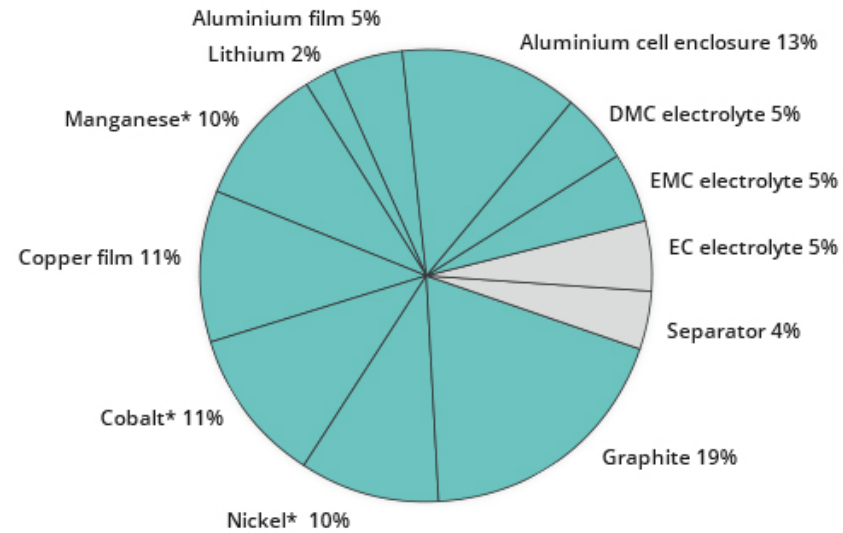
32% - current state of the art



72% - Duesenfeld mechanically



91% - Duesenfeld mechanically + hydro

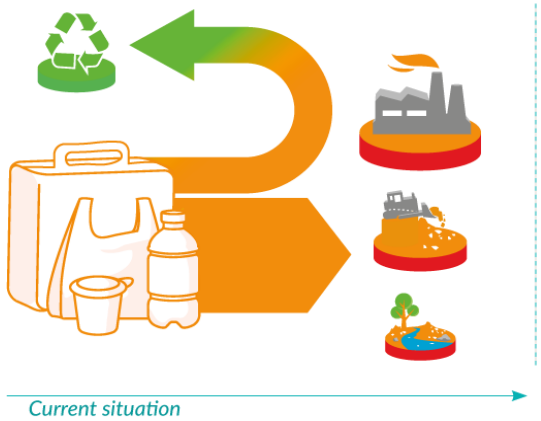


Material recycling Disposal / repurposing as construction material * Oxides shown as elements for simplicity

Comparison of recycling rates at battery cell level without battery housings, fastening systems, screw connections, cabling and Electronics

Source: https://www.duesenfeld.com/recycling_en.html

Design for recycling – An important aspect for future battery development

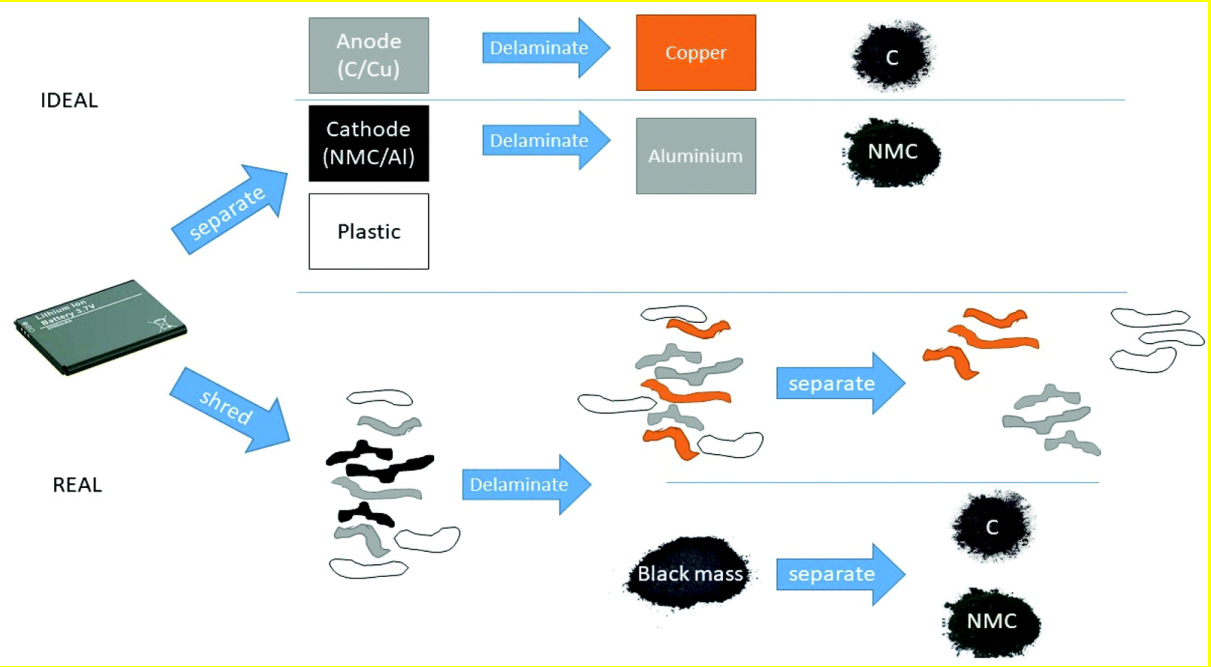


- Lower recycling yield
- Environmental pollution
- High energy consumption
- Less-ecofriendly
- Economically less attractive

Design for recycling

- Improved recyclability
- Losses are minimized (material and energy)
- Sustainable recycling
- Recycling is profitable
- Supporting circular economy-based business models

Schematic diagram of an idealised vs. a real battery recycling process



source: D. L. Thompson et al., Green Chem., 2020, 22, 7585–7603; DOI: 10.1039/d0gc02745f

https://ecodesign-packaging.org/en/guidelines/strategies/design-for-recycling/

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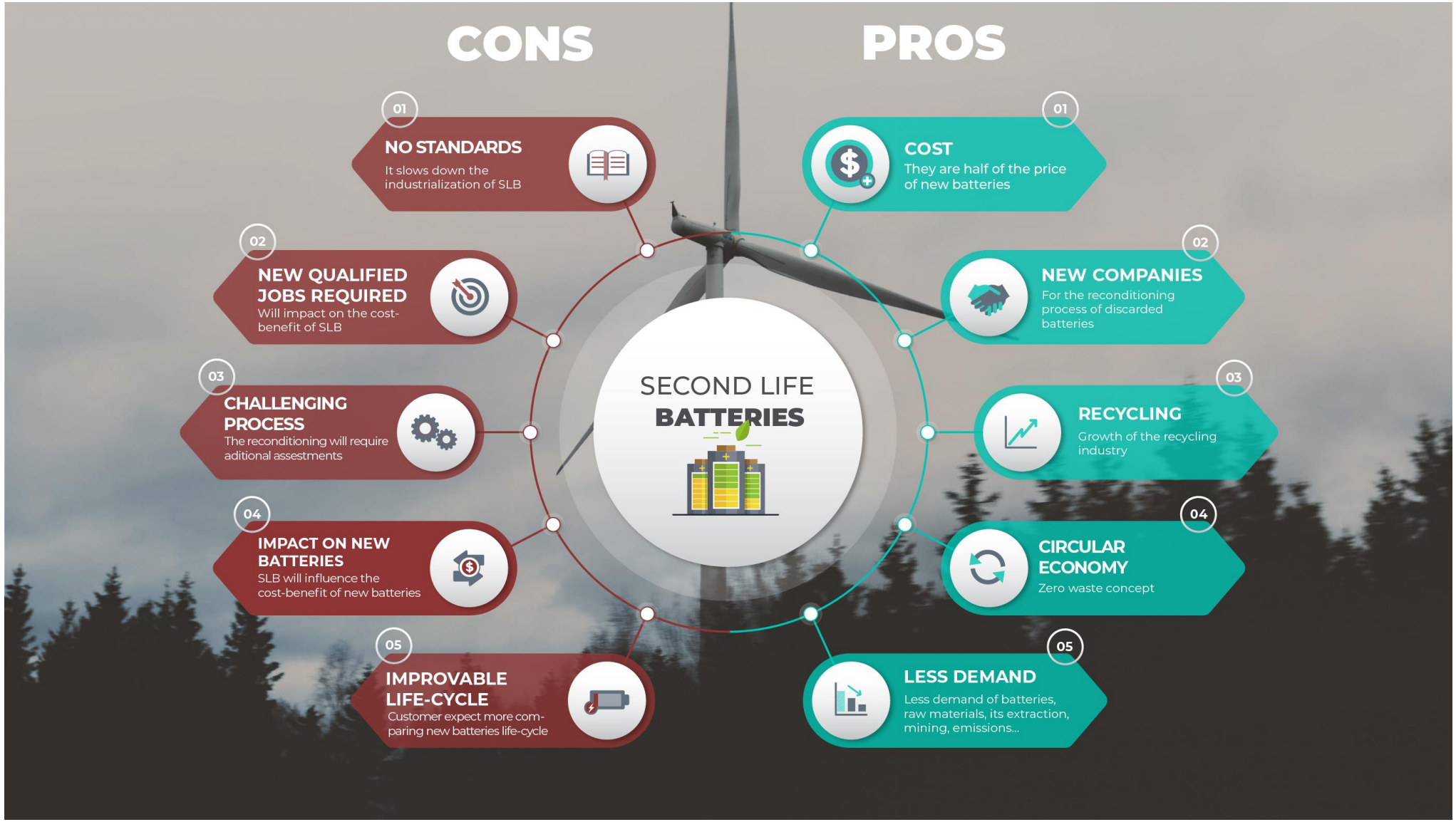
Second life batteries (SLB) – A complementary or competing technology?!



source: https://cicenergigune.com/en/blog/second-life-batteries-sustainable-energy-transition

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Concluding remarks

- Batteries will play crucial role in the green energy transition and at the decarbonization goals
- Clean energy technologies are more mineral-demanded, as the convectional fossil-based technologies
- „Linear-economy” cannot cope with the material demand of the growing battery industry
- Geopolitical dependence of EU battery industry on the battery materials must be buffered
- Global supply chains are prone to break and collapse, this is threatening for the battery industry and the green energy transition
- Battery recycling is crucial for the sustainability, promotes the shift to the circular-economy
- Pyrometallurgy-, hydrometallurgy-, (bio-hydromet.) processes and direct recycling are available for Li-ion battery recycling
- Hydrometallurgy technique is considered as the most suitable according to the EU Battery Directive
- Recycling process must be economic (profitable), ecofriendly, low-carbon footprint, high recycling yield

Köszönöm a figyelmet!

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