Technische Universität Braunschweig

BLB Battery LabFactory Braunschweig

iPAT Institute for Particle Technology

Von Li-Ionen-Altbatterien zur Produktion neuer Li-Ionen-Batterien – Lösungsansätze für geschlossene Stoffkreisläufe

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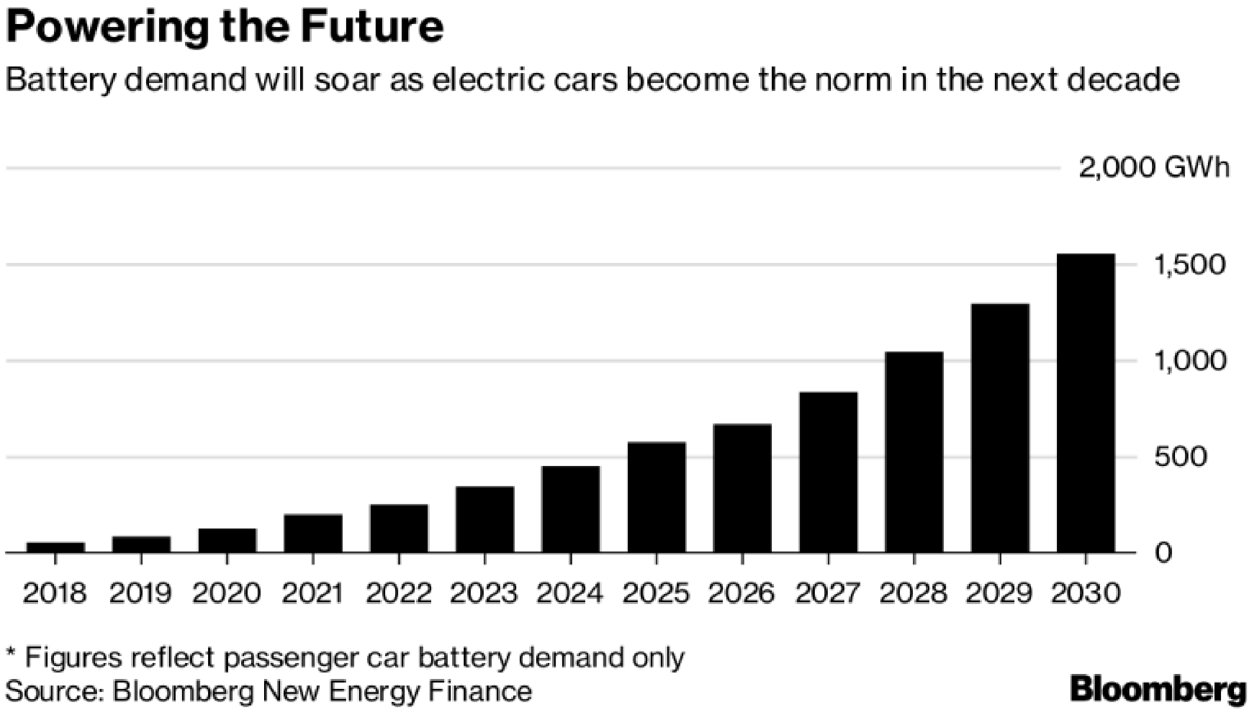
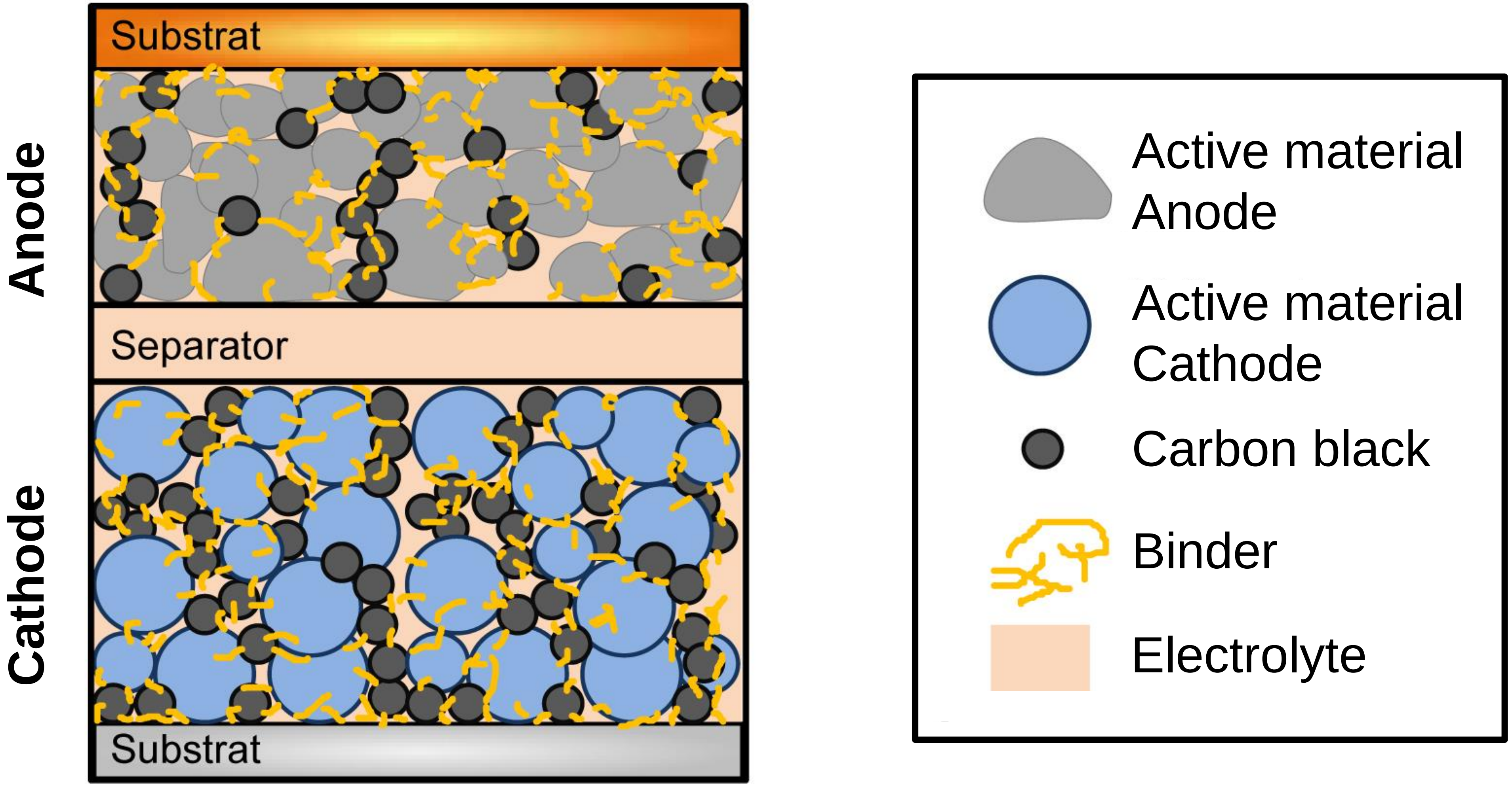
Motivation

- E-mobility and green energy production cause **extreme increase in battery demand**, especially lithium-ion batteries
- Primary raw material reserves are not sufficient to fulfill mid- and longterm demand of battery materials and are ecological not advantageous
- Germany must become **less dependent on material delivery** from foreign countries

→ **Circular production and closed material cycles** are essential for ecological friendly e-mobility and green energy production



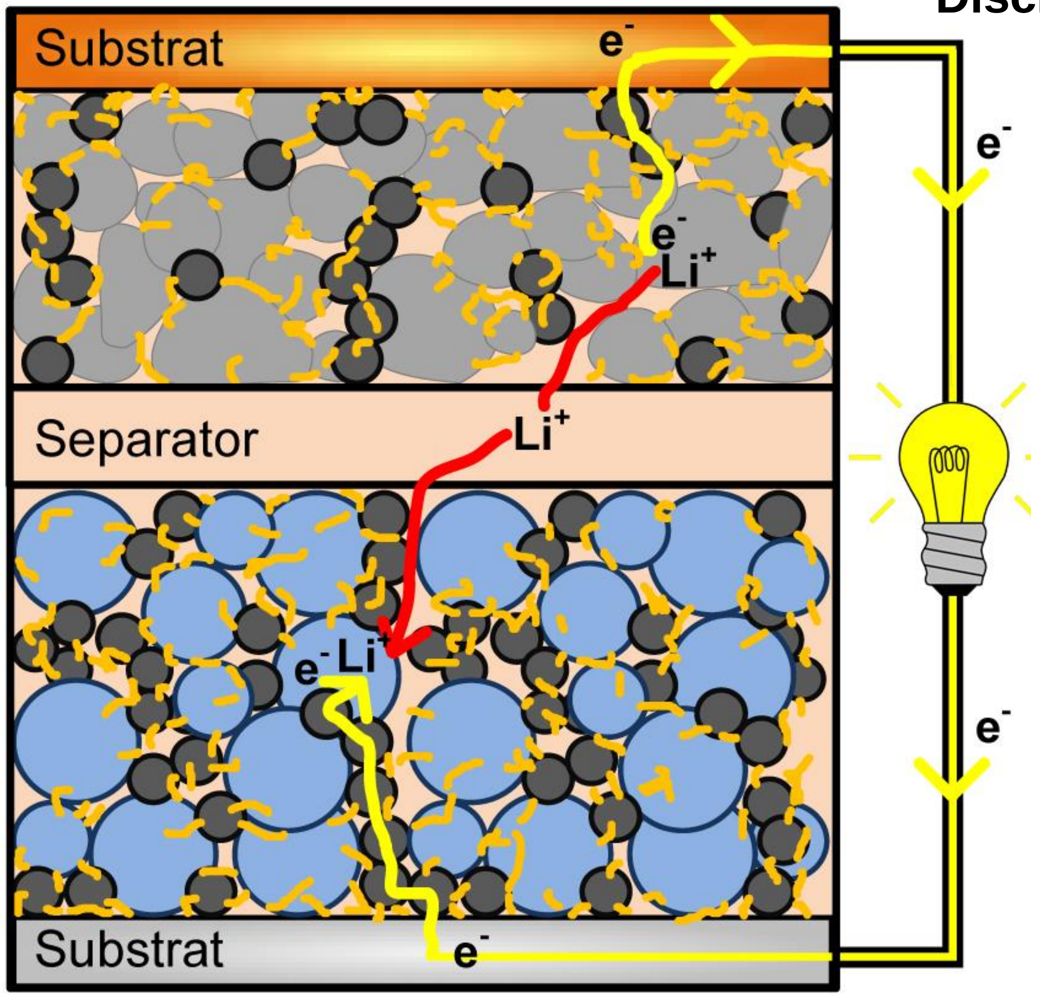
Components and function of Lithium-ion battery



Components and function of Lithium-ion battery

Anode

Cathode



Discharge

Requirements

Energy & Power density

Costs

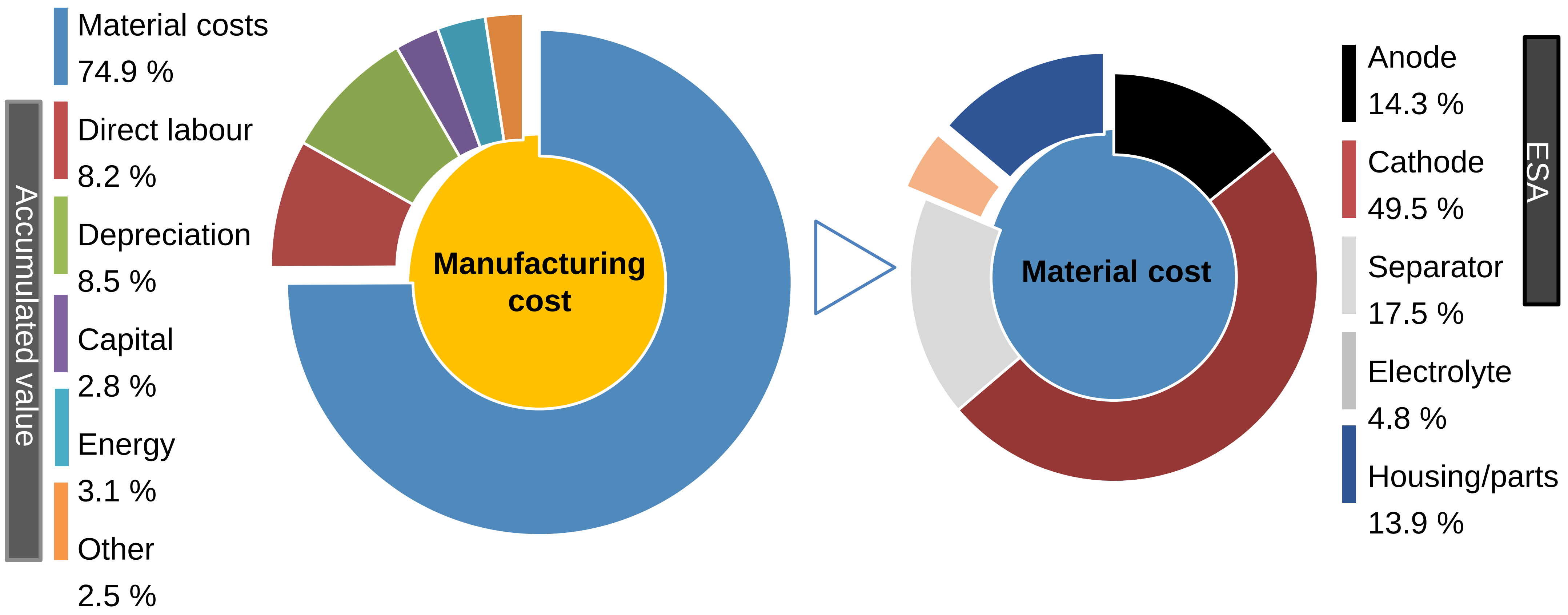
Life time

Sustainability (e.g. CO_2 foot print)

Safety

A. Kwade et.al. (2018) Nature Energy 3 (4), pp. 290-300

Cost breakdown of cell production costs and material costs

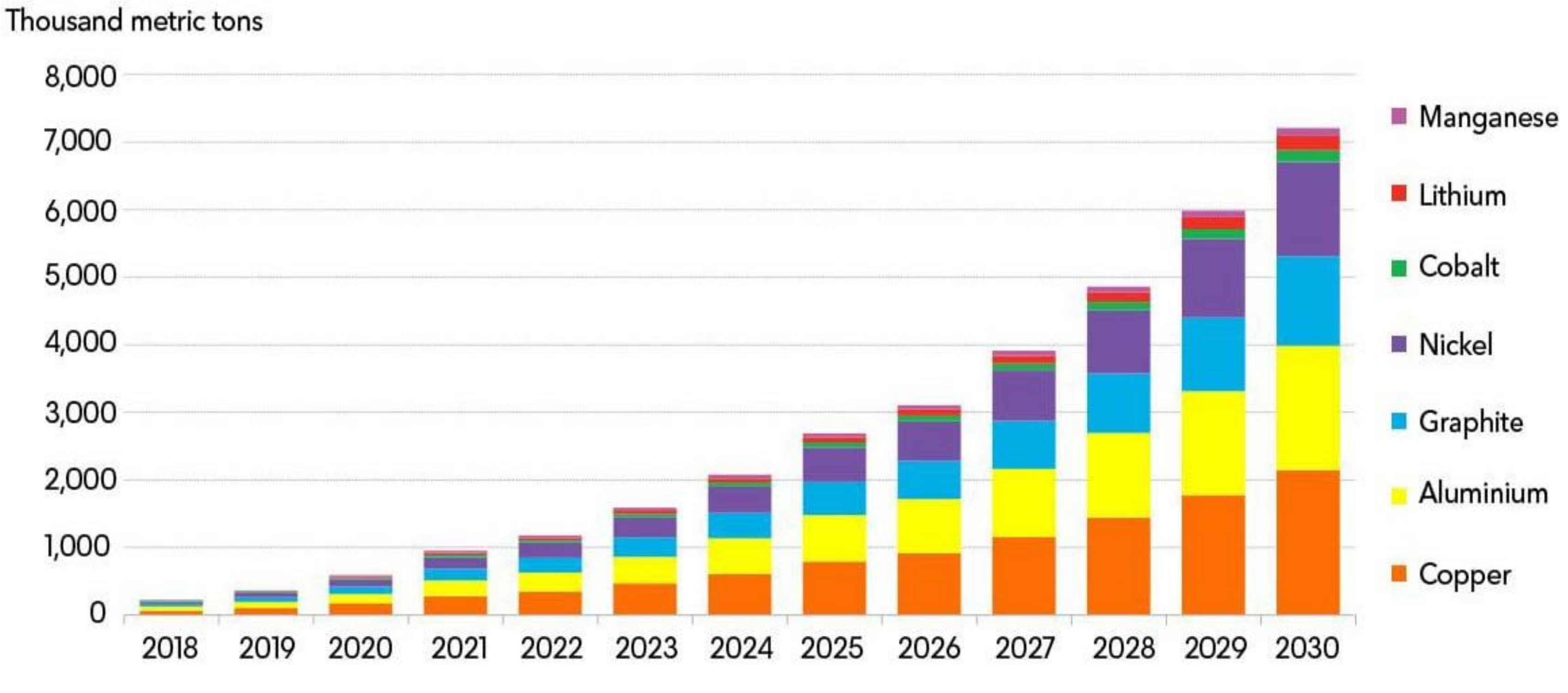


Determination based on C//NMC, PHEV2, 36 Ah

A. Kwade et.al. (2018) Nature Energy 3 (4), pp. 290-300

Demand of materials for battery production

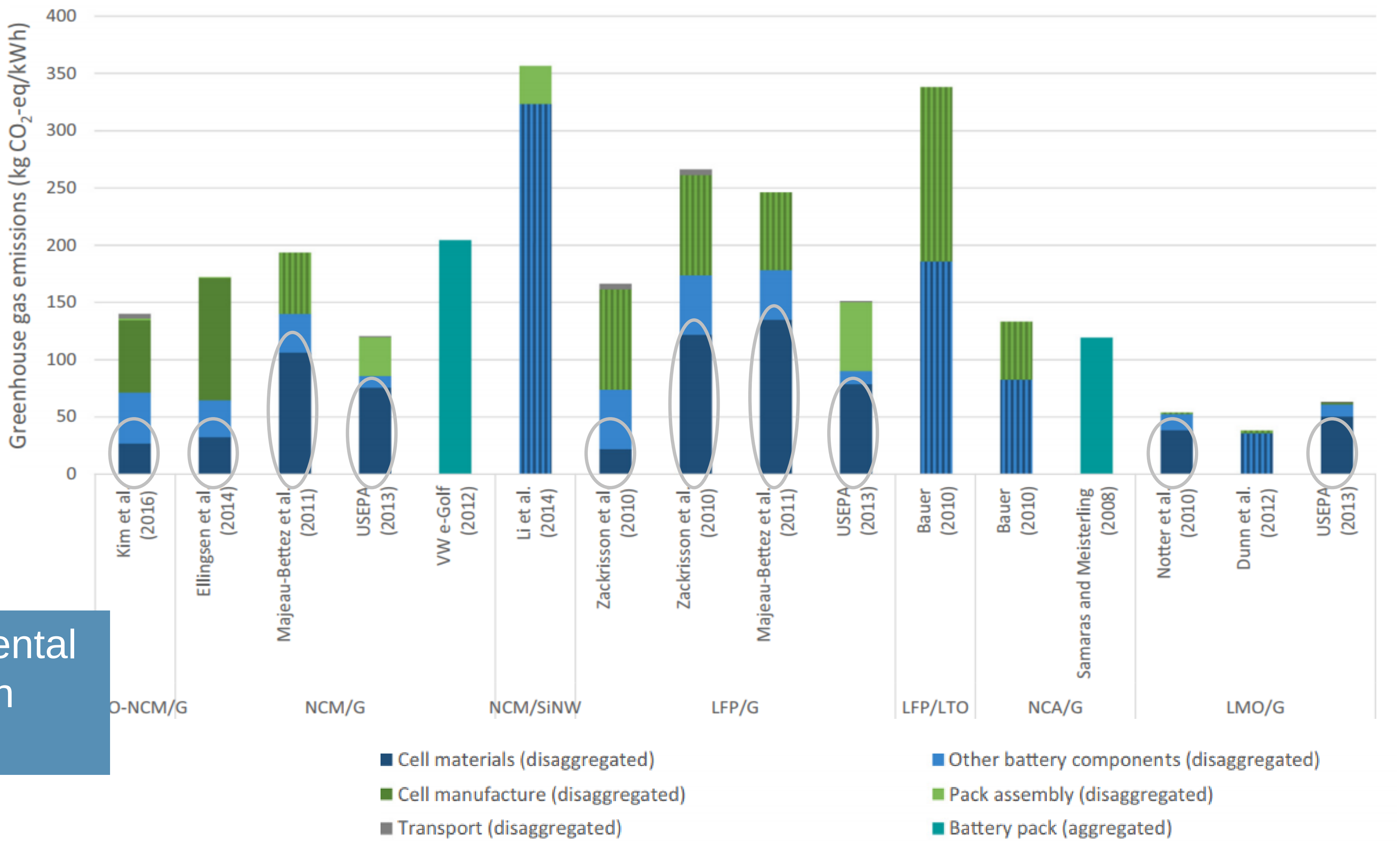
- **Very high demand** of following metals for battery production
  - Nickel (cathode)
  - Graphite (anode)
  - Cupper (current collector, pack wiring)
  - Aluminium (current collector, housing, cathode material)



Source: Electric Vehicle Outlook 2018, Bloomberg New Energy Finance. Note: Copper includes copper current collectors and pack wiring. Aluminium includes aluminium current collectors, cell and pack materials and aluminium in cathode active materials.

High importance of low environmental impact

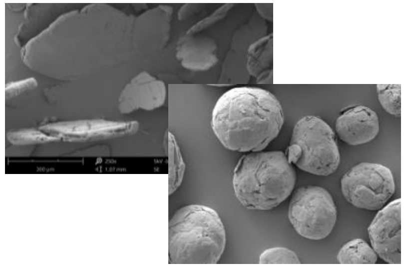
- **Cell materials** have high share with regard to the **environmental impact** of batteries
- Car manufacturer force material supplier and by that **mines** to **minimize environmental impact** (e.g. CO_2 footprint) and production cost

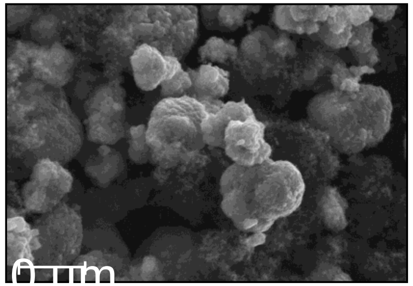


We require new environmental friendly material production technologies

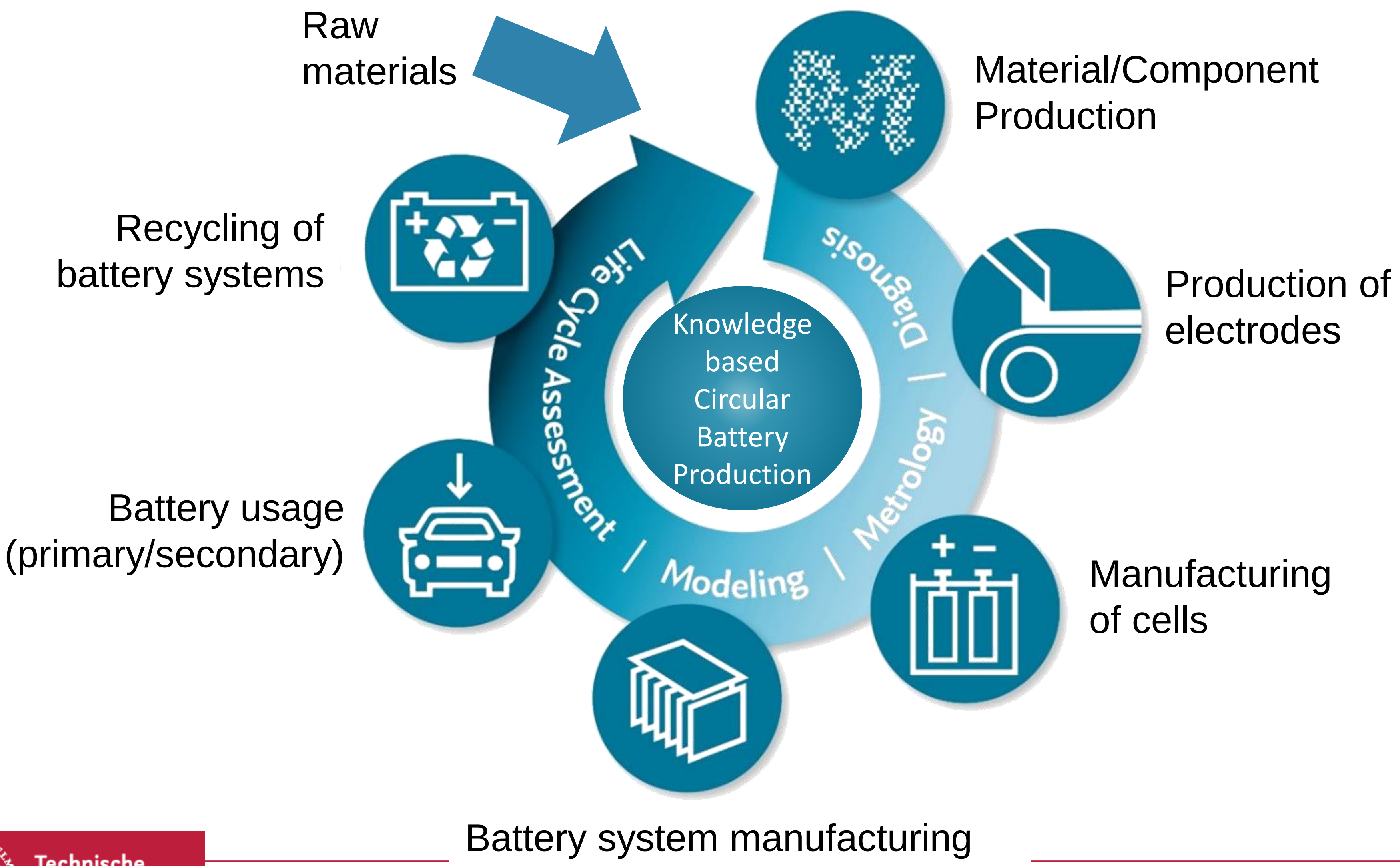
[Ellingsen et al. (2017), Identifying key assumptions and differences in life cycle assessment studies of lithium-ion traction batteries with focus on greenhouse gas emissions, Transportation Research Part D: Transport and Environment, 55:82–90.]

Content





Circular Economy and Production of Batteries



Circular Economy and Production of Batteries

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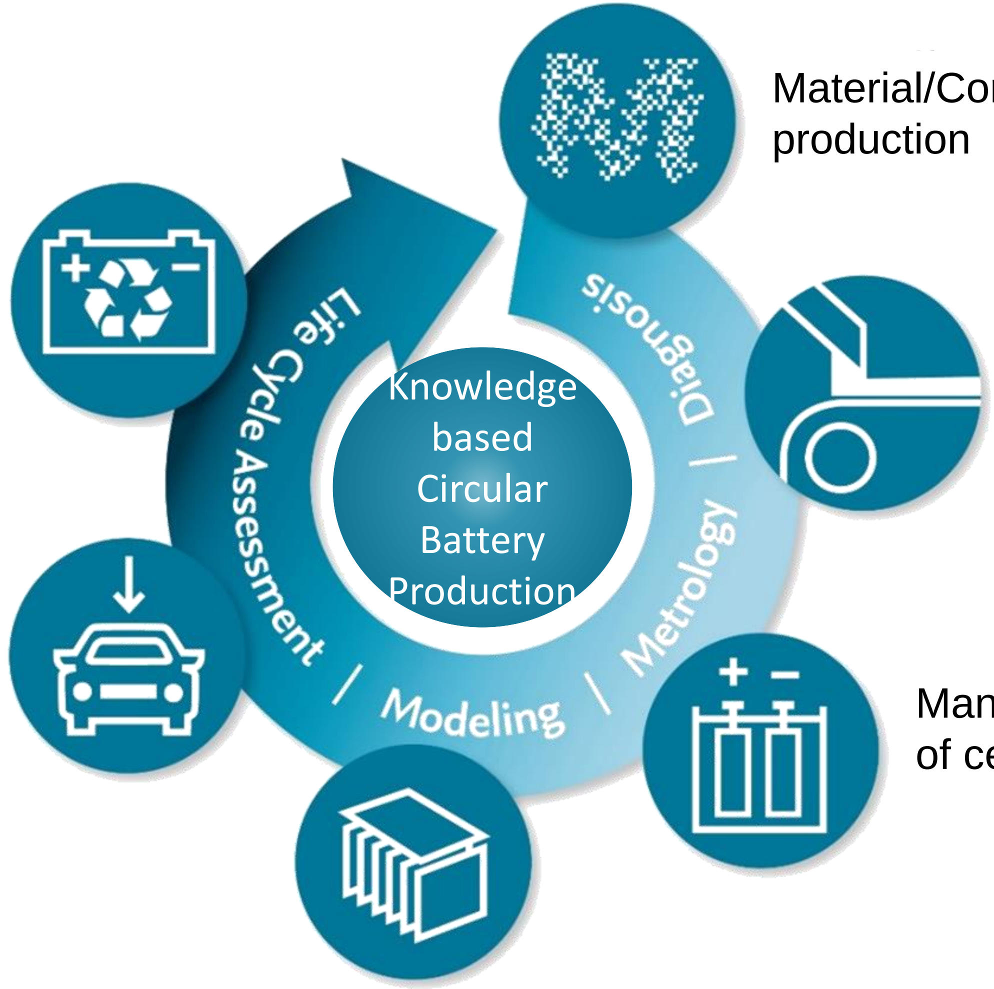
Material/Component production

Recycling of battery systems

Electrode production

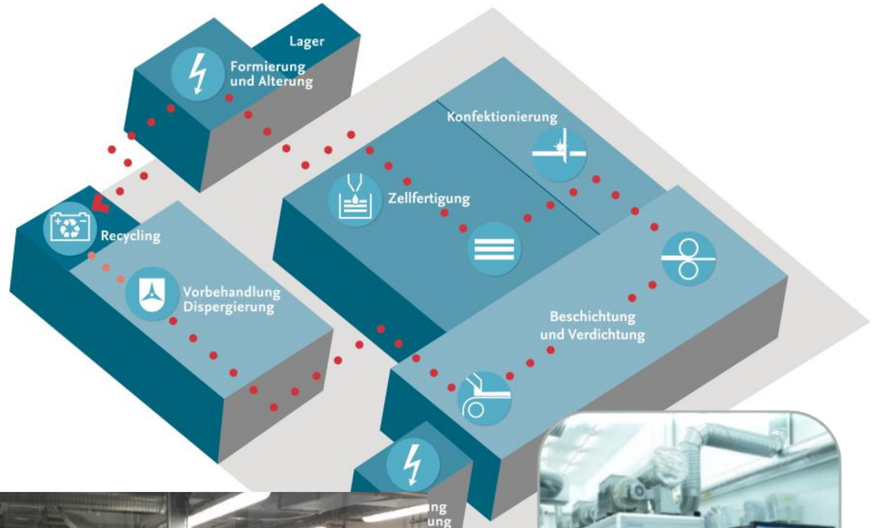
Battery usage (primary/ secondary)

Manufacturing of cells



Battery system manufacturing

Pilot scale battery production facility



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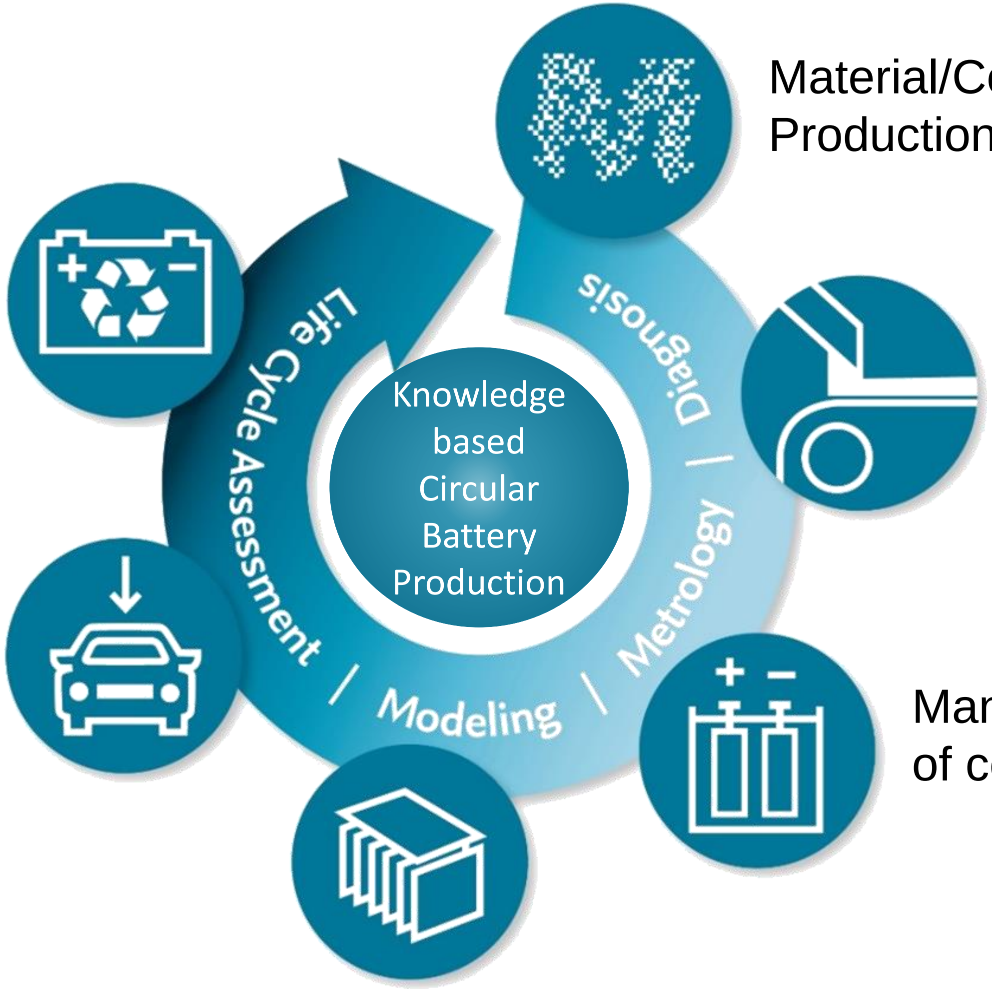
Circular Economy and Production of Batteries

Recycling of battery systems



Material/Component Production

Production of electrodes

Manufacturing of cells

Battery system manufacturing

Battery usage (primary/secondary)

Importance of Battery Recycling
Number of End-of-Life Battery Systems and components

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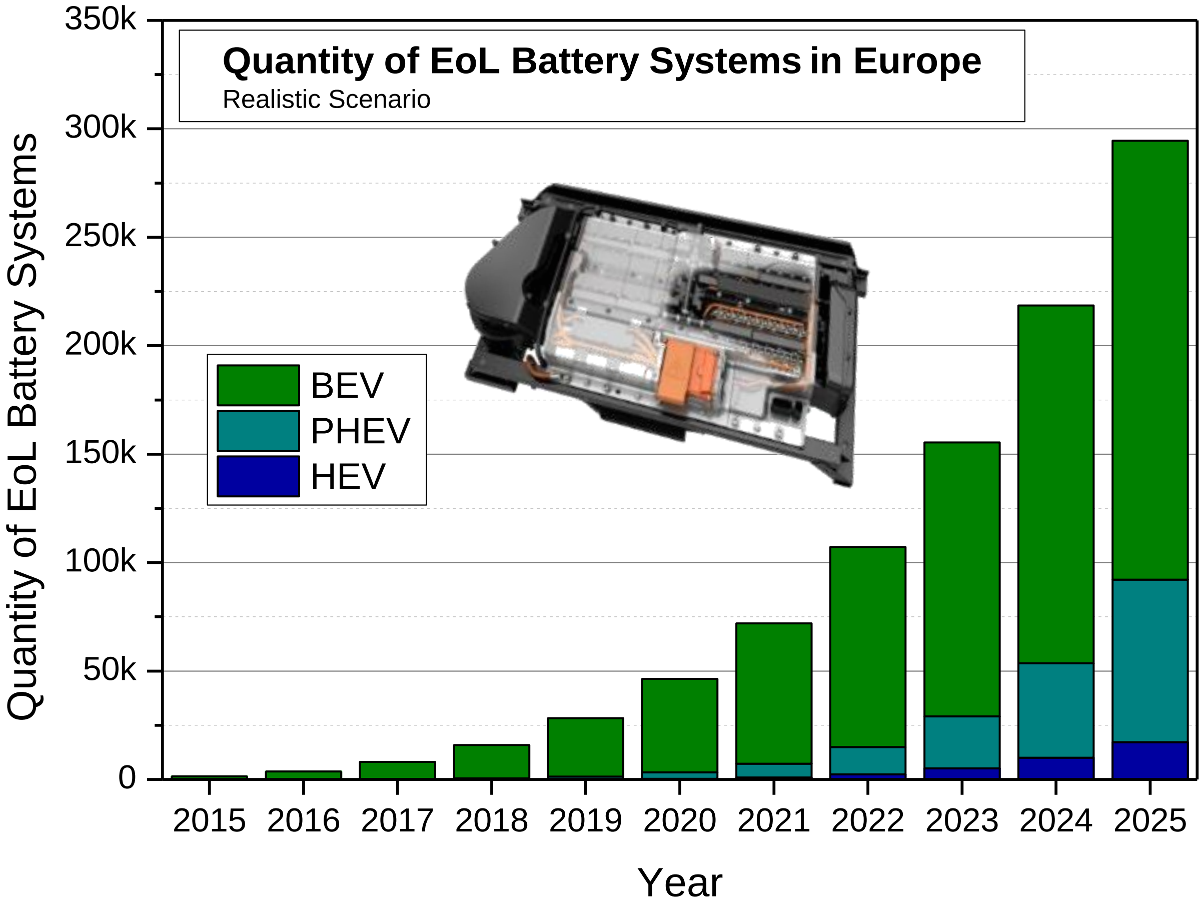

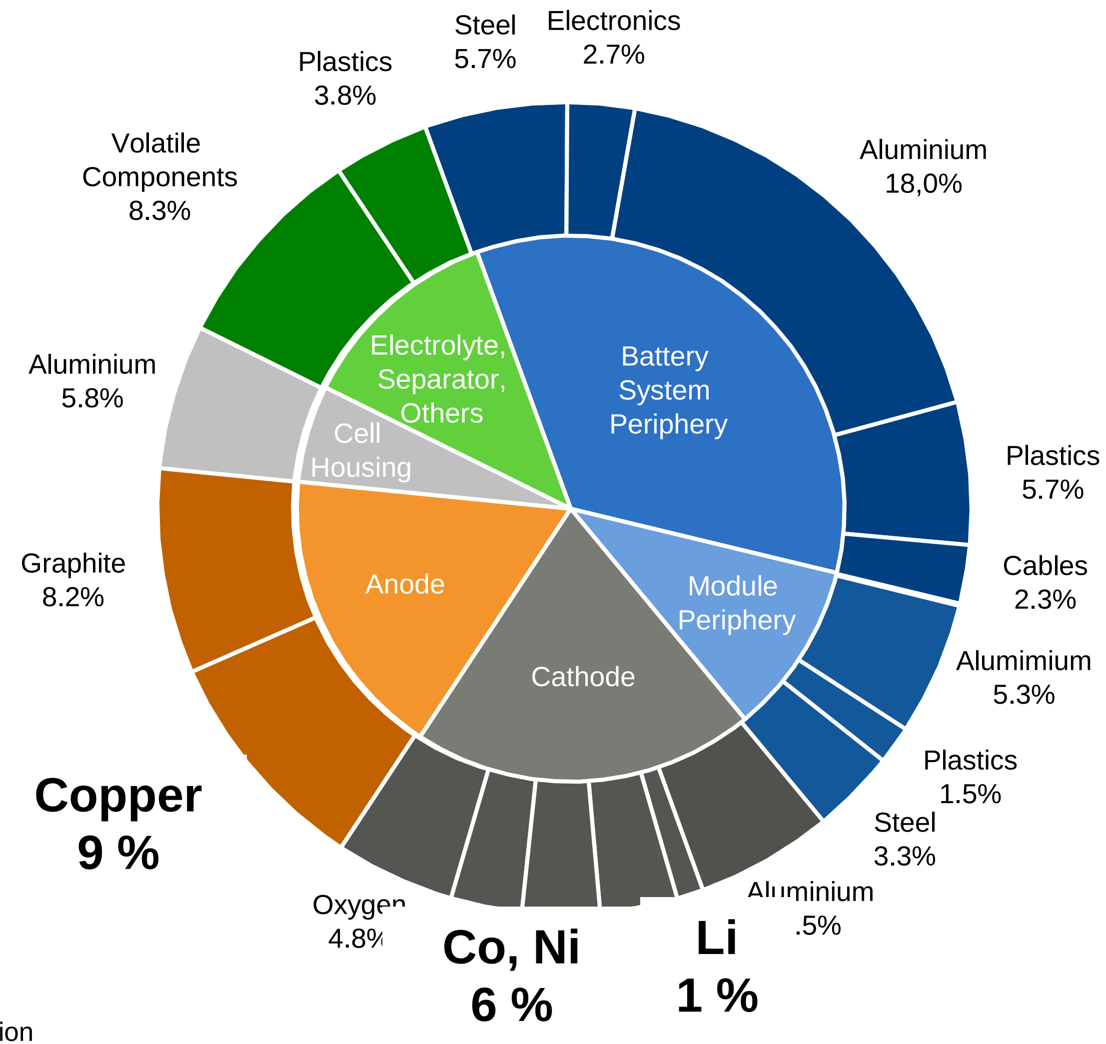

Source: Institute of Automotive Management and Industrial Production

Technische Universität Braunschweig

A. Kwade, J. Diekmann (2017) Recycling of Lithium-Ion Batteries: The LithoRec Way, Springer

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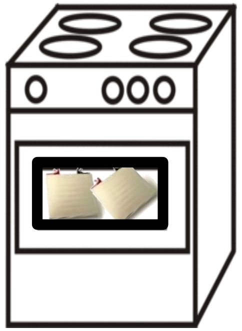
Unit operations of battery recycling

Deactivation of cells

- Thermal Pretreatment
- Discharging
- Freezing of Electrolyte
- Short circuit (e.g. in water)



Mechanical Processing

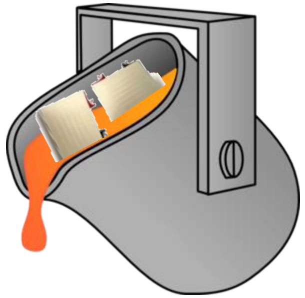
- Deassembling
- Crushing / Milling
- Classifying (sieving, air classification)
- Sorting (e.g. magnetic separation)

Pyro-metallurgy

Smelting of

- Battery Moduls
- Electrode Scraps
- Active Material Powder

→ Regaining of Co, Ni, Cu

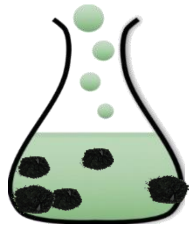


Hydro-metallurgy

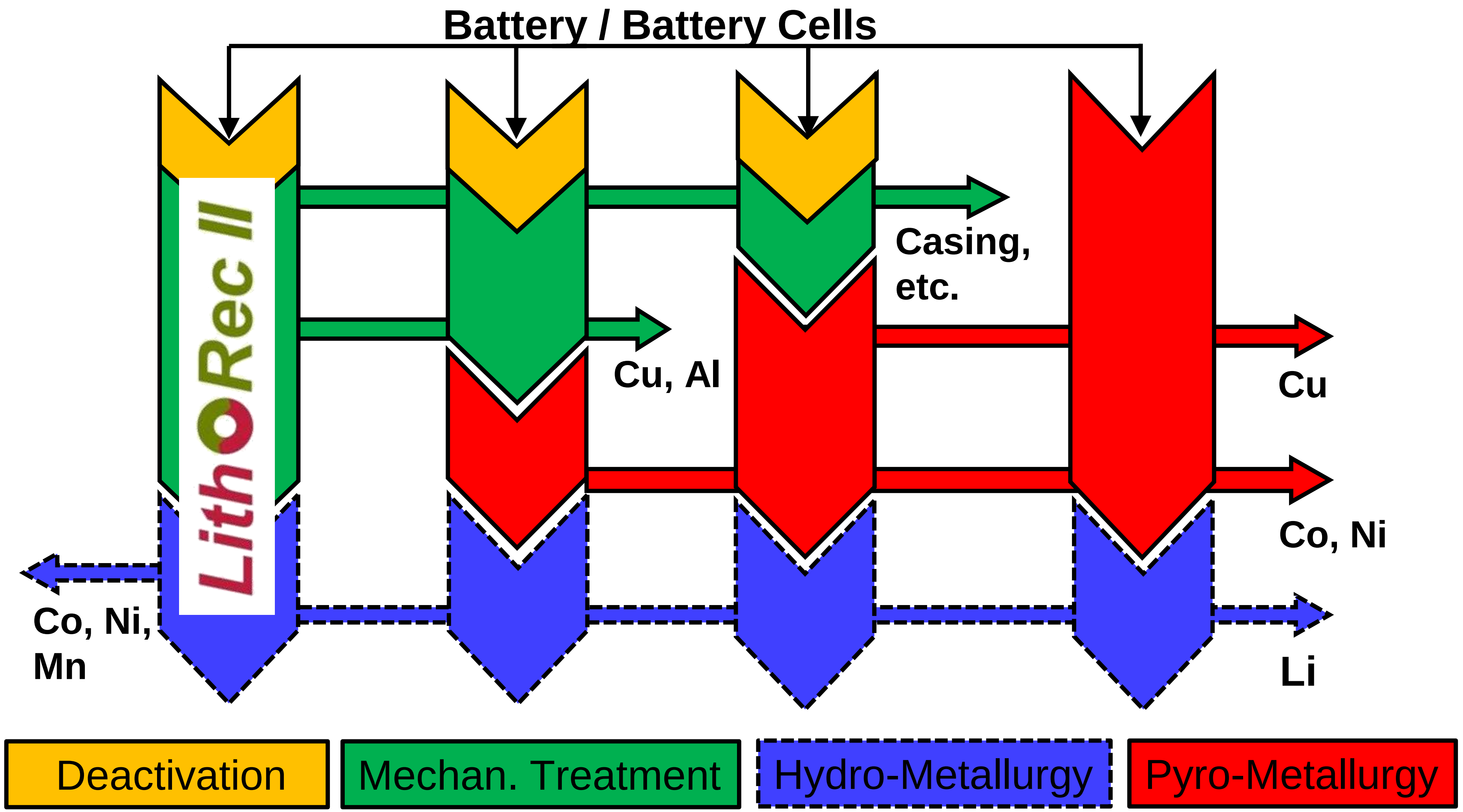
Chemical Processes

- Leaching
- Extraction
- Cristallisation
- Precipitation

→ Regaining of Metals Co, Ni, Li from separated powders or slag



Possible solutions with recovery of lithium



Lithorec process overview

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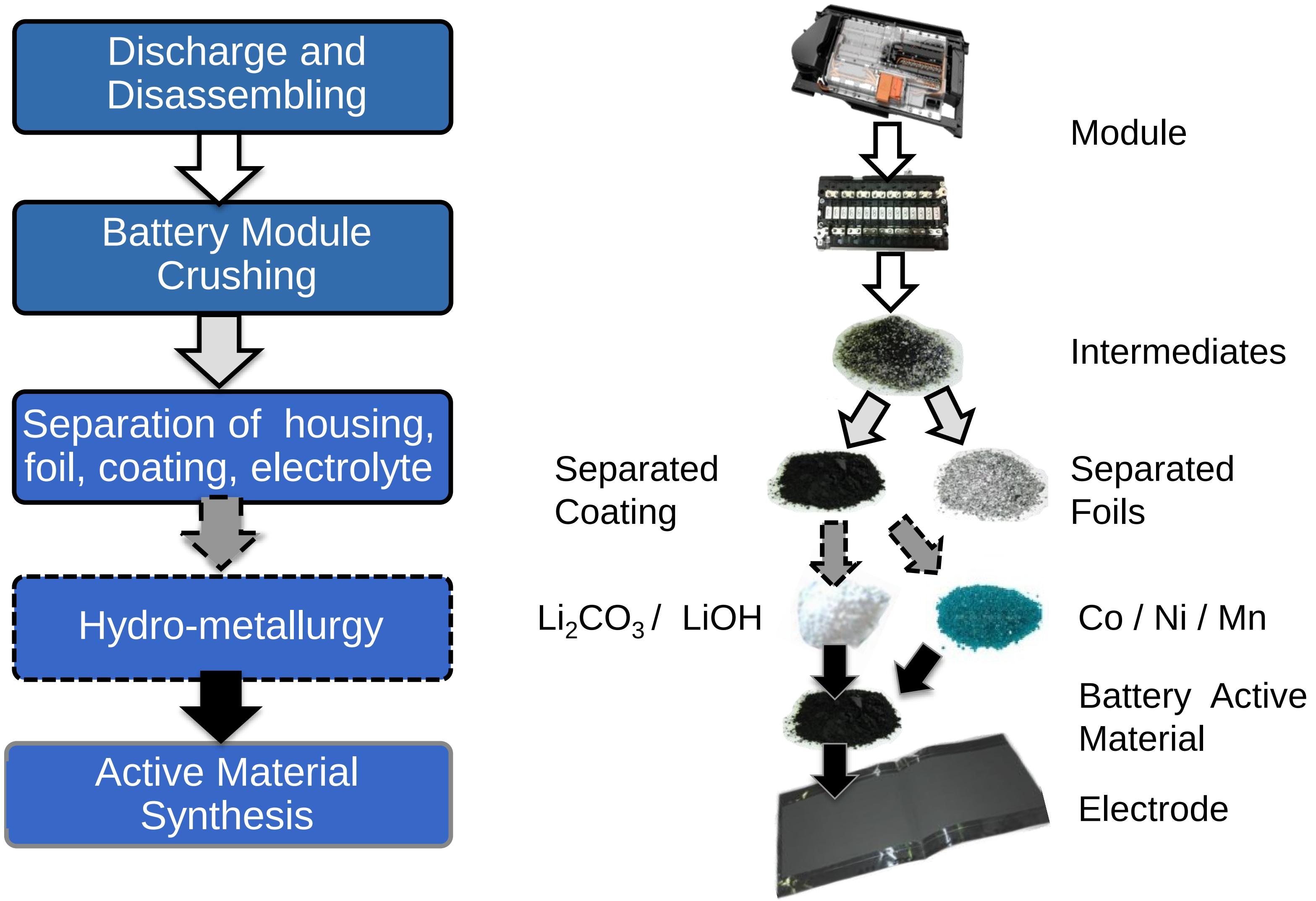
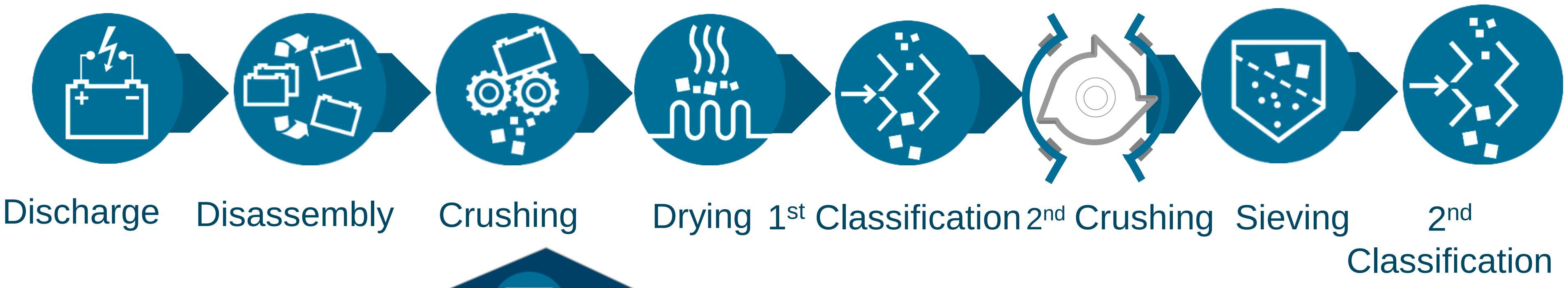
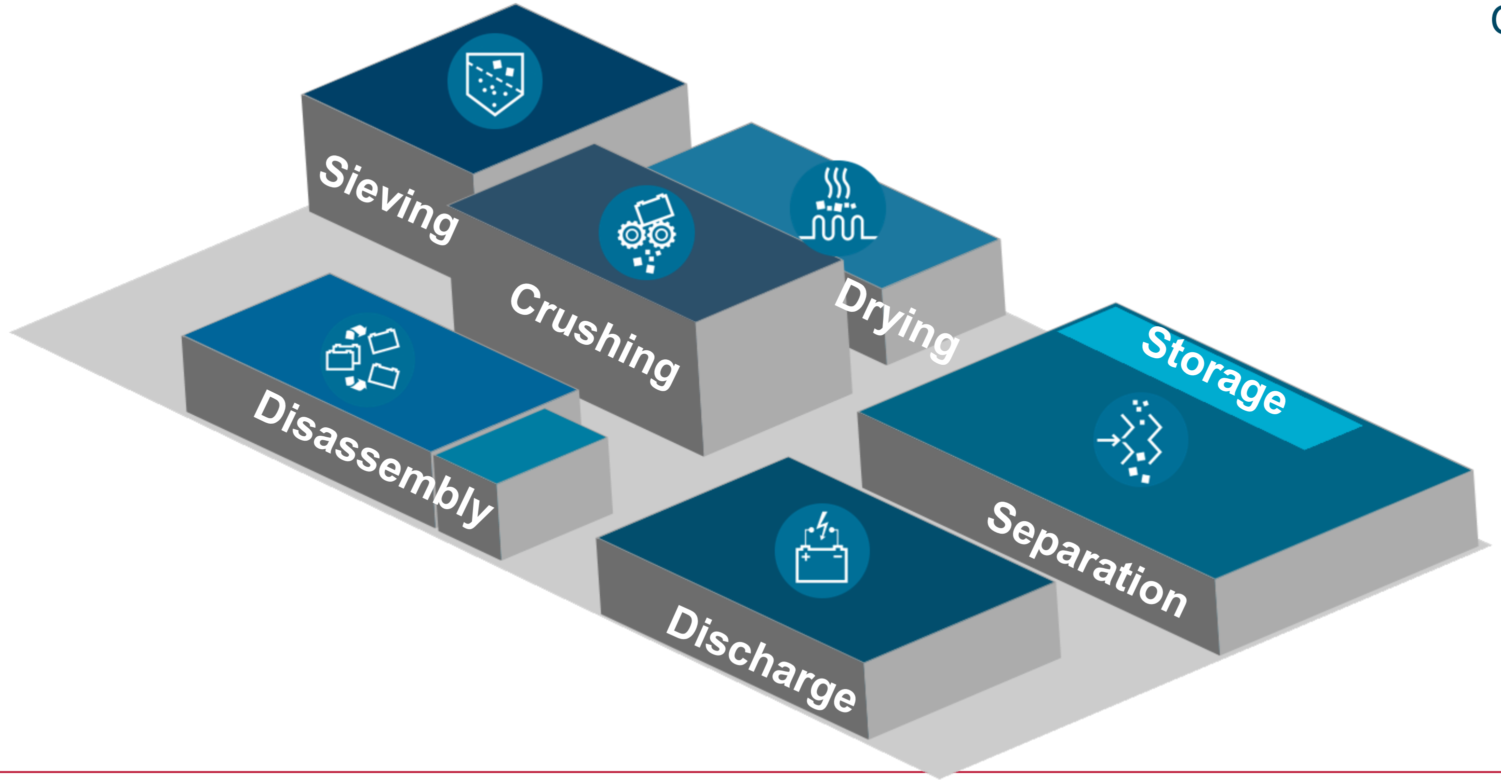


C. Hanisch, T. Loellhoeffel, J. Diekmann, K.J. Markley, W. Haselrieder, A. Kwade (2015). Journal of Cleaner Production 108, pp. 1-11

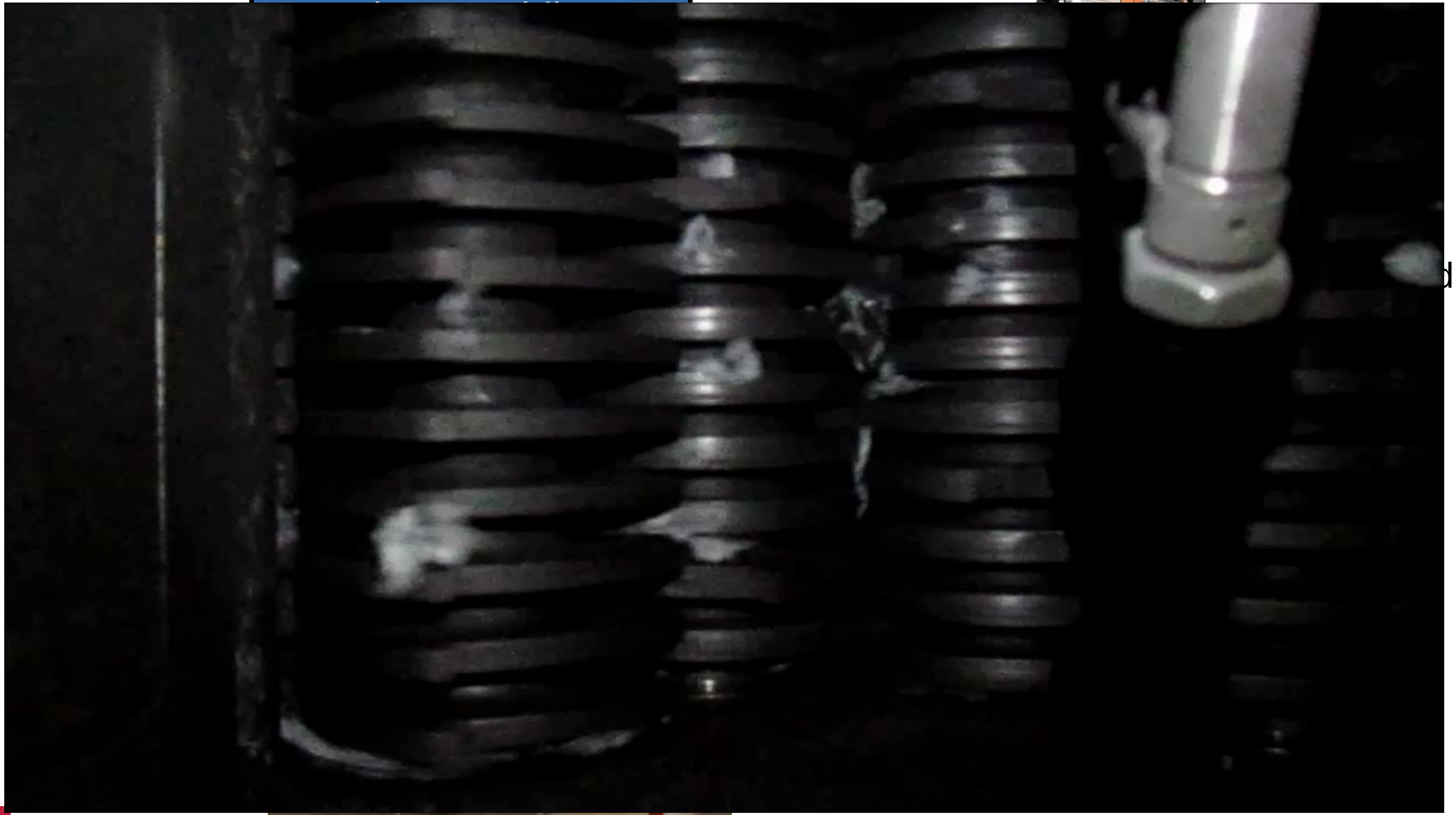
Process Chain for Demonstration Plant





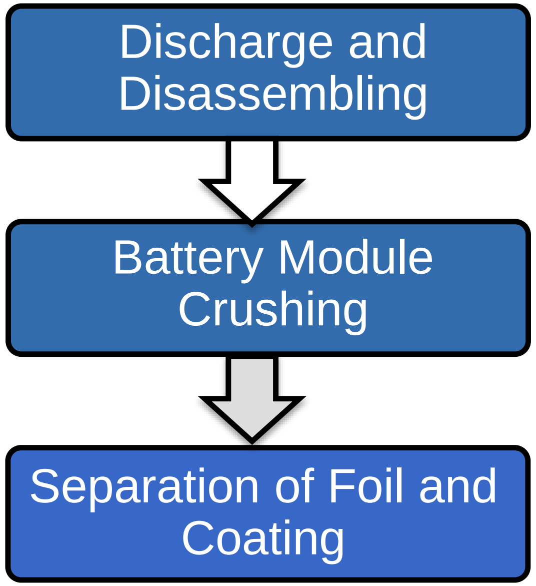
Lithorec process overview

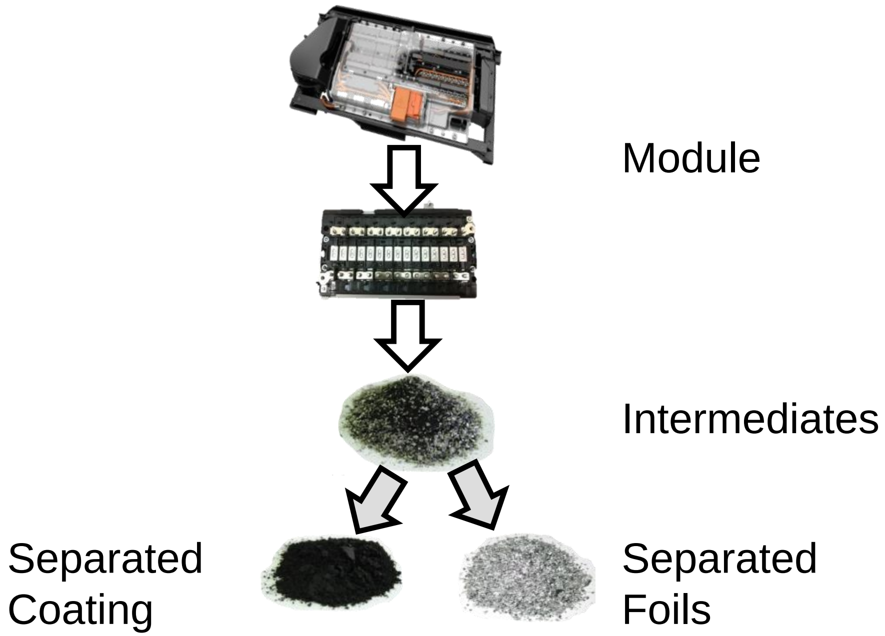
Discharge and



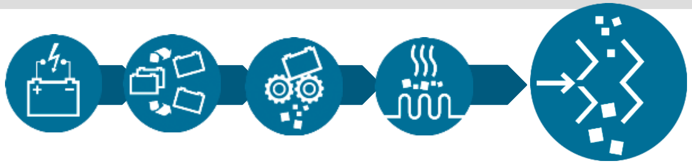
diates

Lithorec process overview

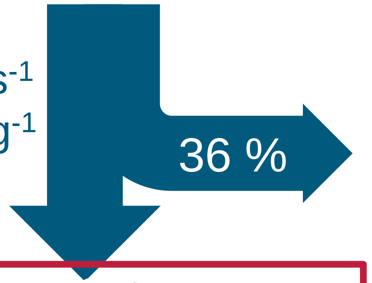




1st Air-Classification



v_S 3,34 m s^{-1}
μ_S 190 g kg^{-1}



heavy parts

Cu-, Al- Foil, Separator, Plastics, Black Mass

Al module
26.6 %

Copper
5.0 %

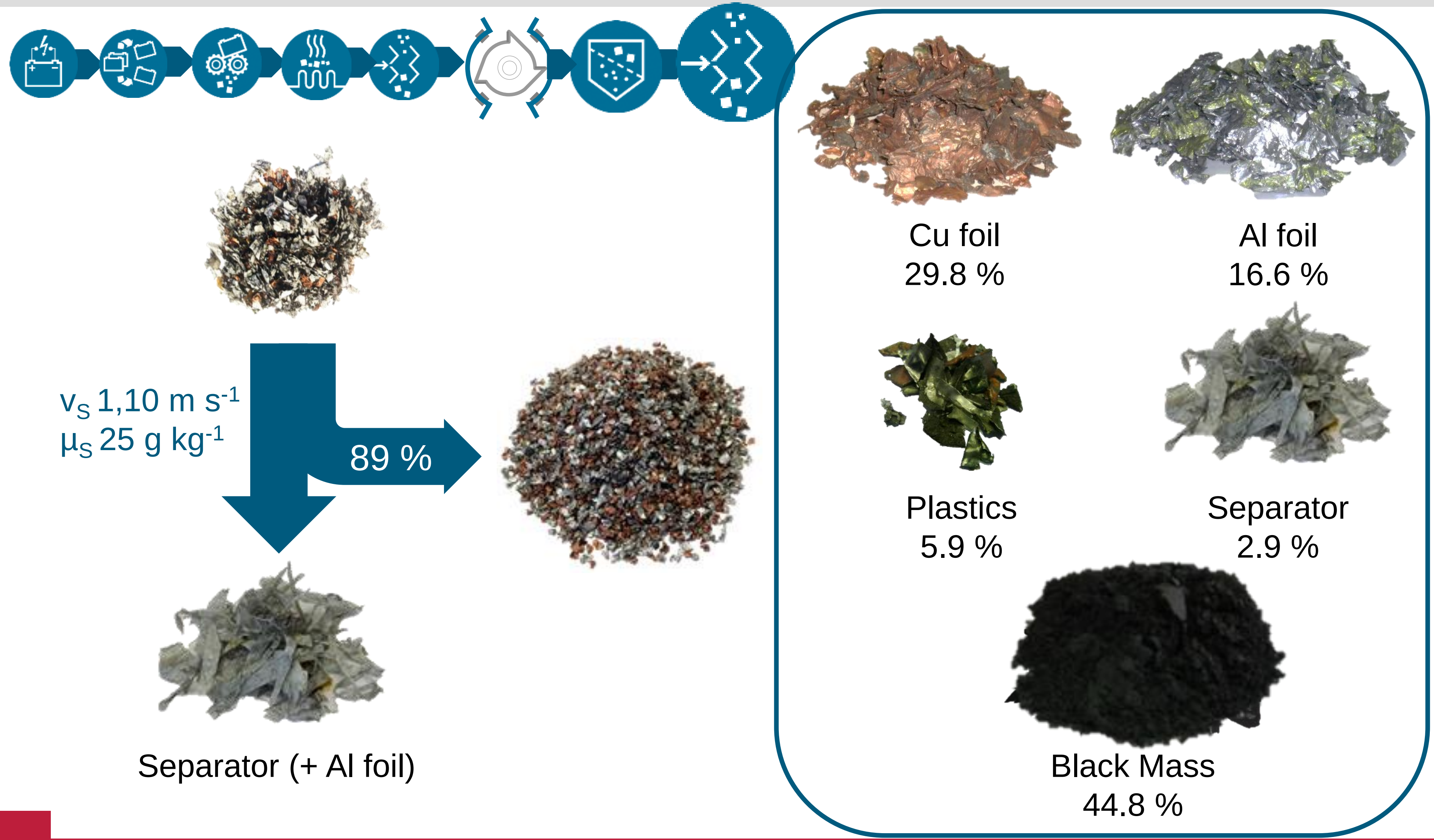
Al housing
47.7 %

Plastics
4.0 %

Steel
13.8 %

Inclusions
2.9 %

2nd Air-Classification



Fine sieving of fine/light fraction
Yield and purity black mass

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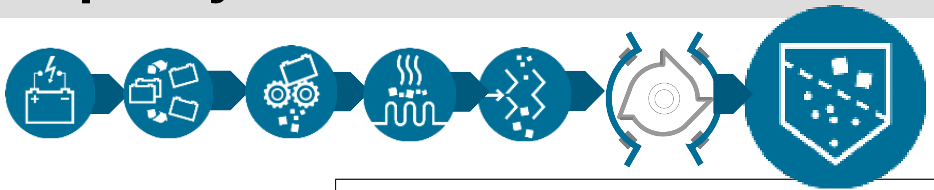
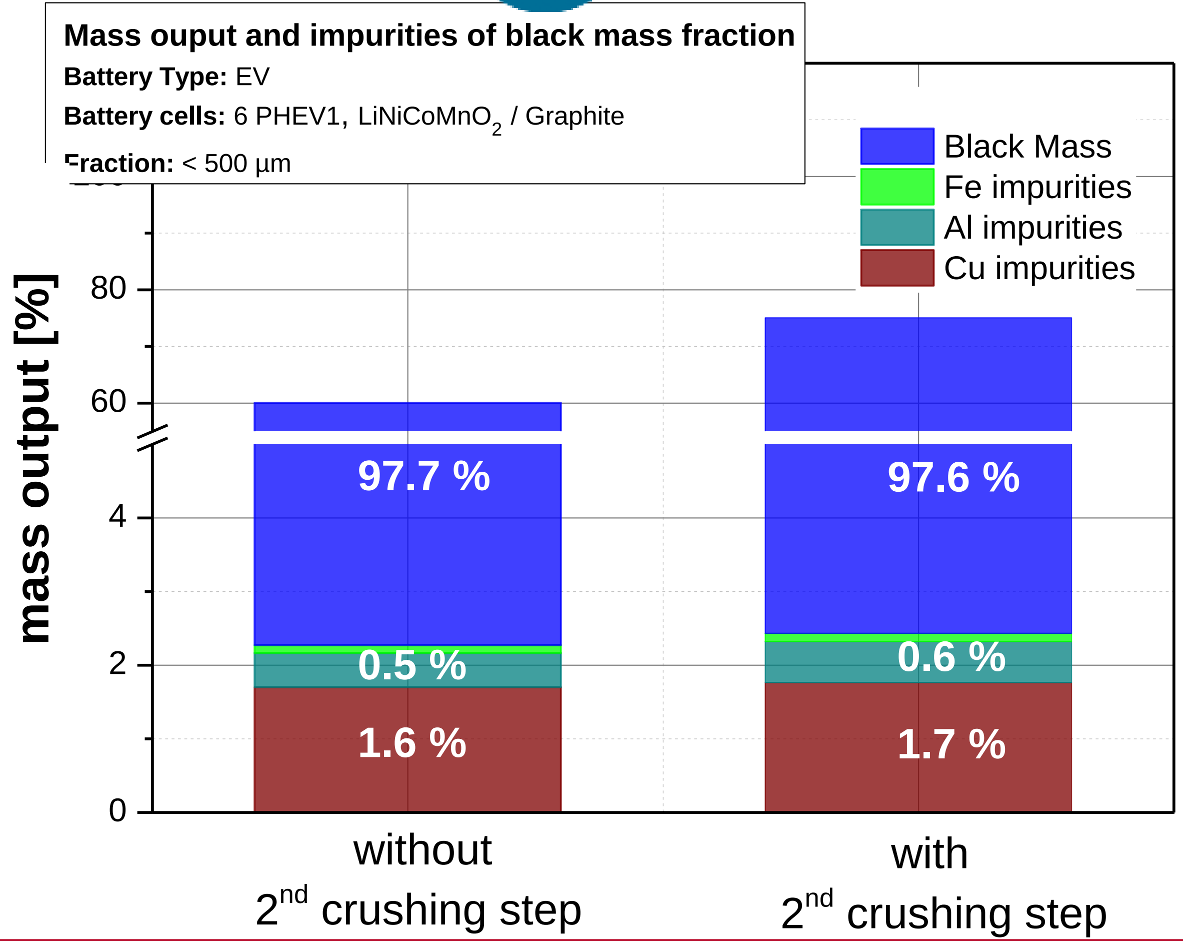
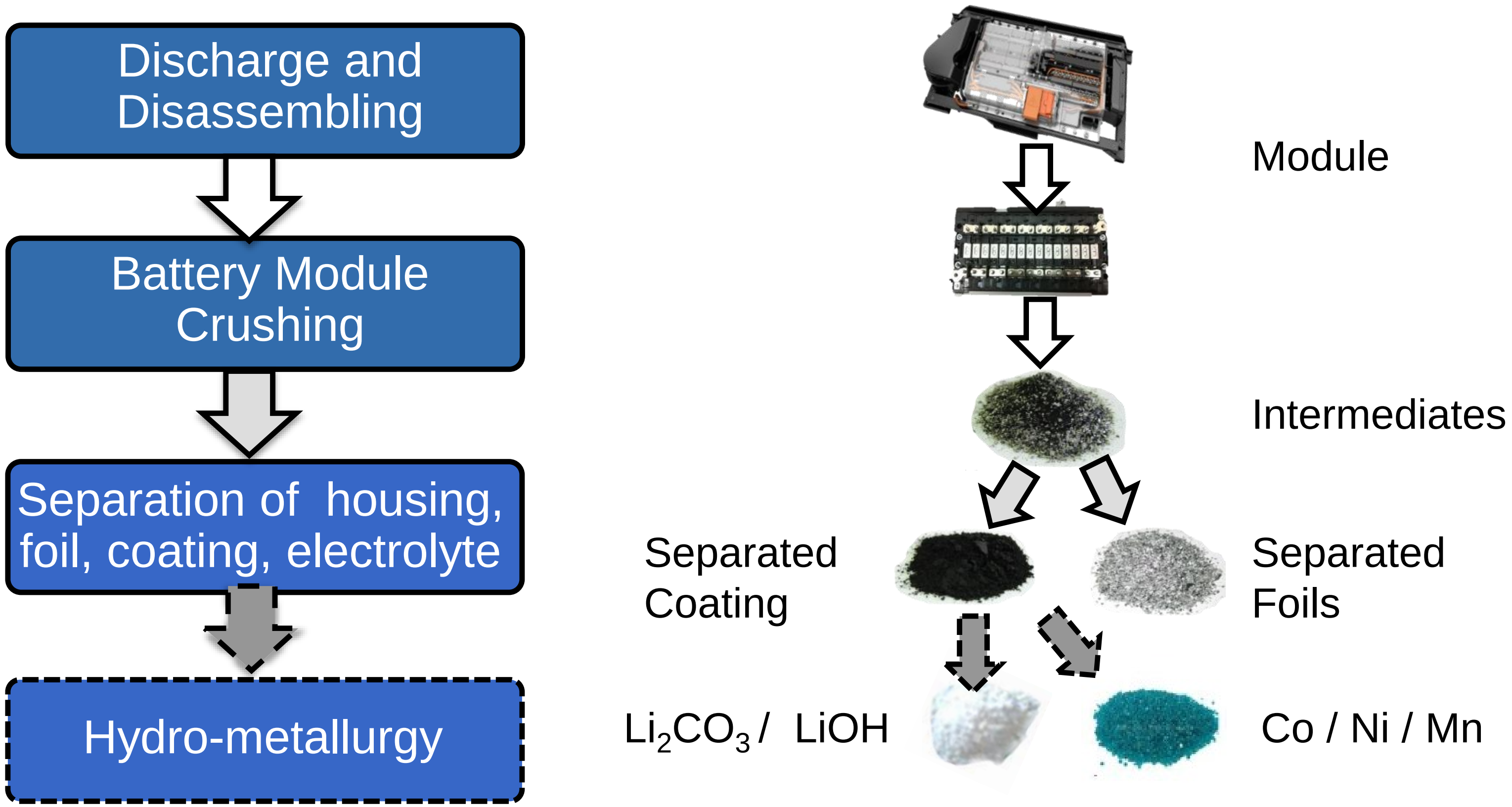


Black mass recoverd by sieving at 200 µm



Black mass recovery rate > 75% at this point

Lithorec process overview



A. Kwade et.al. (2018) Nature Energy 3 (4), pp. 290-300

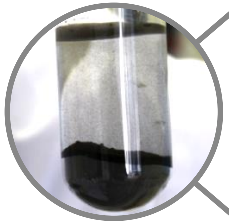
Recycling
Hydrometallurgical treatment

Active material

- Cathode
- Residual cross contamination (Al, Fe, Cu)

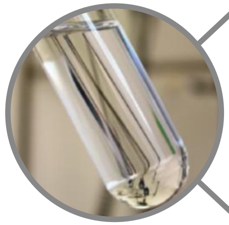
Acidic desintegration of active material

- Dissolution of metal components



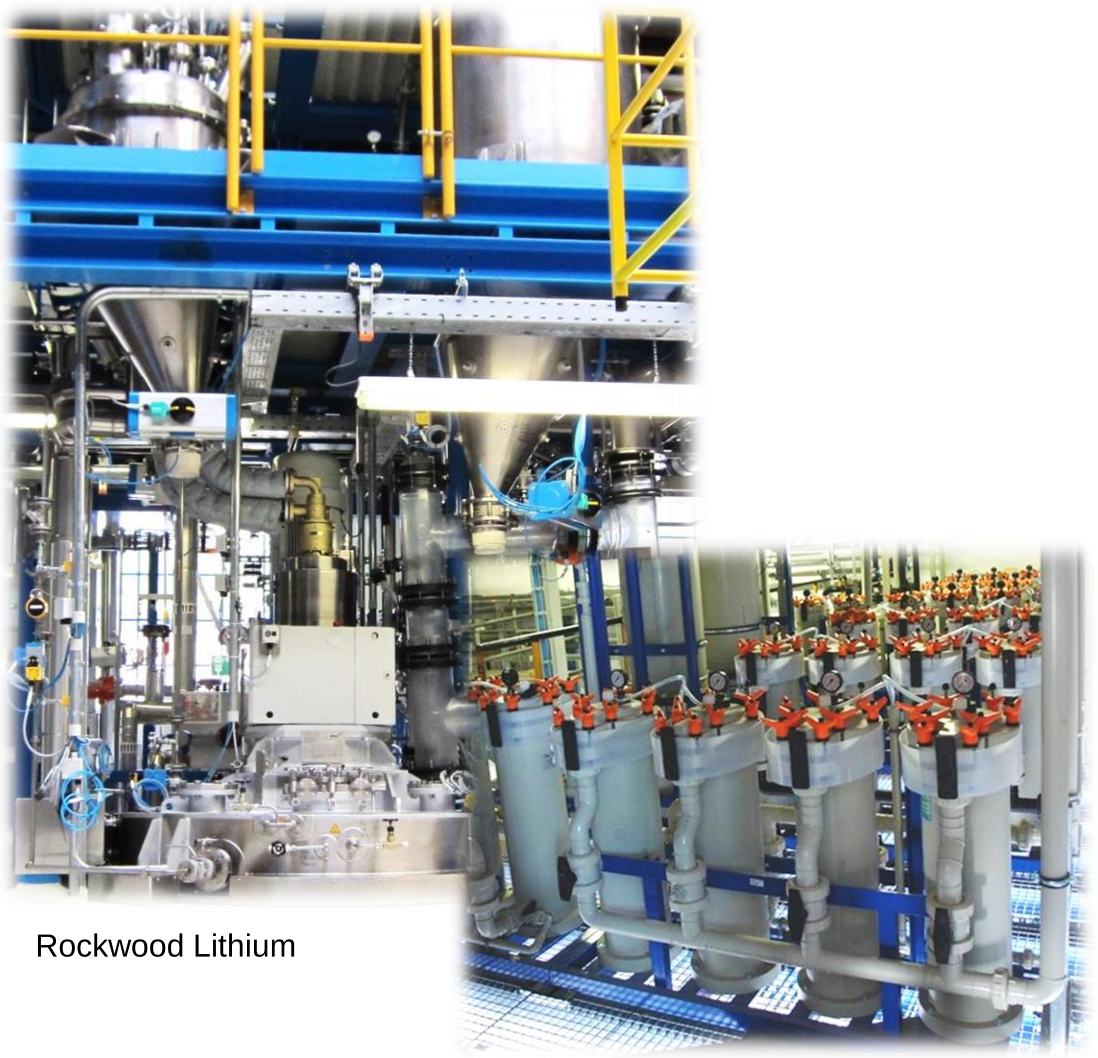
Solid separation

- Metal salt solution
- Solids remaining



Precipitation

- of transition metal salts
- Preservation of a Lithium-Salt-Solution



Rockwood Lithium

Recycling Efficiency
based on material recycling

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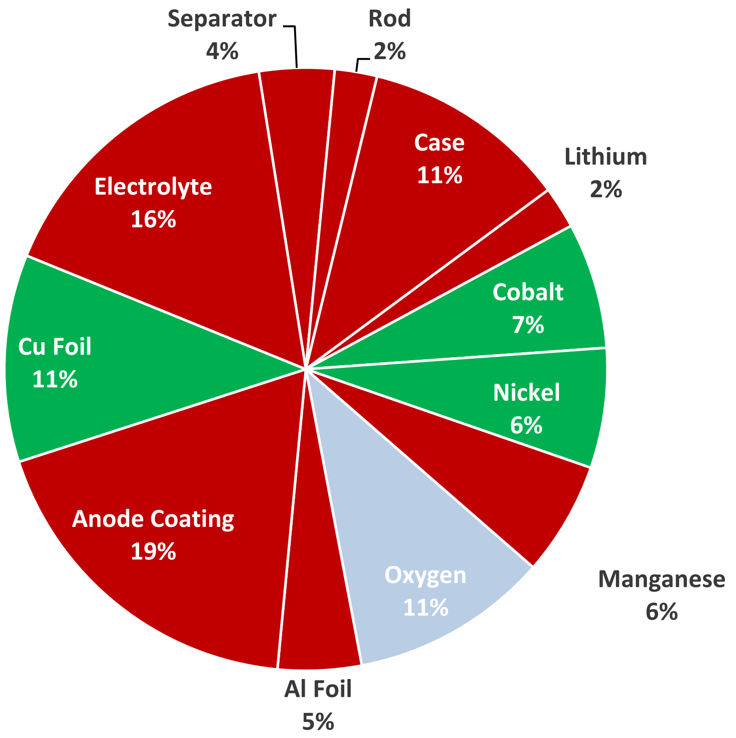
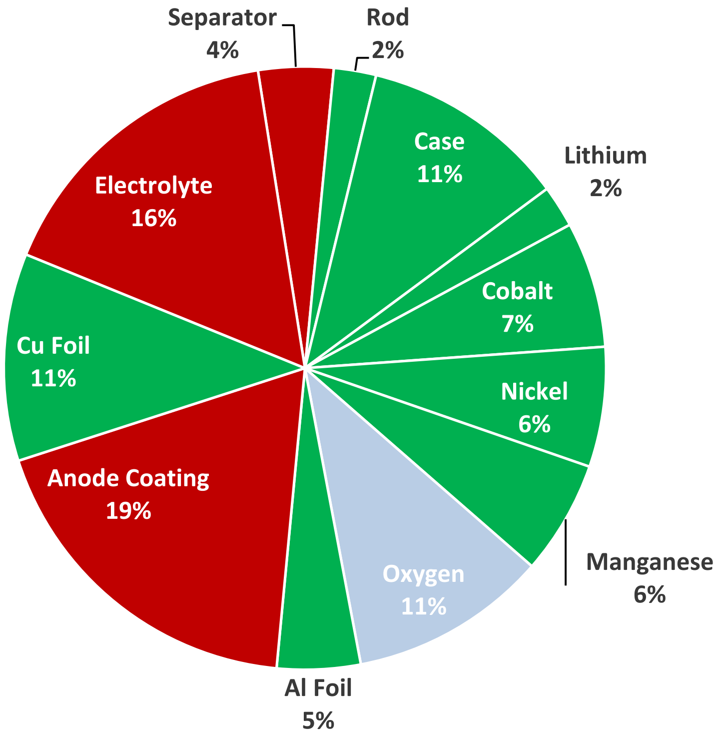
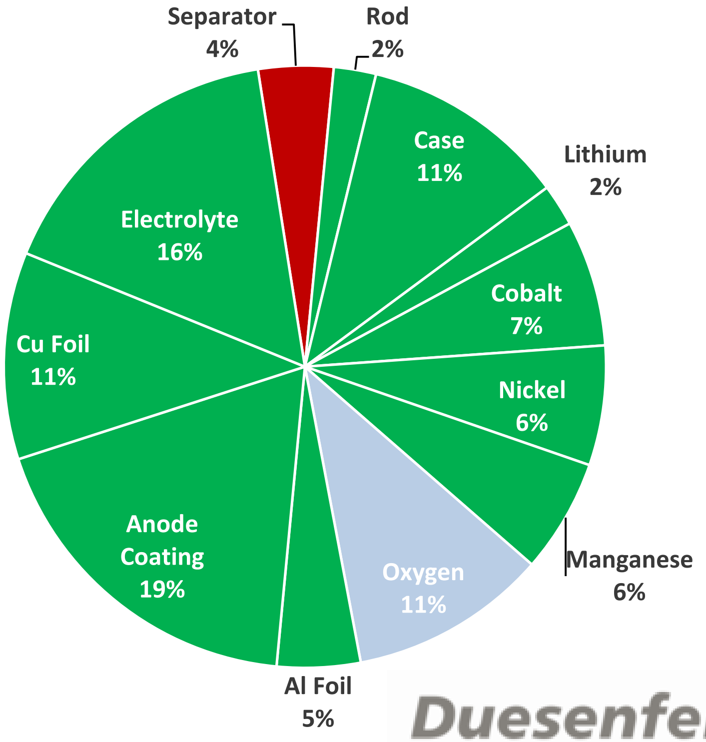
State of the art
(mainly pyrometallurgy)
≈ 30%



Available technology
(Mechanical treatment, hydrometallurgy)
≈ 80% *



Advanced technology
(Mechanical treatment, hydrometallurgy)
> 95%*



Duesenfeld

Other recycling or disposal   Material recycling

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* on battery cell level, normalized after substraction of oxygen

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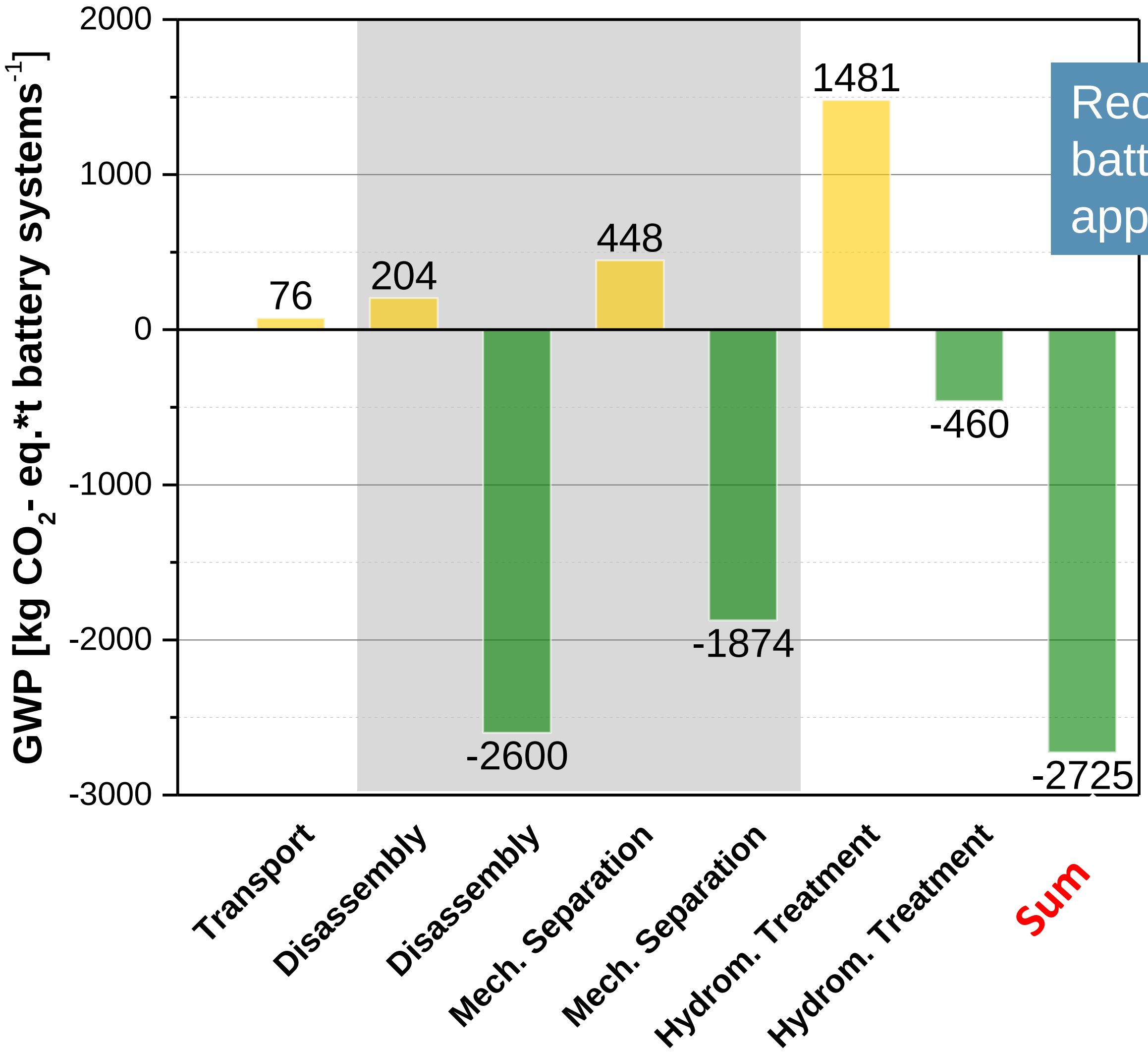
Ecobalance LithoRec-Process

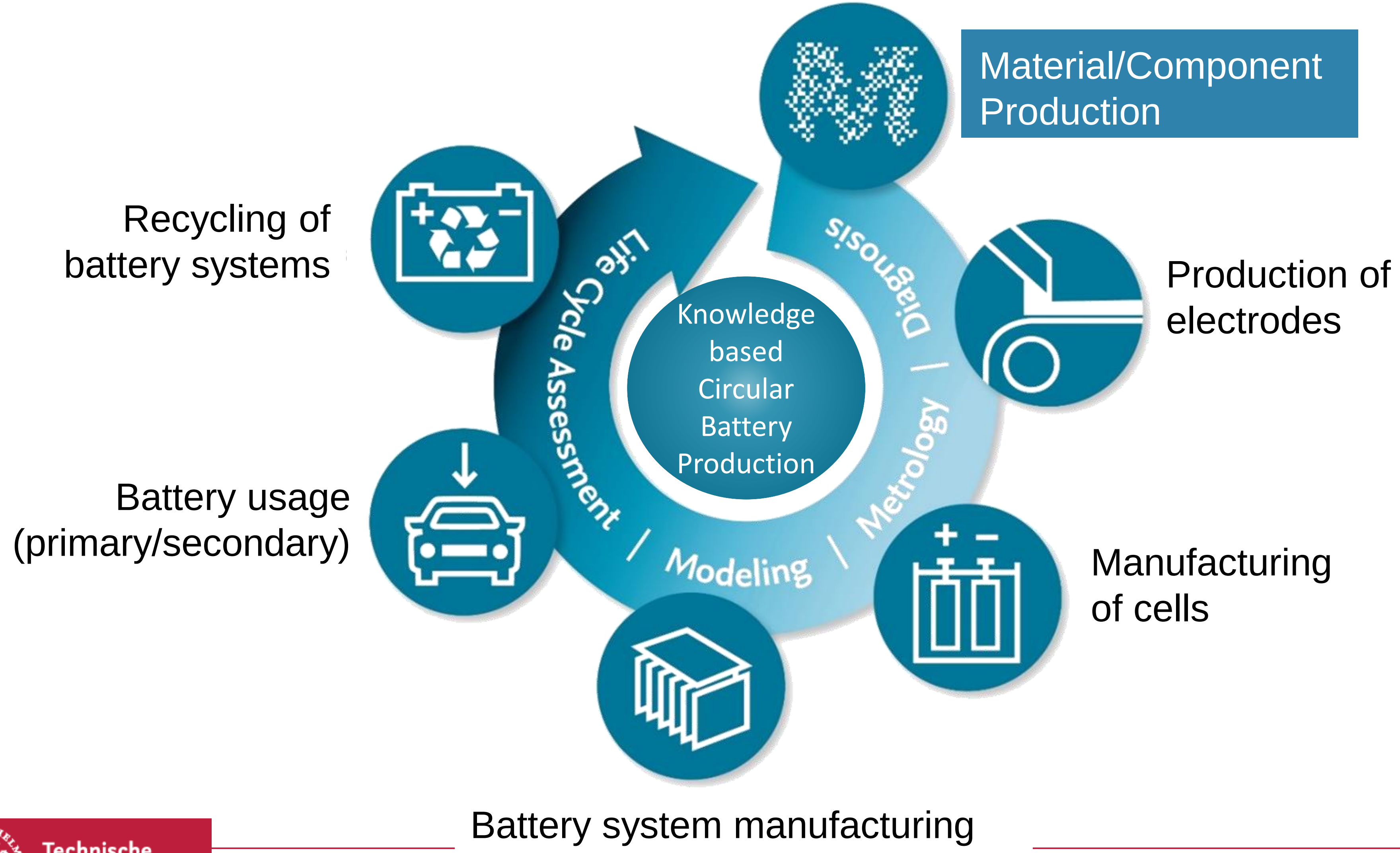
Öko-Institut e.V.



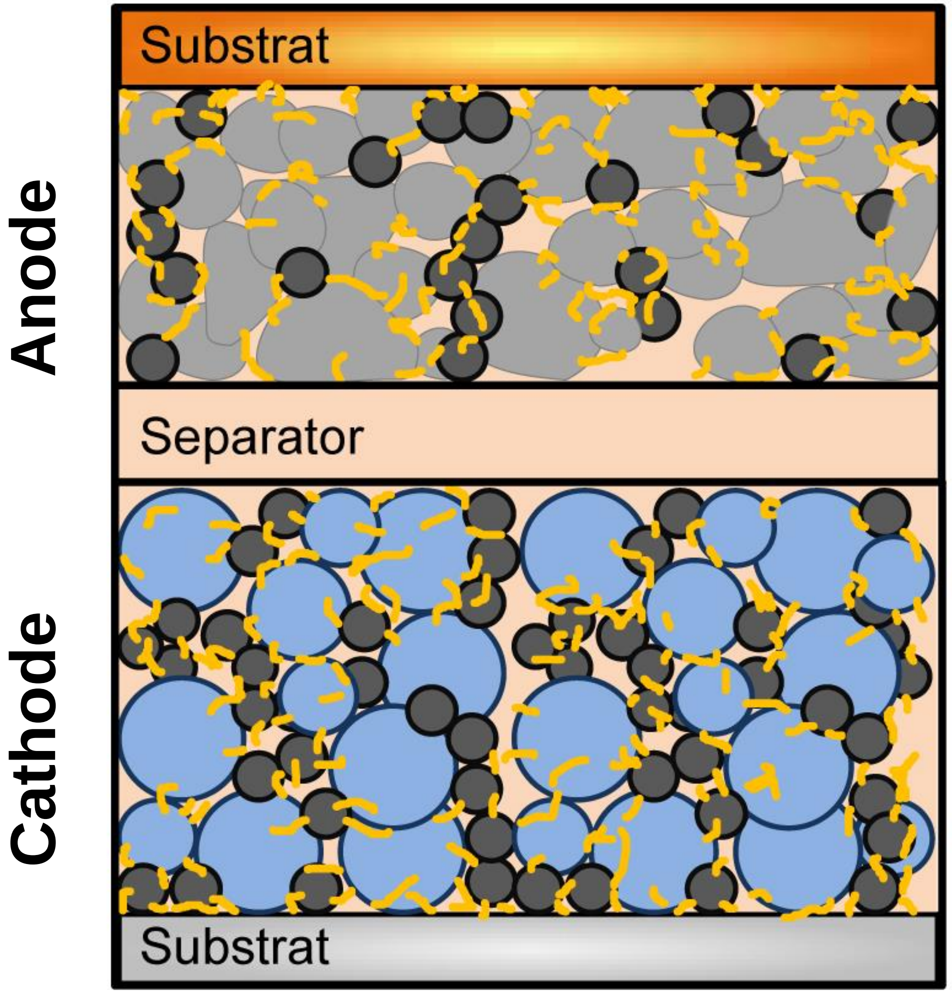
Recycling of 1 ton of NMC based batteries results in a reduction of approximately 2.7 ton of CO_2

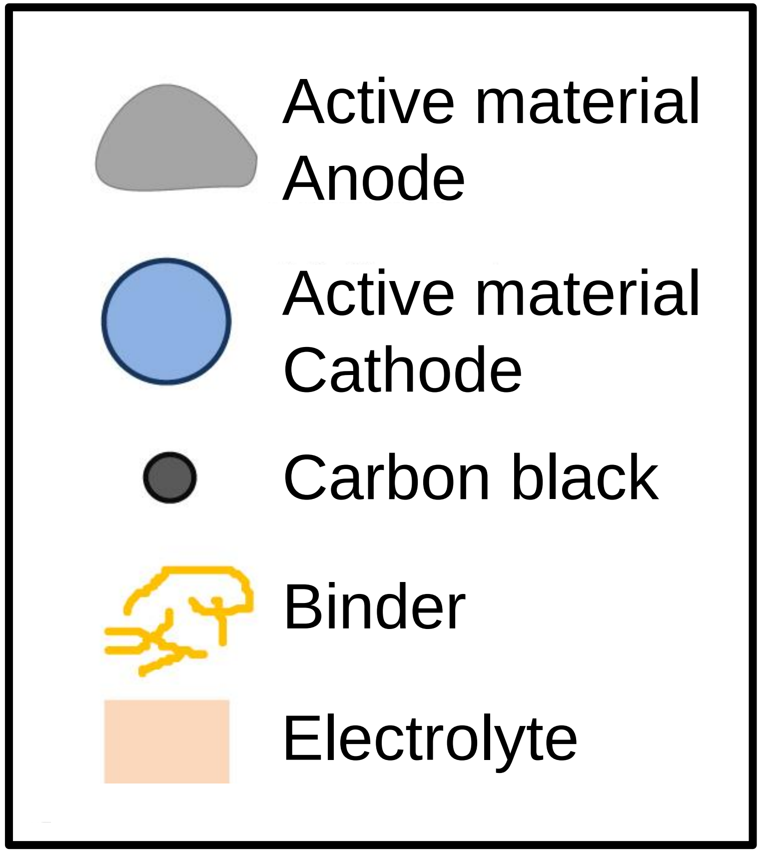
Source: Abschlussbericht zur Ökobilanz des LithoRec II –Verfahrens, Öko-Institut e.V.

Circular Economy and Production of Batteries



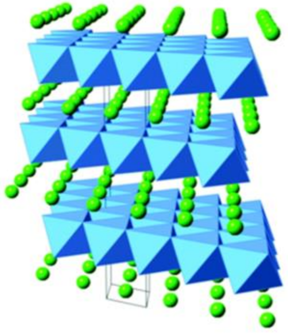
Active materials of Lithium-ion battery



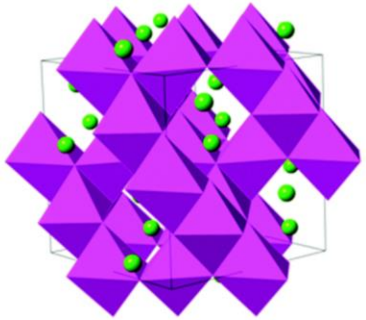


Active materials for the cathode

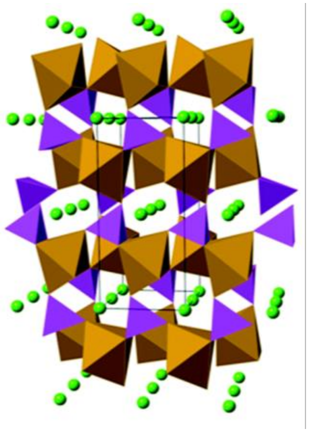
- **Lithium metal oxides** with morphology of **layered oxide**
  - $LiCoO_2$
  - $LiNMO_2$ (N, M = Ni, Co, Mn in different amounts N + M = 1)
    - e.g. **$LiNiMnCoO_2$** (NMC 111, NMC 622, NMC 811)
    - e.g. **$LiNiCoAlO_2$** (NCA)



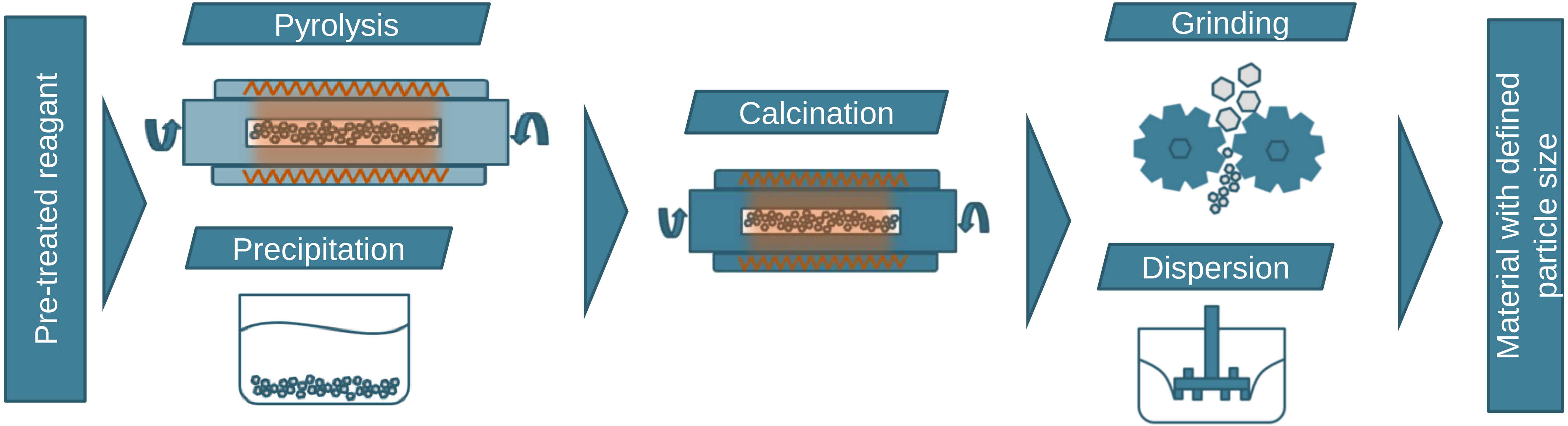
- **Lithium metal oxides with morphology of spinels**
  - LiM_2O_4 (M = Mn, Ni, Co)



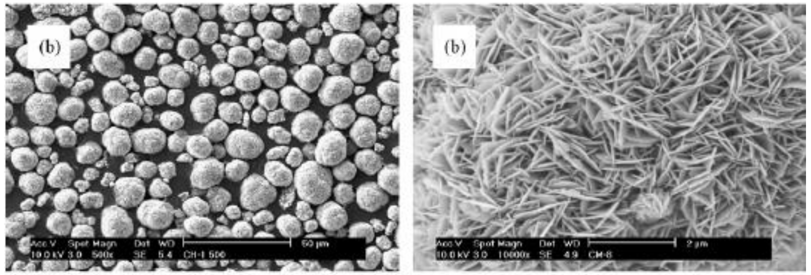
- **Lithium metal phosphates**
  - $LiMPO_4$ (M = Fe, Co, Ni, Mn) e.g. **$LiFePO_4$**



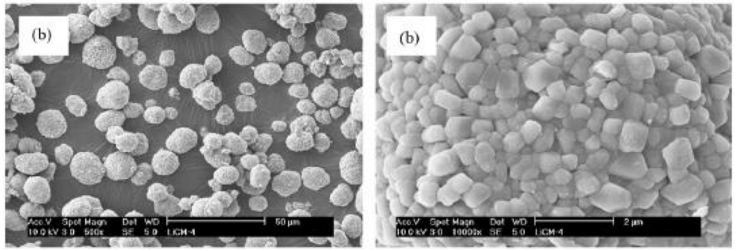
Synthesis of cathode material



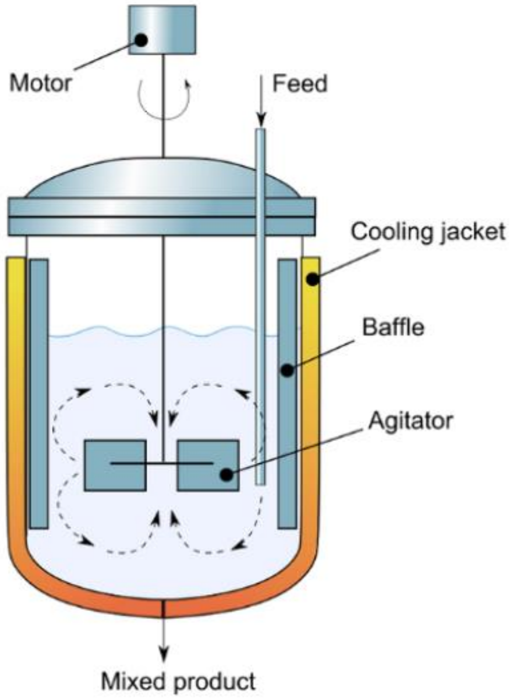
NMC Precursor after precipitation



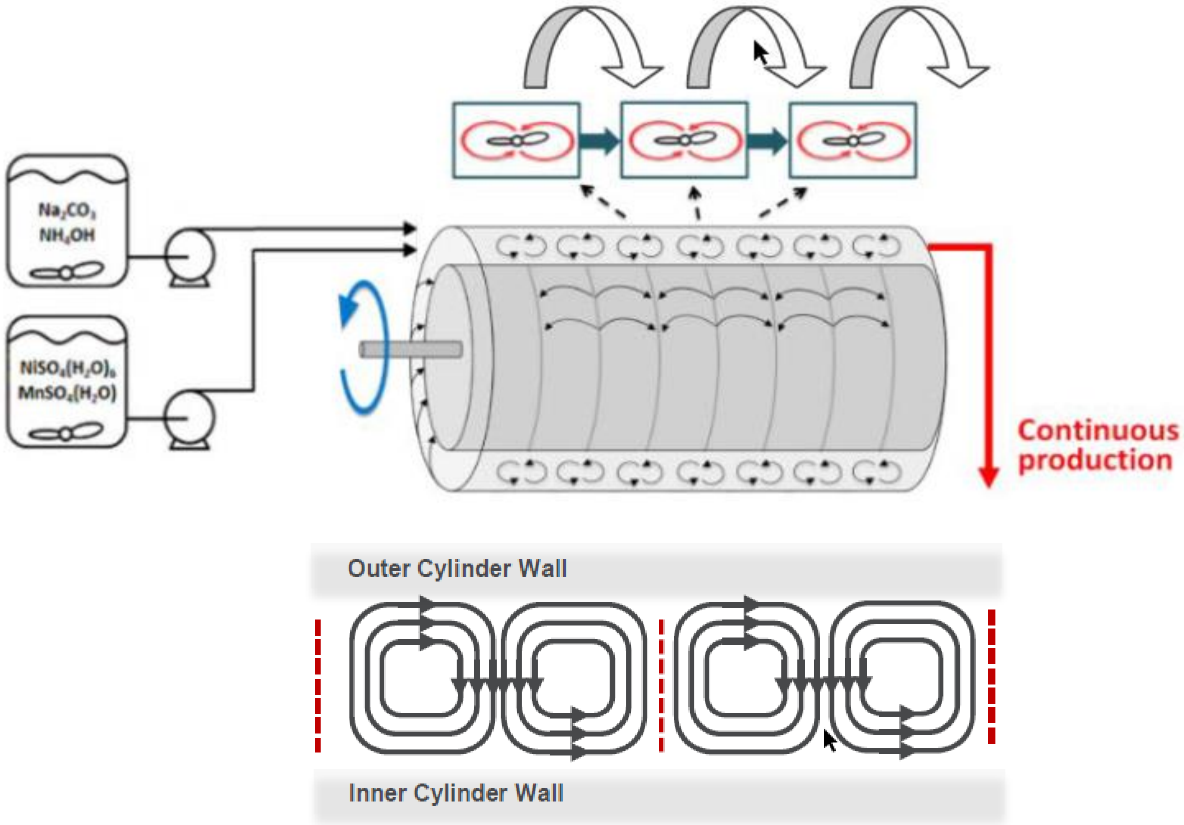
NMC after calcination



Production and preparation of cathode active materials



Continuous Stirred Tank Reactor



Taylor Vortex Reactor

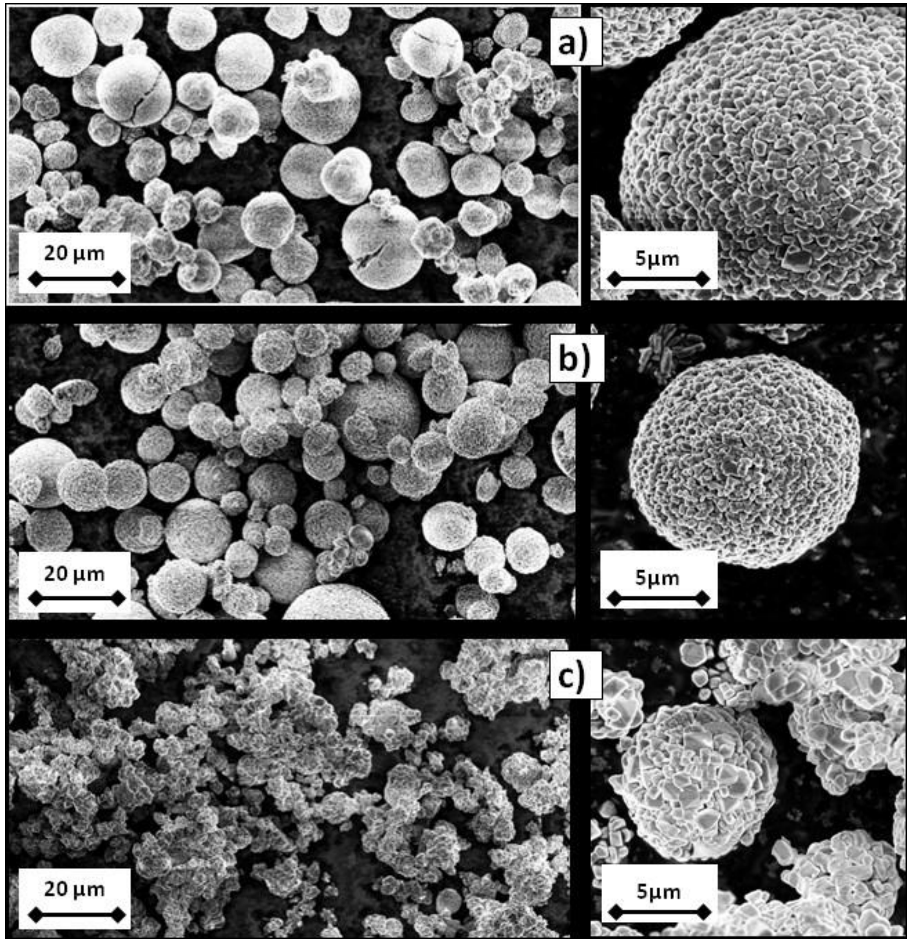
Source: www.anl.gov

SEM-Images of Re-Synthesized NCM

Reference
- From pure metal salts

Rejects
- From electrode production rejects

Cycled
- From resynthe-sized spent cells



- **Increase** of BET-surface area
  - Reference 0.23 $m^2\ g^{-1}$
  - Rejects 0.28 $m^2\ g^{-1}$
  - Cycled 0.60 $m^2\ g^{-1}$

- **Reference and Rejects are closer** in BET-surface area
- Reason is **secondary particle shape** as a result of particle conditioning

- **Aluminium content increases** as main impurity

/ $g \cdot L^{-1}$	Reference	Rejects	Cycled
Li	-	0.56	6.46
Ni	34.00	39.00	39.00
Co	34.00	38.00	37.70
Mn	32.00	32.00	33.60
Al	< 0.02	0.24	1.48
Cu	< 0.01	<0.01	0.10
Fe	< 0.01	<0.01	0.03
Mg	-	0.01	0.03
Si	< 0.01	0.01	0.11

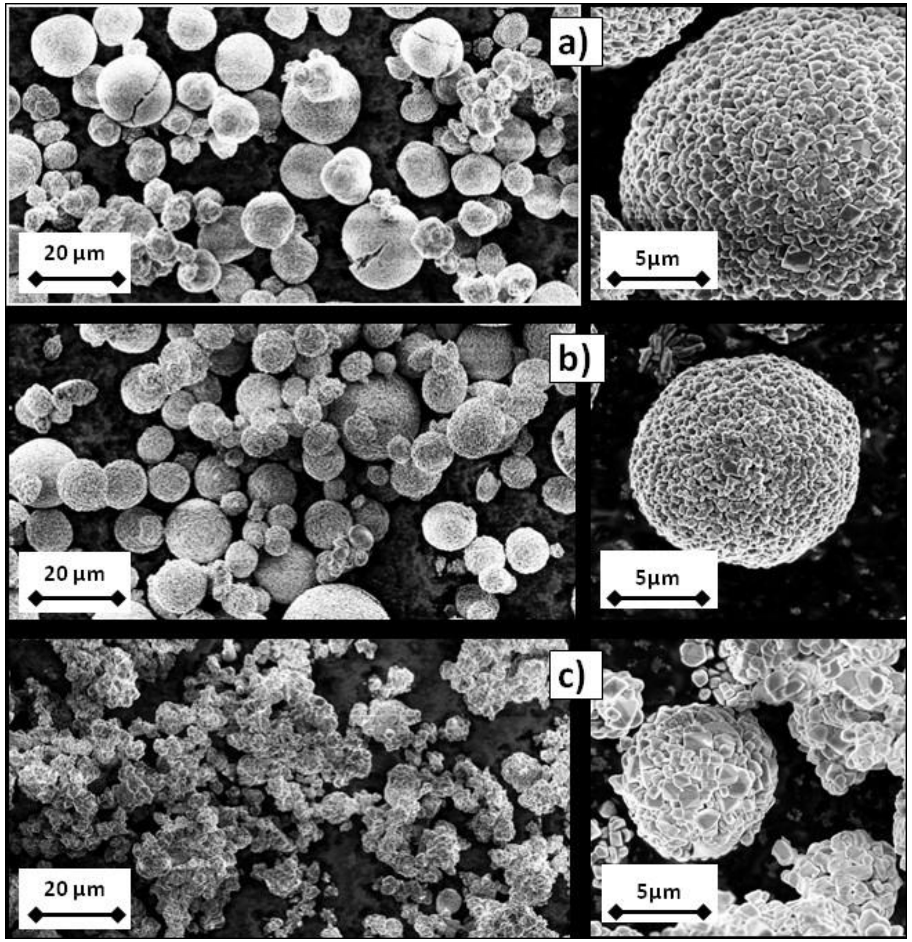
Source: S. Krueger, C. Hanisch, A. Kwade, M. Winter, S. Nowak, Effect of Impurities Caused by a Recycling Process on the Electrochemical Performance of Li[Ni0.33Co0.33Mn0.33]O2, Journal of Electroanalytical Chemistry (2014), doi: http://dx.doi.org/10.1016/j.jelechem.2014.05.017

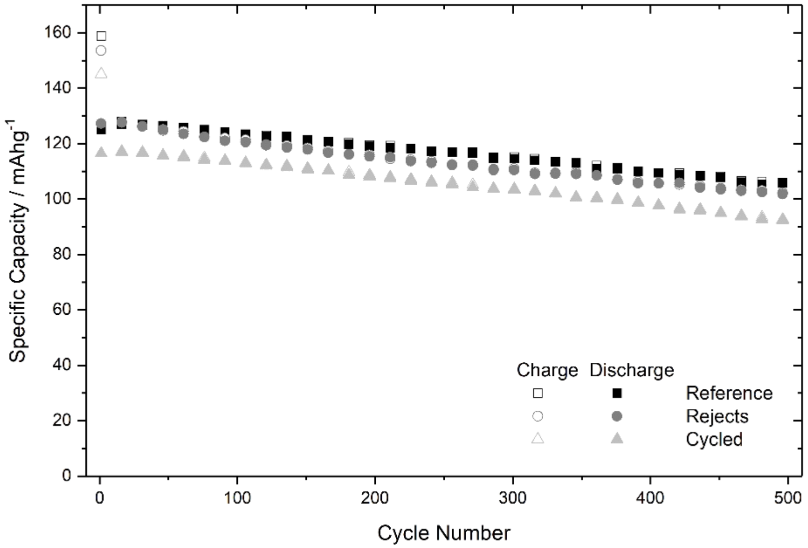
Electrochemical Performance of Re-Synthesized NCM - Material

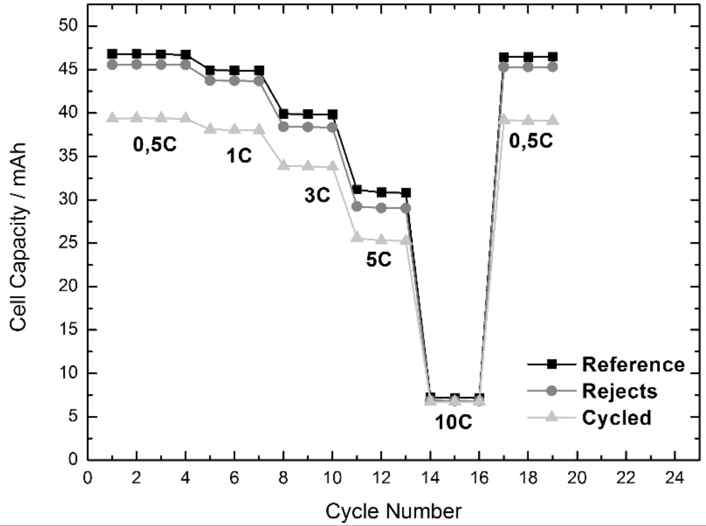
Reference
- From pure metal salts

Rejects
- From electrode production rejects

Cycled
- From resynthe-sized spent cells







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Re-Synthesized Graphite – Recycling Strategies

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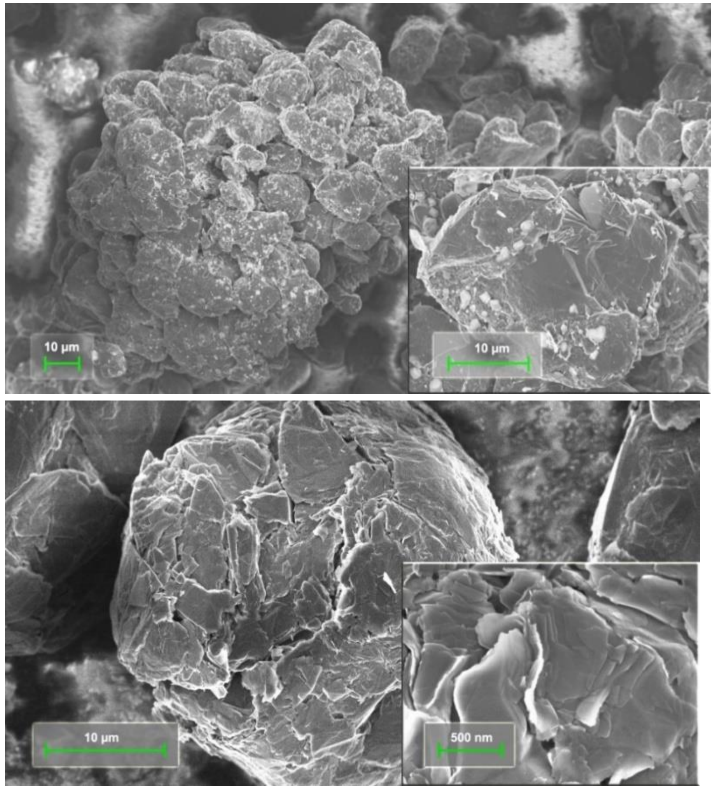
Graphite recycling strategies

Washing steps, removal of SEI and binder

Thermal evaporation of volatile electrolyte compounds

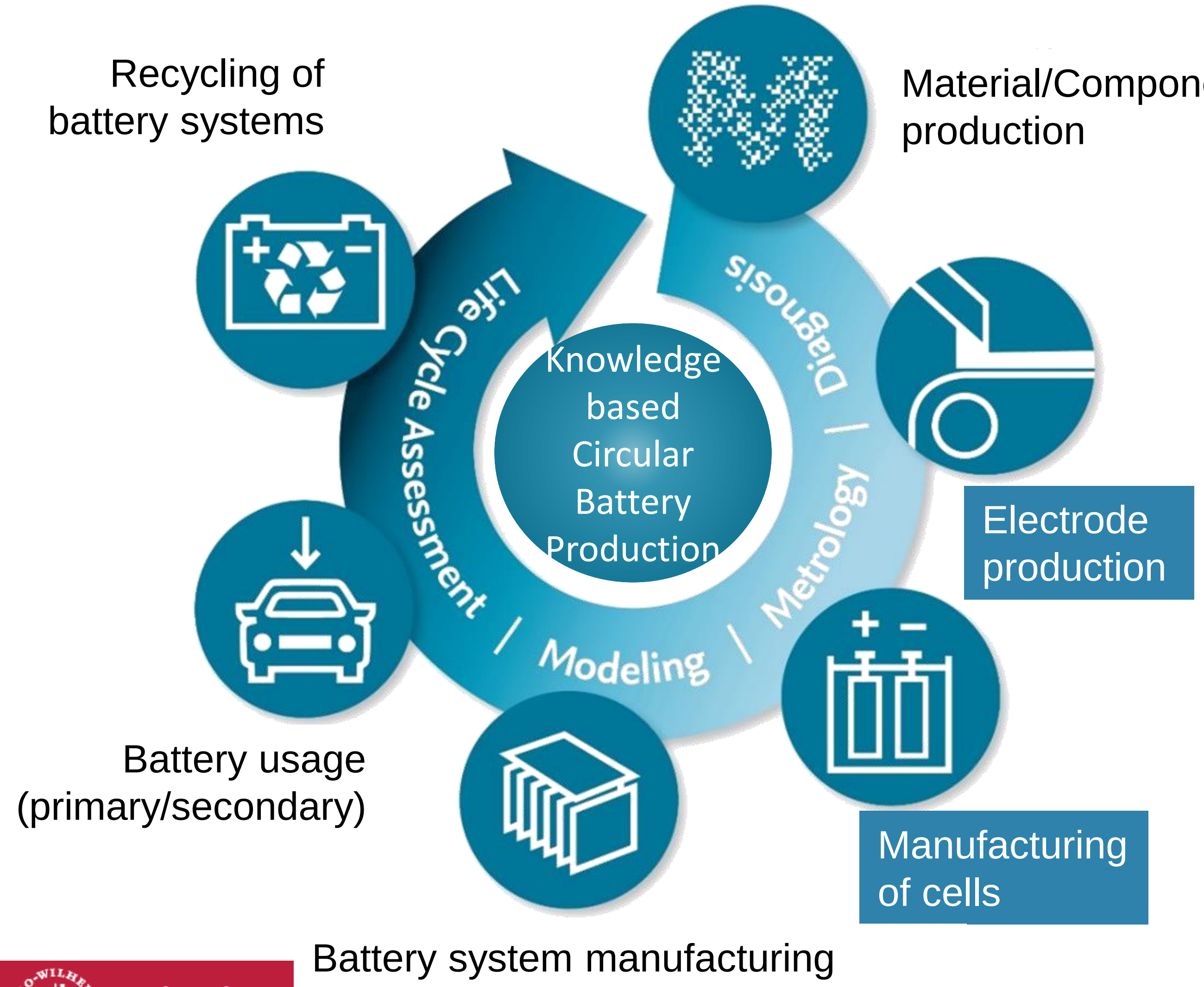
Electrolyte extraction with subcritical CO_2 in combination with acetonitrile

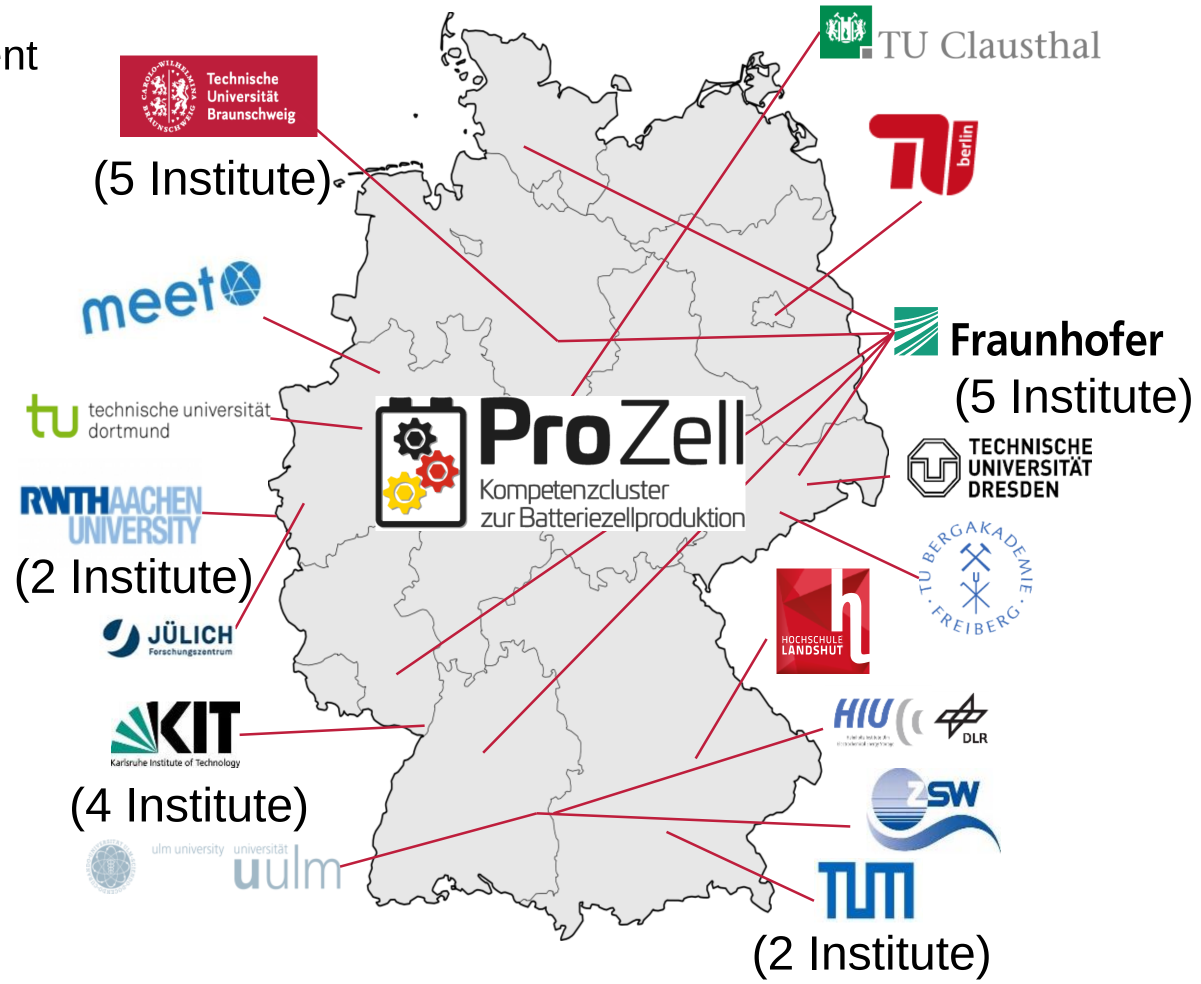
Thermal evaporation of volatile electrolyte compounds



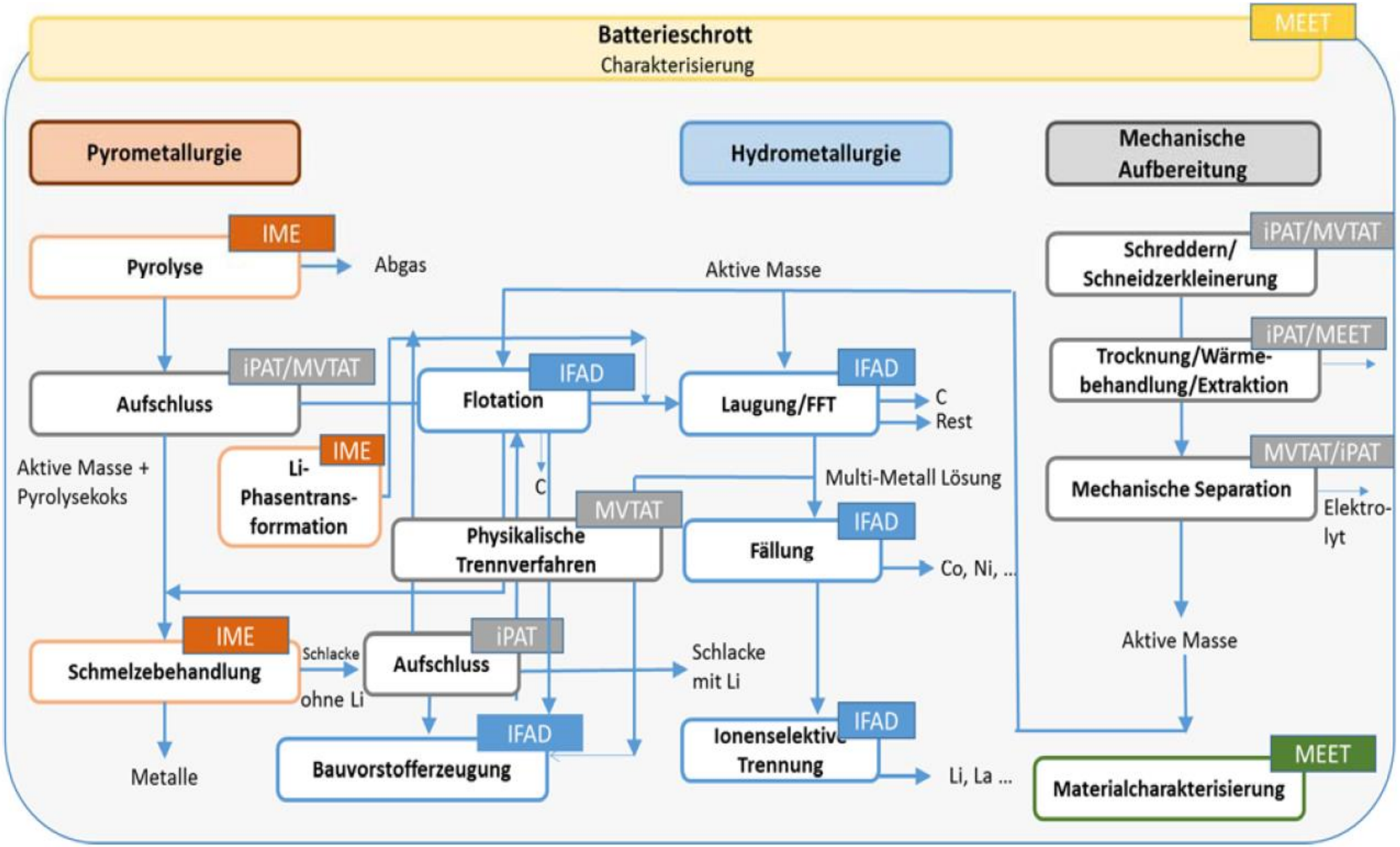
Source: Rothermel S, Evertz M, Kasnatscheew J, Qi X, Grützke M, Winter M, Nowak S (2016) Graphite recycling from Spent Lithium Ion Batteries. ChemSusChem [accepted]. doi:10.1002/cssc.201601062

Production of Battery cells – German competency cluster on battery cell production ProZell



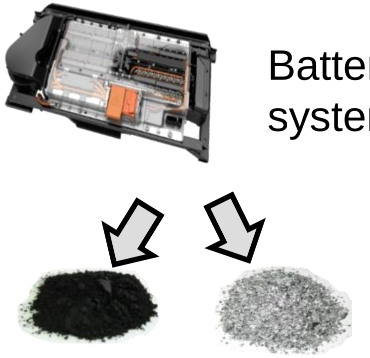


New german wide academic recycling platform „INNOREC“ within German competency cluster ProZell

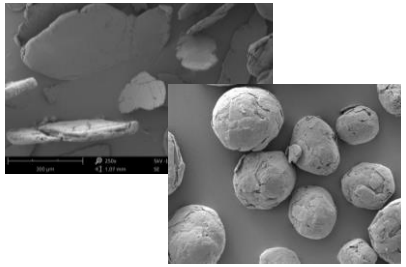


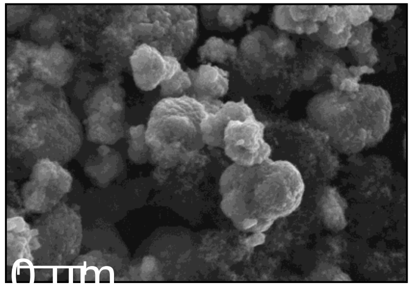
Conclusions
Closed material circuits within circular battery production

- **Demand of battery cells** and consequently required raw materials and synthesized active materials **rise tremendously** in the future
- **Sustainable processes especially for materials** are very important to fulfill environmental goals of car manufacturer (e.g. CO_2 footprint)
- In the future **recycling of spent batteries and re-synthesis of active materials from spent lithium battery systems** are decisive
  - to close material cycle,
  - to decrease dependency on primary raw materials and
  - to minimize ecological impact of battery production.
- **Mechanical-hydrometallurgical recycling** process developed in Niedersachsen is advantageous compared to other processes
- Recycling and Re-Synthesis of battery materials should be **future key technology of Niedersachsen**



Battery system

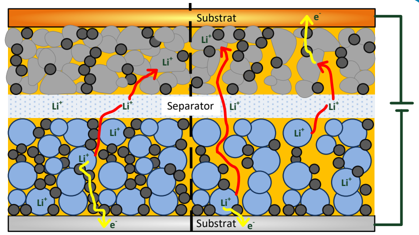




Challenges of future recycling processes – Diversity of battery materials and technologies

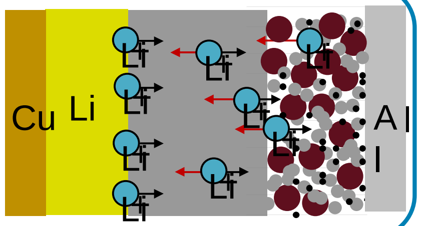
iPAT
Institute for Particle Technology

Lithium-Ion
Sodium-Ion



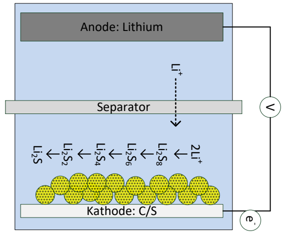
Lithium/Sodium-Metaloxide vs. Graphit/Si
Solvent based electrolyte

All-Solid-State



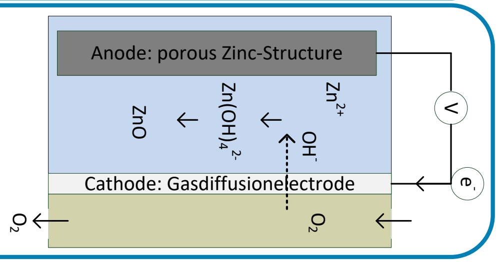
Lithiummetaloxide vs. Li
Solid state electrolyte

Lithium-Sulfur



Sulfur-Carbon-Composite vs. Li
Solvent based or solid state electrolyte

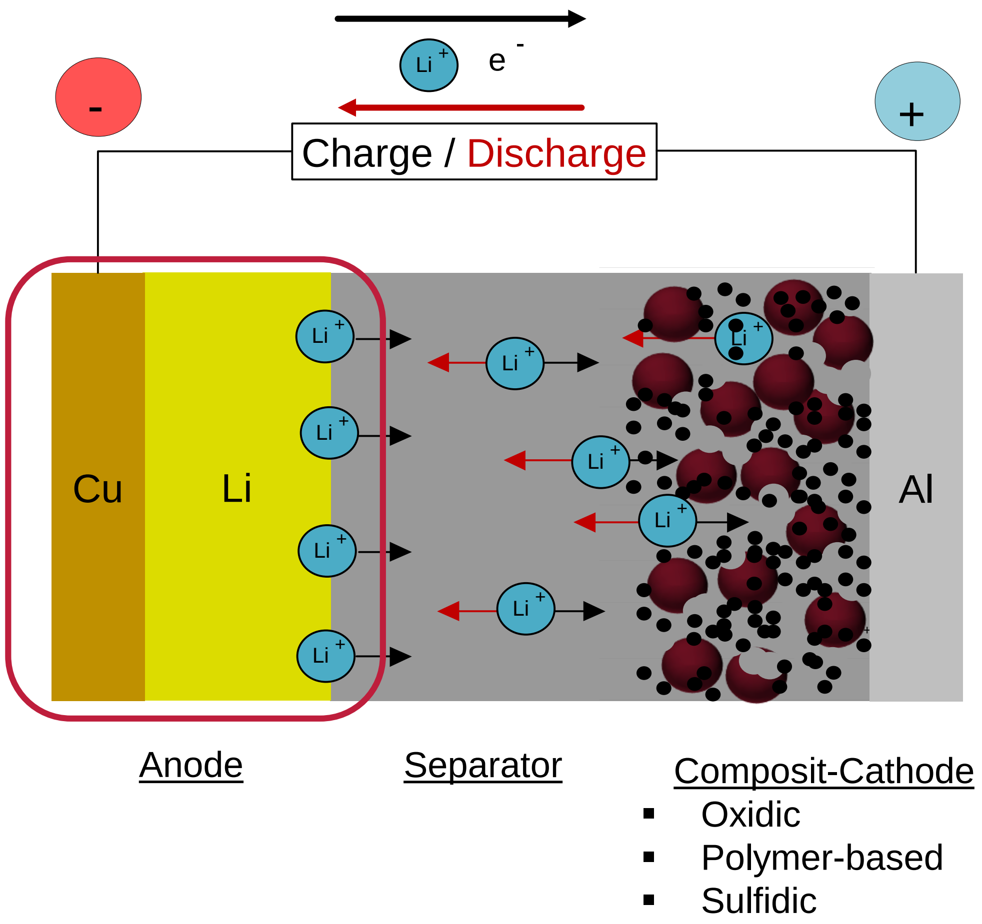
Metal-Air Batteries



Gasdiffusion electrode vs. metal (z.B. Lithium, Zinc)
Solvent based electrolyte

Challenges in Recycling of All Solid State Batteries

iPAT Institute for Particle Technology



Challenges in Process Technology:

- Shredding of the systems / cells only possible under protective atmosphere
- Li-metal is very reactive
- Dissolving the Li-metal in water
- In aqueous systems formation of LiOH with release of H_2
- Polymer-based solid electrolytes: Removal of valuable cathode active materials (NCM) e.g. by swelling or dissolving polymers (PEO)
- Sulfidic solid electrolytes: Danger of release of H_2S and other sulphur compounds

Thank you very much

.... for the support by

Bundesministerium für Bildung und Forschung

Bundesministerium für Wirtschaft und Energie

Deutsche Forschungsgemeinschaft DFG

….for the great work of my
PhD-students and co-workers,
especially
Sabrina Zellmer
Julian Mayer

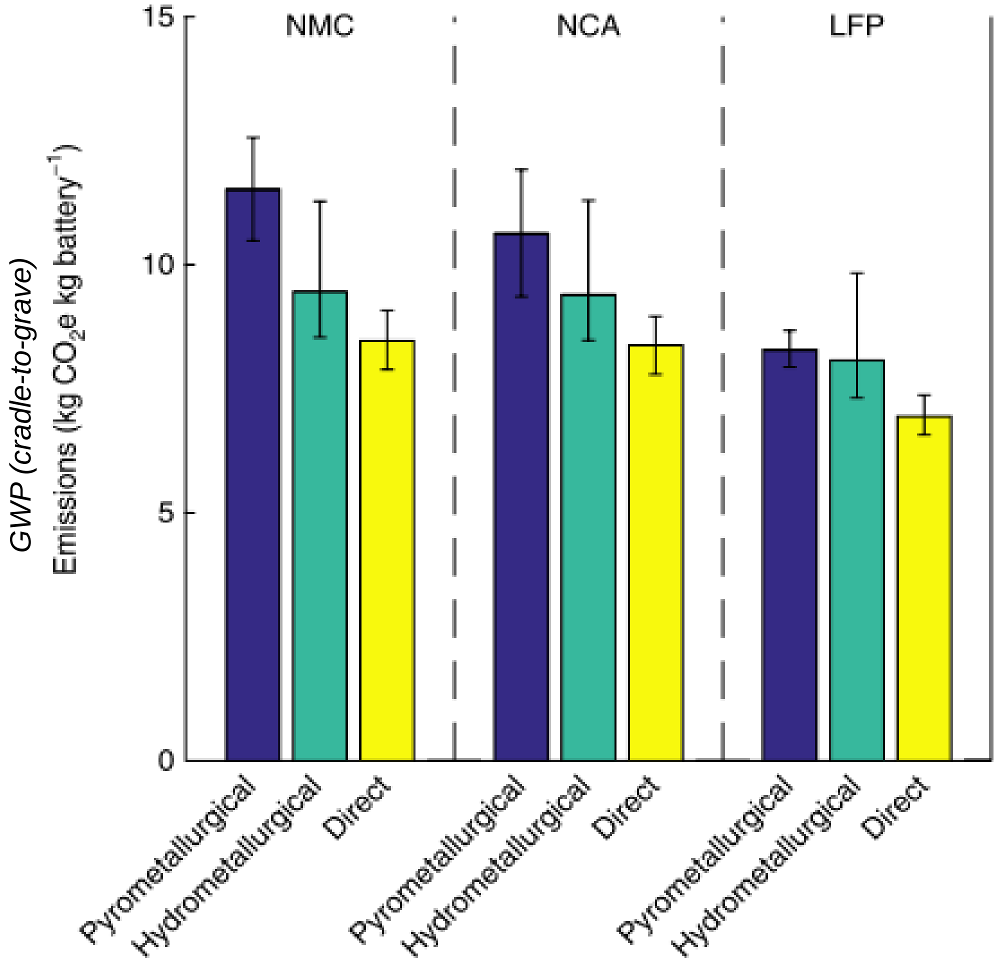
… for your attention

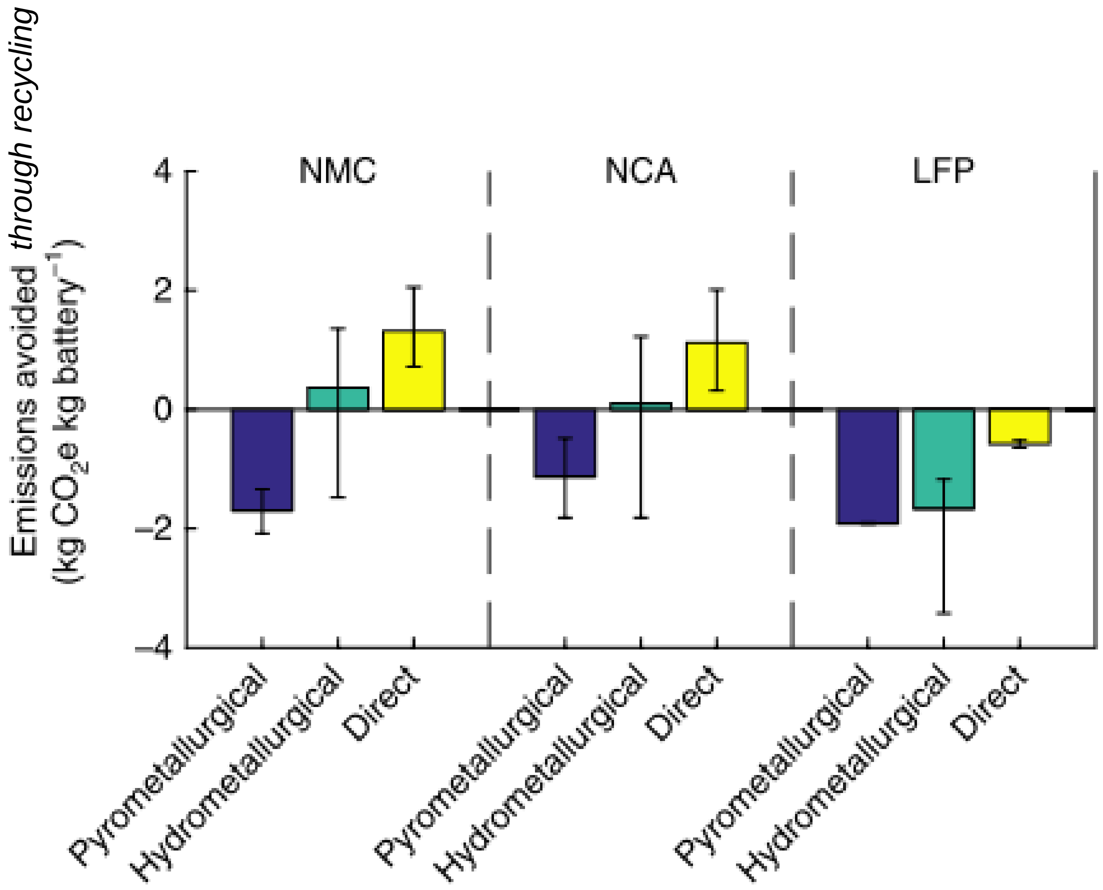
IBPC 2019

INTERNATIONAL BATTERY PRODUCTION CONFERENCE

4 to 6 November 2019

Estimation of recycling burdens remains a challenge



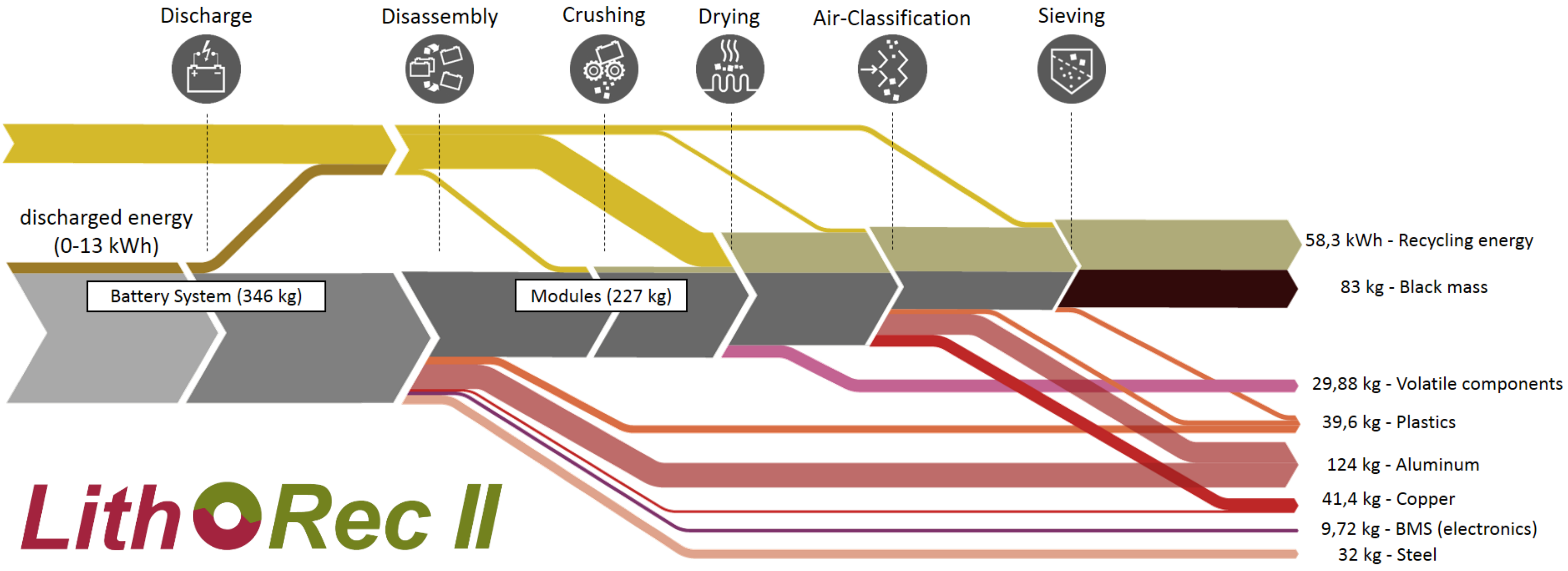


Source: Ciez R E, Whitacre J F (2019) Examining different recycling processes for lithium-ion batteries. *Nature Sustainability*. 2(2):148–156.

Recycling burdens of battery recycling

Methodology | Step 3: Impacts

1 Product Analysis | 2 Target Materials | 3 Net Env. Impacts | 4 Allocation



Source: Cerdas et al. (2018) Environmental Aspects of the Recycling of Lithium-Ion Traction Batteries, in *Recycling of Lithium-Ion Batteries : the LithoRec Way*, pp. 267–288.