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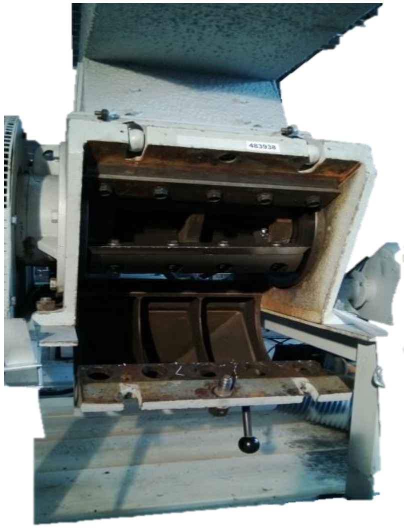
Recycling of Lithium-Ion Batteries

Christian Hanisch, c.hanisch@lion-eng.de

Outline

- **Recycling of Lithium Ion Batteries**
- **Different Industrial and Research Processes and Recycling Yields**
- **Safety Issues in Battery Recycling and how to deal with them**
- **Recent Developments in Recycling of LIB from EVs**
- **Recycling of LIB-Production Rejects**



Recycling of Lithium-Ion Batteries

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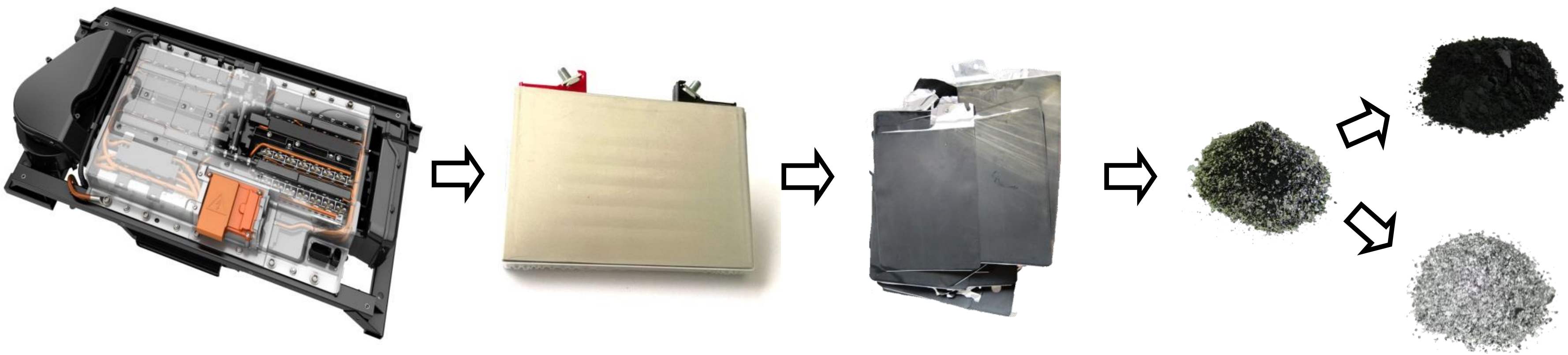
Composition of a traction battery



Battery system — **Battery cells** — **Electrodes** — **Current collector + Active material**

Reference: [TU Braunschweig]

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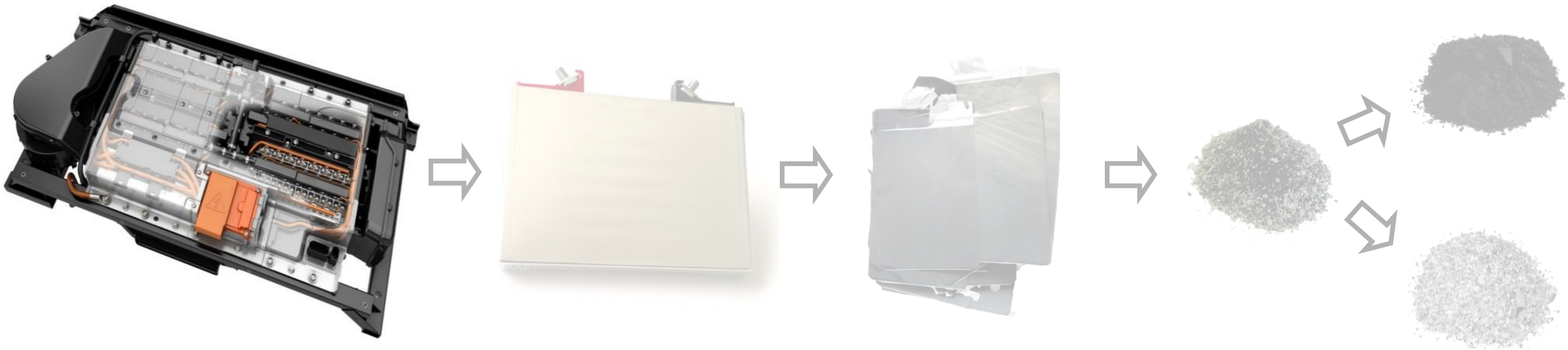
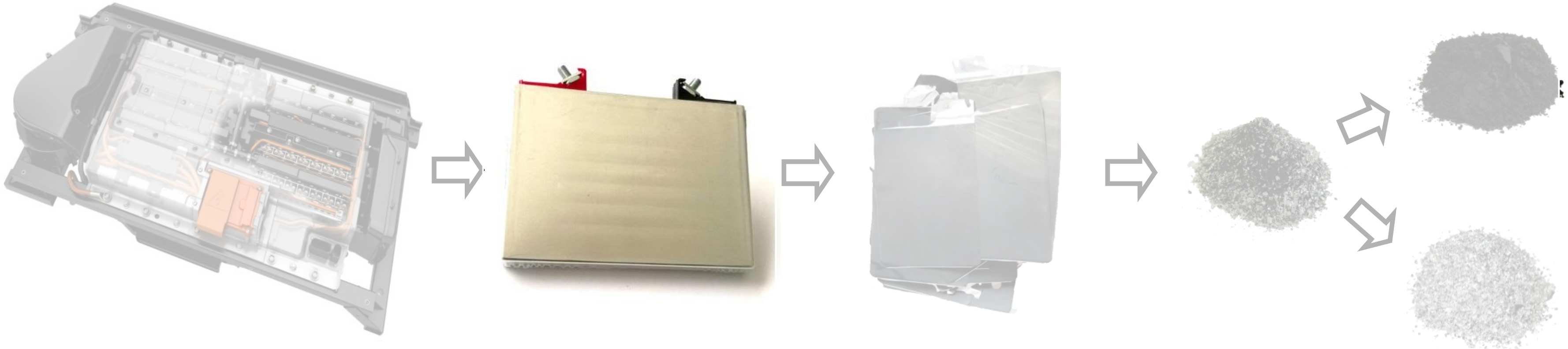


Battery system level:

50-70%	Battery cells	→ Further treatment (next slide)	
15-45%	Casing	→ Smelting	→ Steel, aluminum
2-6%	Wiring	→ Separation	→ Smelting→ Copper, plastic
2-3%	Electronics, PCB	→ Separation	→ Iron, copper, aluminum, residua
0-3%	Cooling tubes, casing parts	→ Granulation	→ Plastic
0-3%	Busbars → Separation	→ Copper, Plastic	
1-2%	Screws, metal parts	→ Reuse, remelt	→ Iron
<1%	Rubber, tape, etc.	→ Waste	

Reference: TU Braunschweig

Composition of a traction battery



Battery cell level:

ca. 65%	Electrodes	→ Further treatment (next slide)	
10-15%	Steel / Aluminum casing	→ Smelting	→ Aluminum, steel
10-20%	Electrolyte	→ Recovery	→ Valuable solvents, electrolytic salt
		→ Incineration?	
2 - 5%	Further parts	→ Smelting	→ Steel, copper, aluminum
ca. 3%	Separator/Foils	→ Incineration	

Reference: TU Braunschweig

Composition of a traction battery

Electrode level:

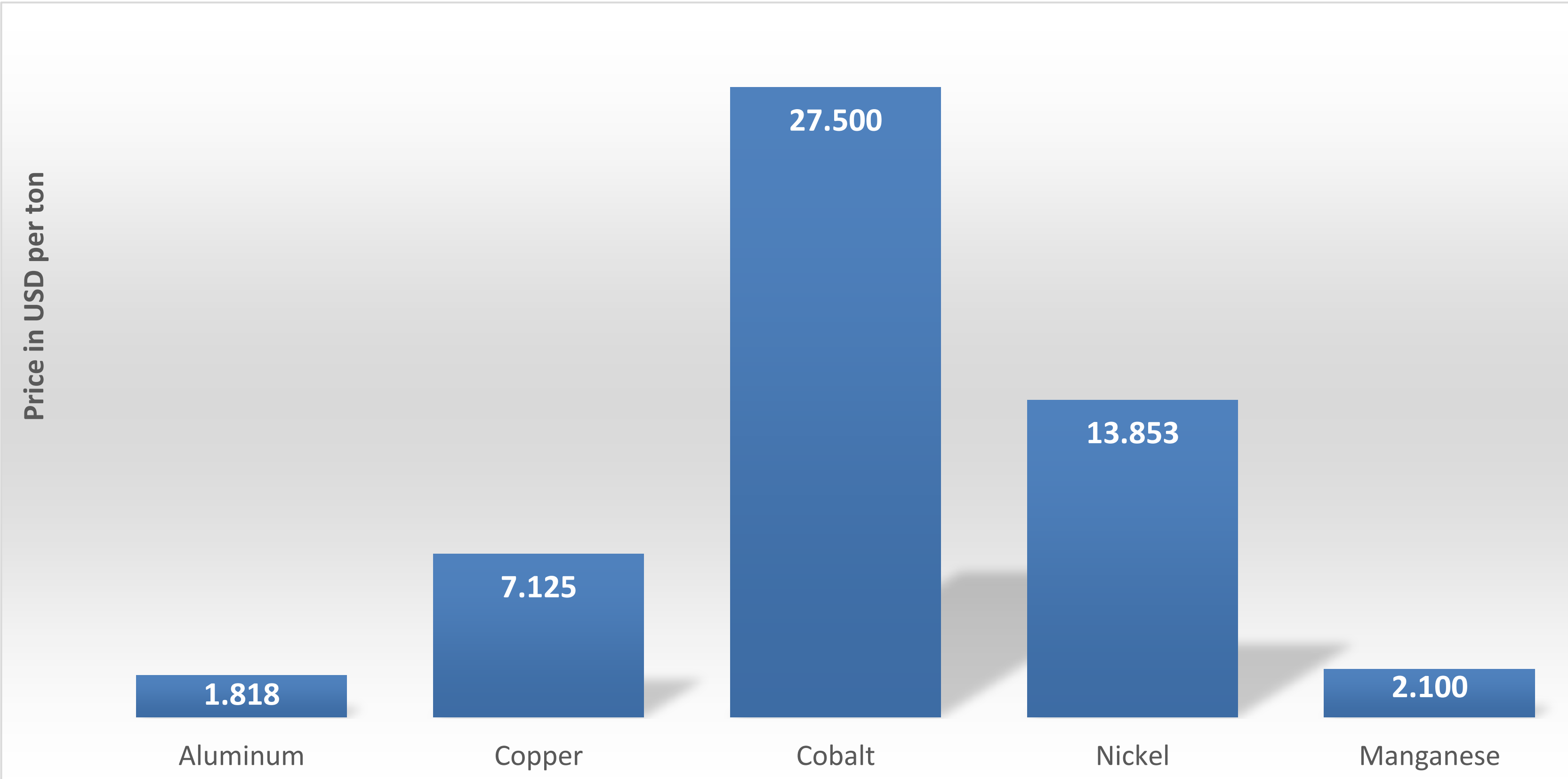
15%	Copper foil	→ Briquetting	→ Smelting
8%	Aluminum foil	→ Briquetting	→ Smelting
31%	Anode coating	→ Hydrometallurgy	→ Lithium, organic residues
46%	Cathode coating	→ Hydrometallurgy	→ Lithium, Ni/Co/Mn-solution.

↓

New active materials

Reference: TU Braunschweig

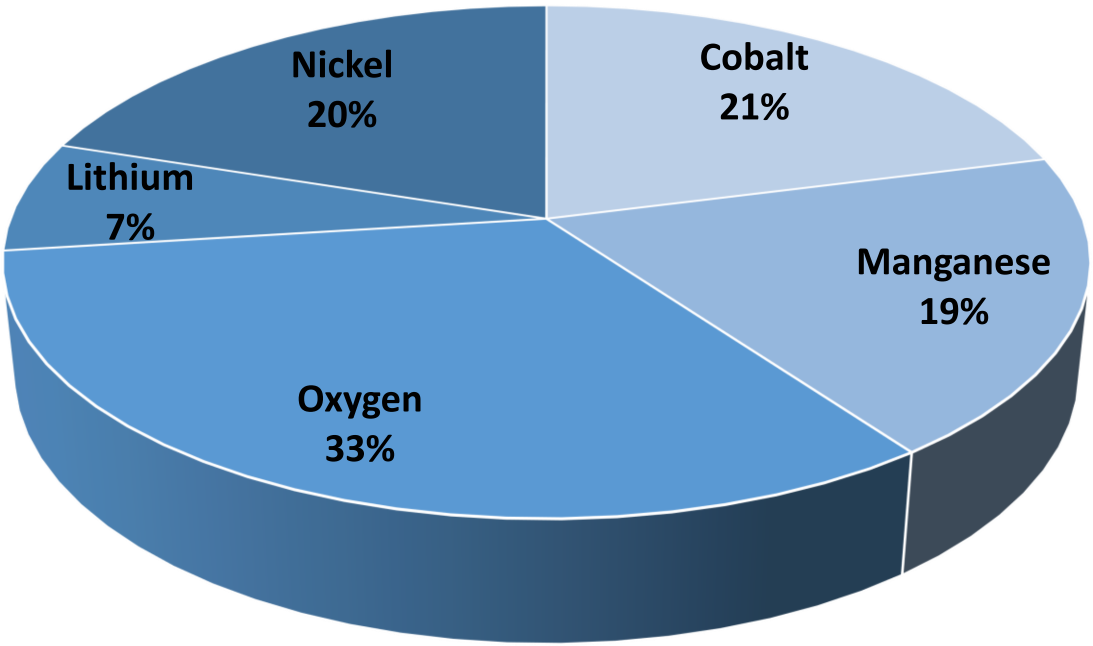
Current world market prices



Prospective active materials: More and more spinel and olivine structures (e.g. LFP) without cobalt and nickel

Lithium-ion battery cell

Stoichiometric compostion of the active material lithium-nickel-cobalt-manganese-oxide $Li(NiCoMn)_{1/3}O_2$



Per 200 battery cells:

- ca. 4 kg lithium
- ca. 12 kg nickel
- ca. 12 kg cobalt
- ca. 10 kg manganese

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Unit operations of battery recycling

Deactivation	Mech. treatment	Pyrometallurgy	Hydrometallurgy
▪ Thermal pretreatment ▪ Discharge ▪ Freezing of the electrolyte	▪ Shredding ▪ Classifying (e.g. sieving, separating) ▪ Sorting (e.g. magnetic separation)	Smelting of the ▪ whole battery ▪ cells ▪ electrodes ▪ active materials → Recovery of transition metals Co, Ni	Chemical processes ▪ Leaching ▪ Extraction ▪ Crystallization ▪ Precipitation → Recovery of pure metals from ▪ Active materials ▪ Slag

Further information: **Recycling of Lithium-Ion Batteries**
Christian Hanisch, Jan Diekmann, Alexander Stieger, Wolfgang Haselrieder, Arno Kwade
Handbook of Clean Energy Systems - Volume 5 Energy Storage, 2015 edited by Jinyue Yan, Luisa F. Cabeza, Ramteen Sioshansi, 01/2015: chapter 27: pages 2865-2888; John Wiley & Sons, Ltd.., ISBN: 978-1-118-38858-7

Reference: TU Braunschweig

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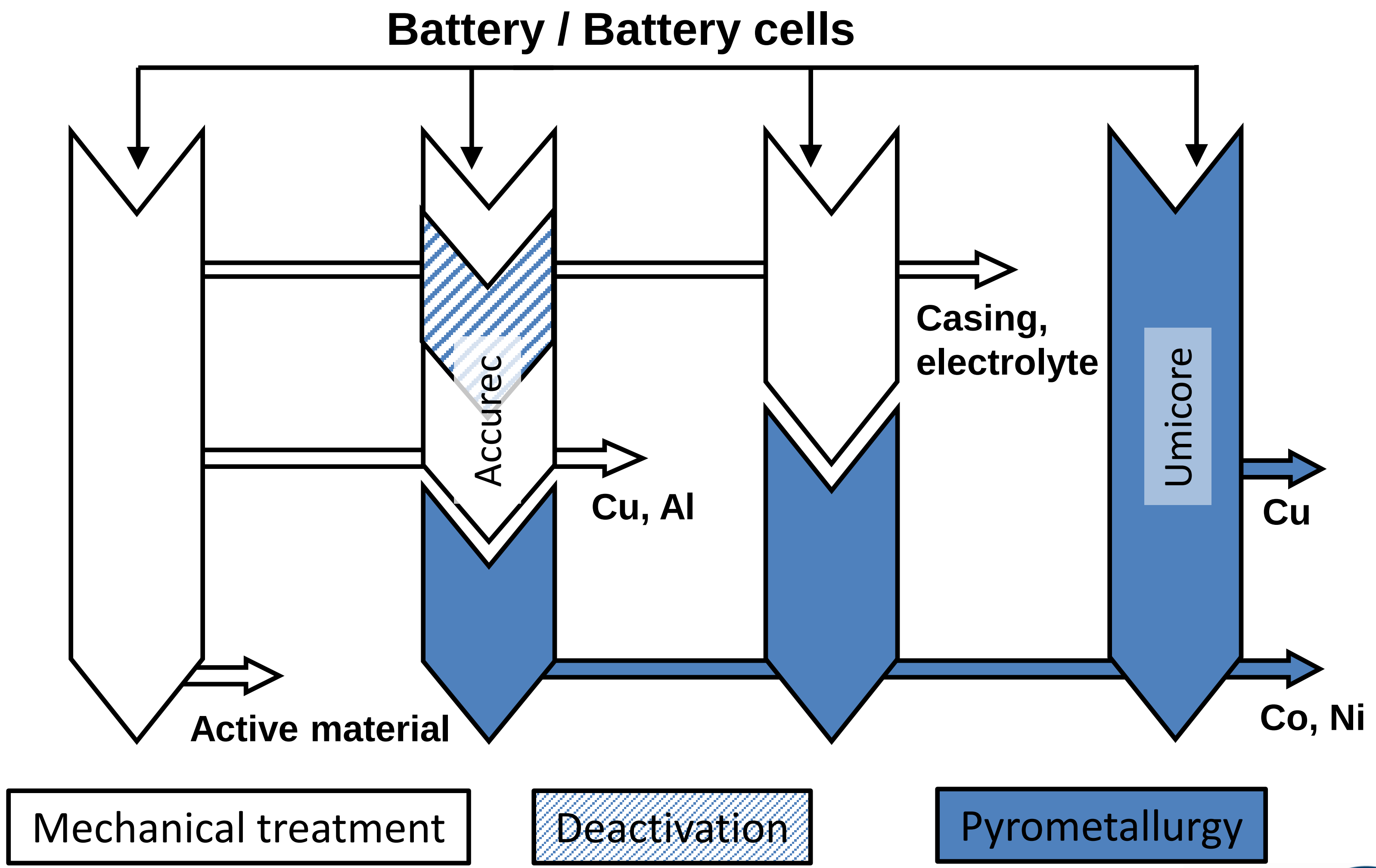
Process routes



Reference: [TU Braunschweig] Further information: [Recycling of Lithium-Ion Batteries]

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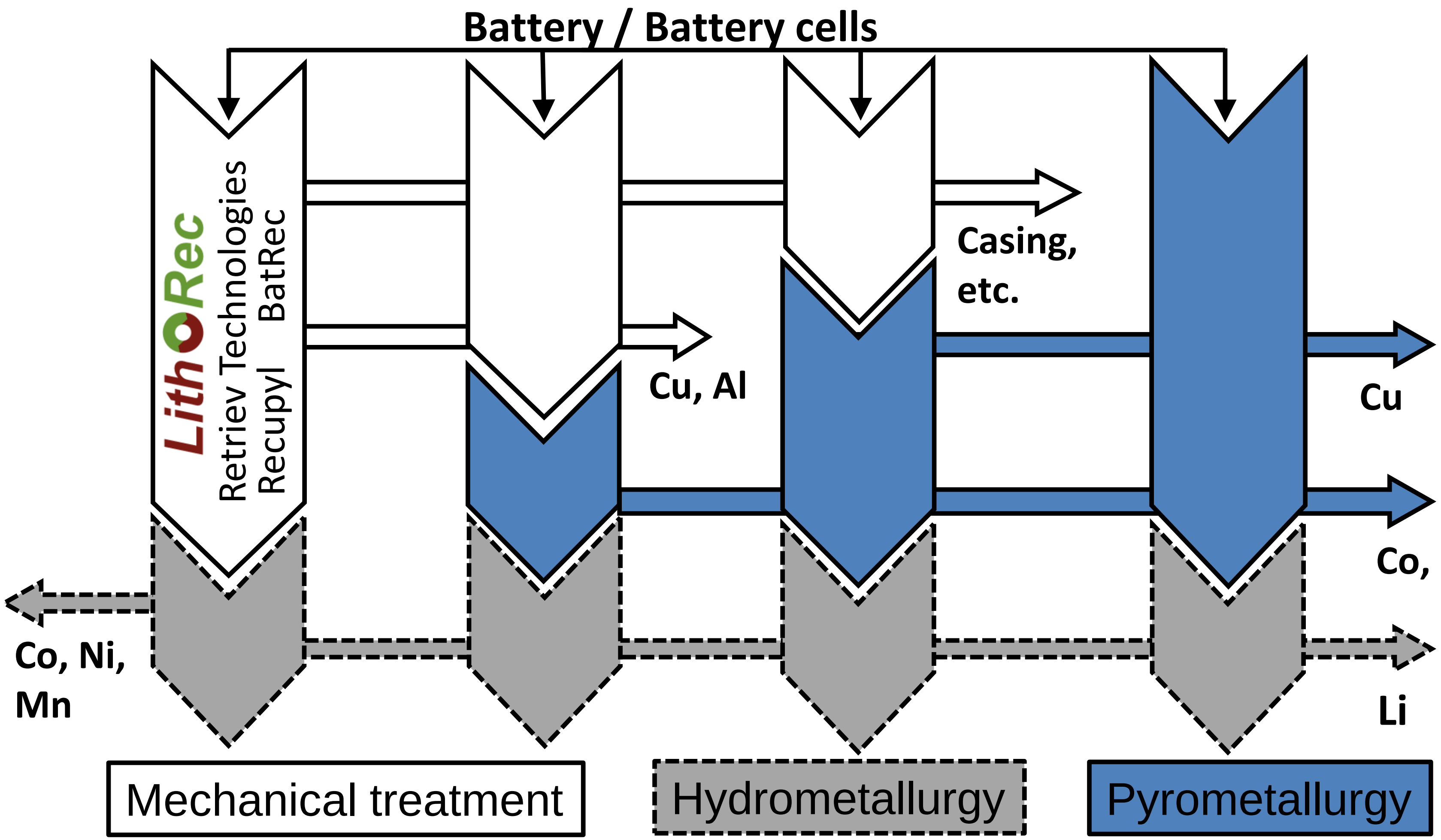

Reference: TU Braunschweig   Further information: Recycling of Lithium-Ion Batteries

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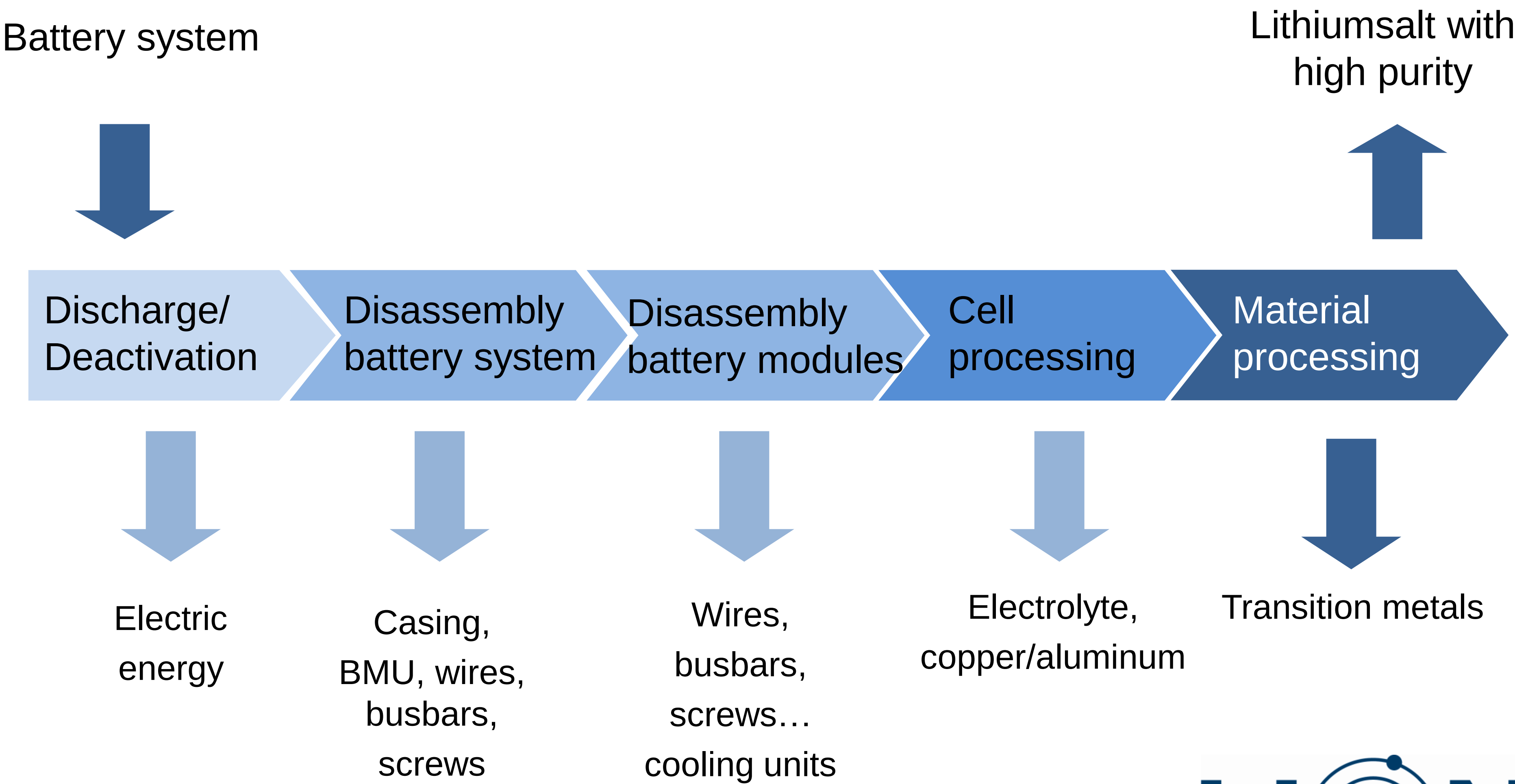
Basic structure of the process chain



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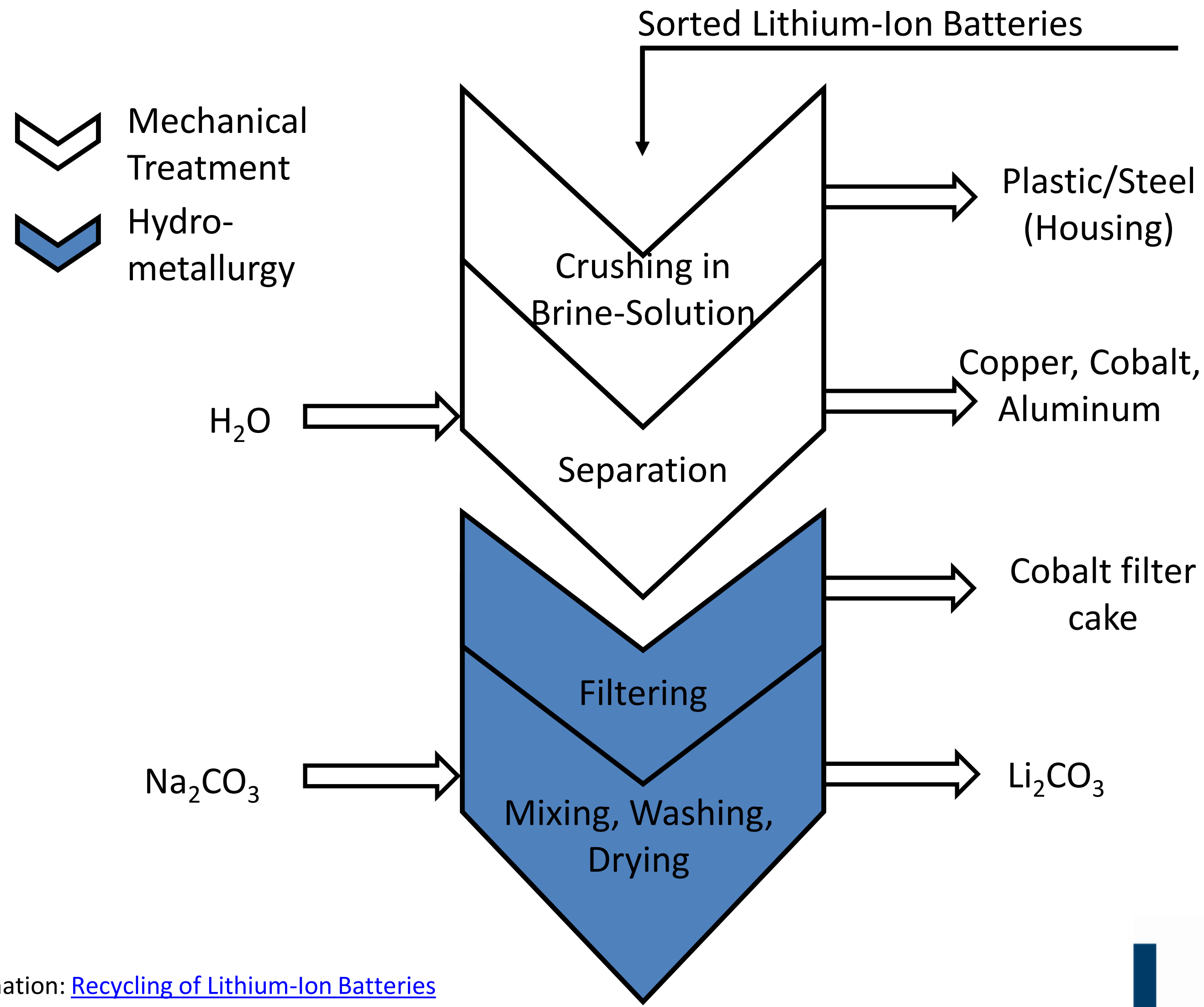
Retriev Technologies Inc.



Further information: Recycling of Lithium-Ion Batteries

Basic process chain *LithoRec II*

Cell shredding

↓

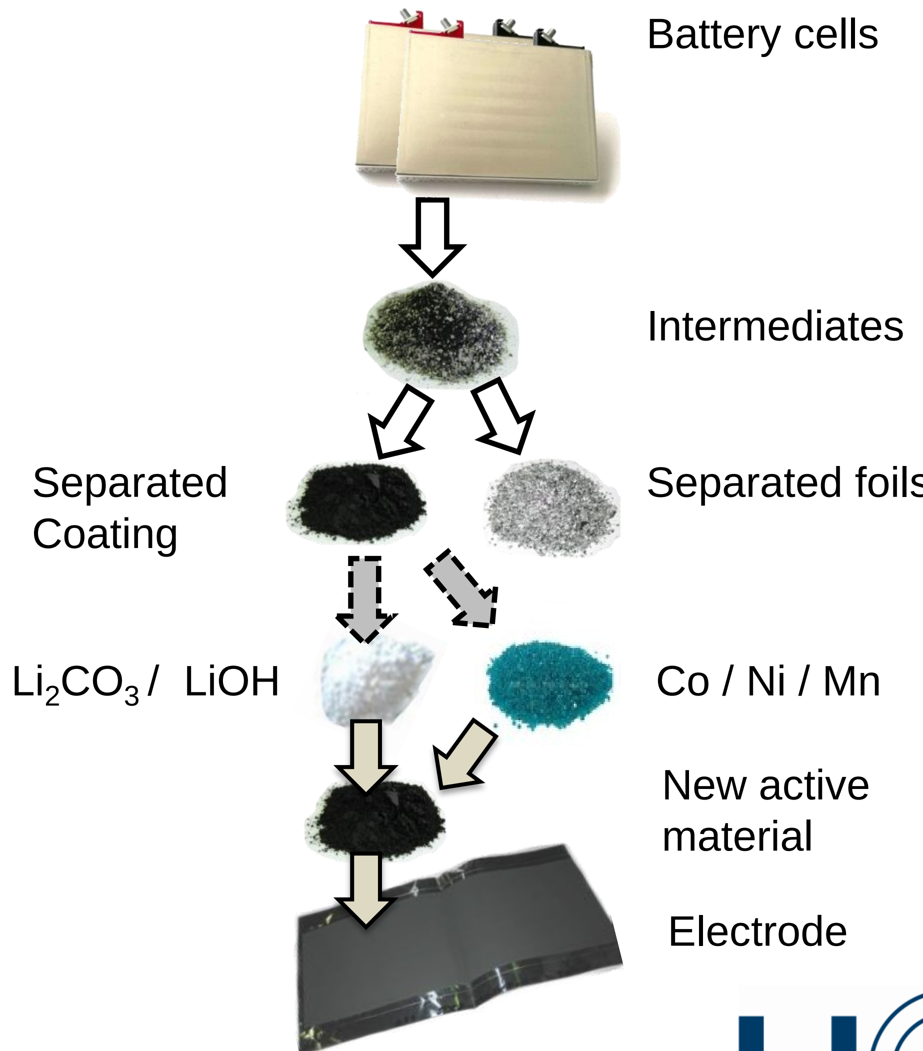
Separation of foil and coating

↓

Hydrometallurgy

↓

Synthesis of active material



Reference: [TU Braunschweig]

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Basic process chain LithoRec II

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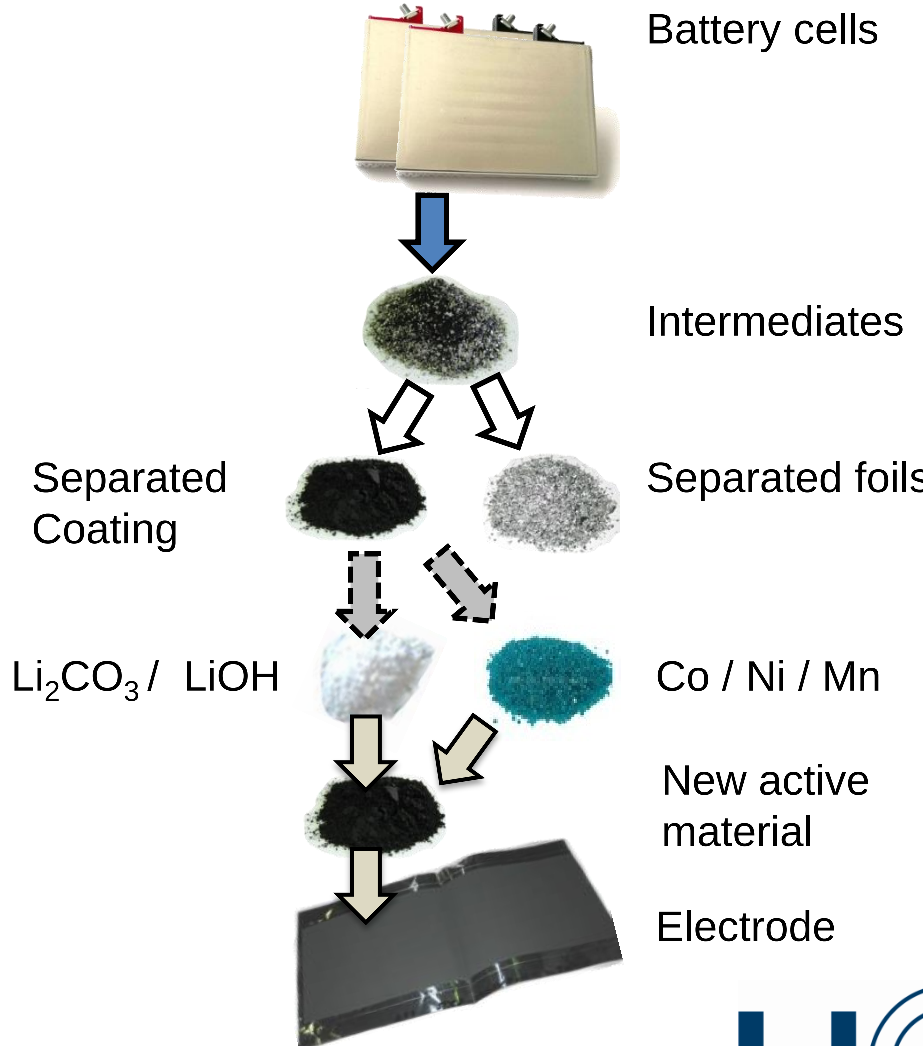


Reference: [TU Braunschweig]

Example: Cell shredding and sorting

Cells / Modules

Pre shredding

Fe ← Magnetic separation

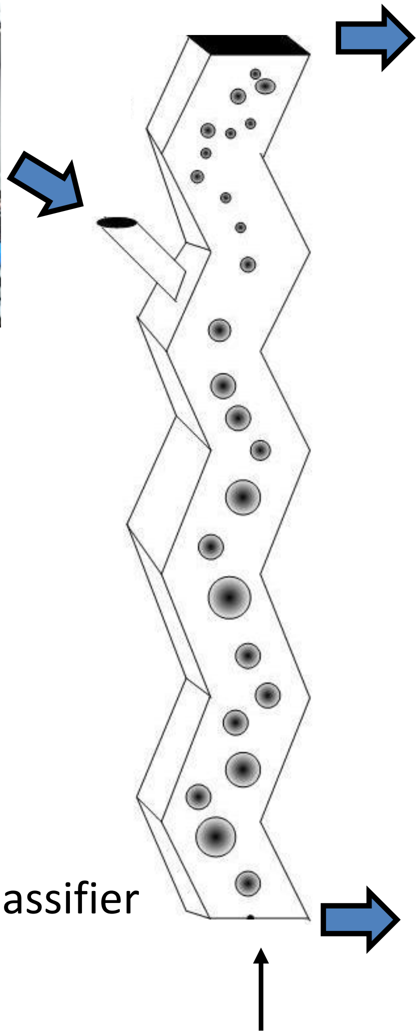
Heavy fraction: Steel-/Al-Casing ← Cross flow sifter

Separator foil ← Pneumatic table

Electrode fragments

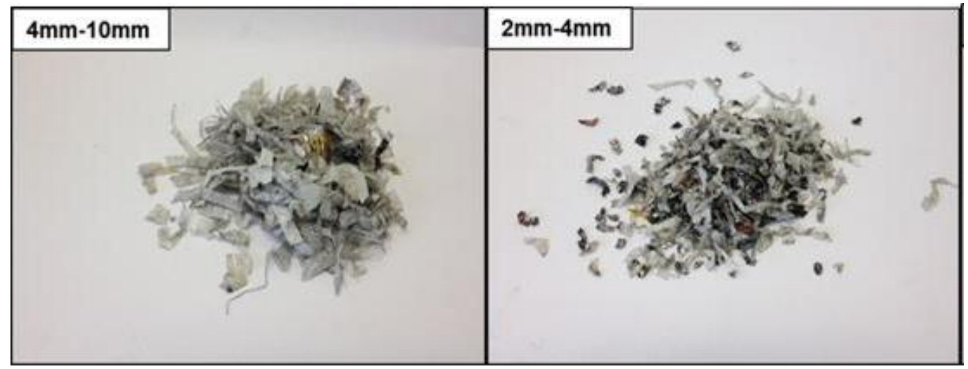
Reference: TU Braunschweig

Air Classification and Sieving

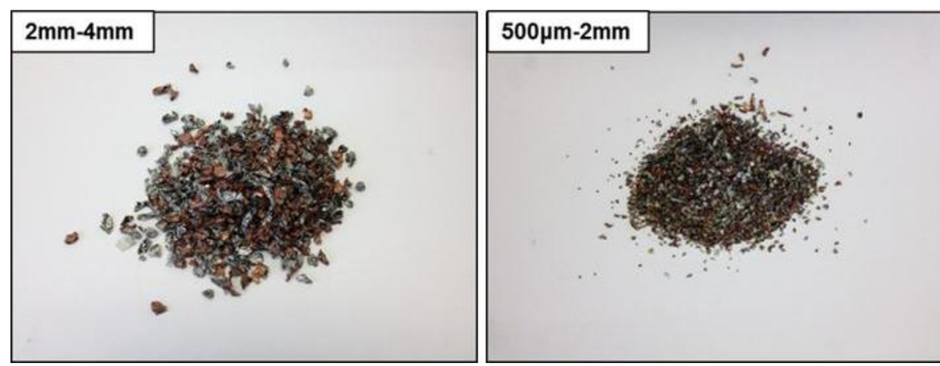


Zigzag-Classifier

Air jet



Light fraction



Heavy fraction

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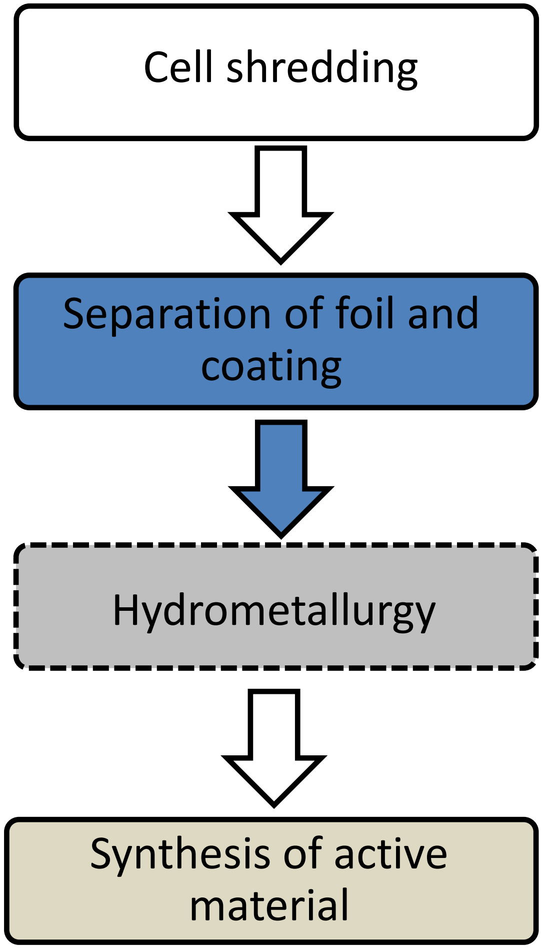
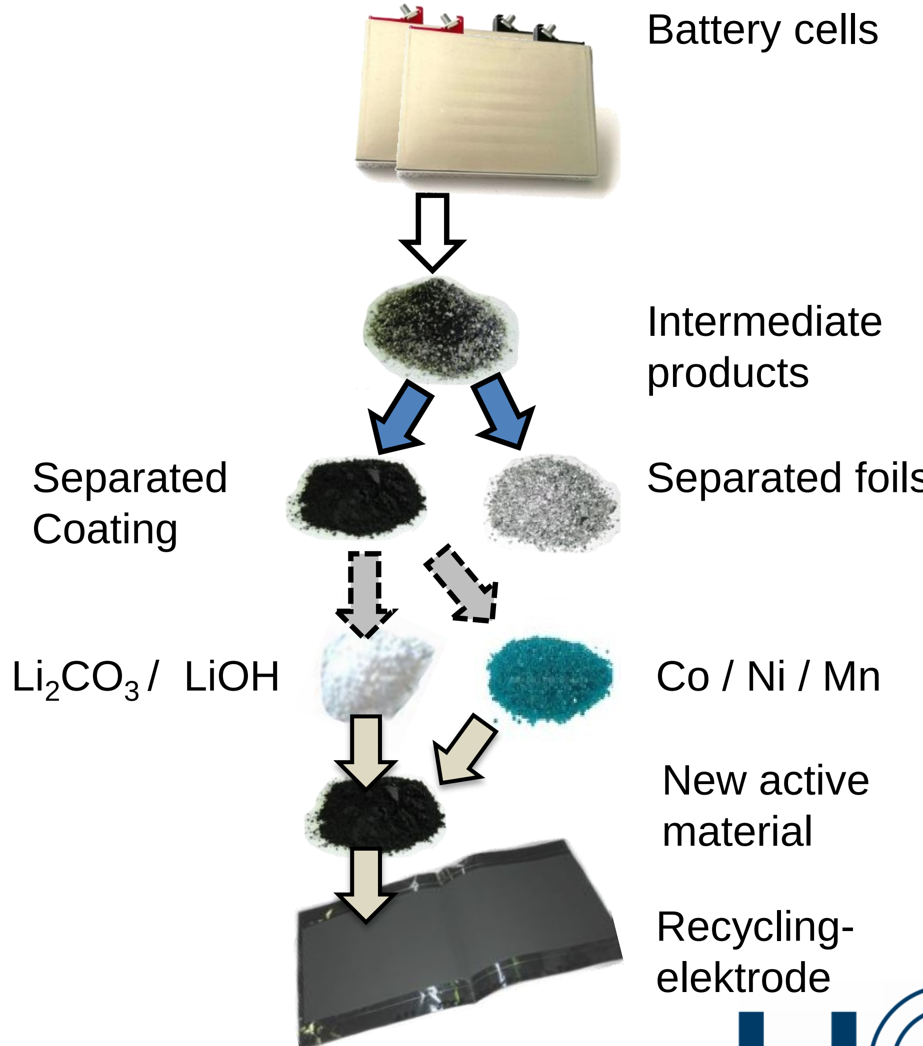
Basic process chain *LithoRec II*





Reference: TU Braunschweig

Measurements in Recycling of LIB

Compound Separation Efficiency

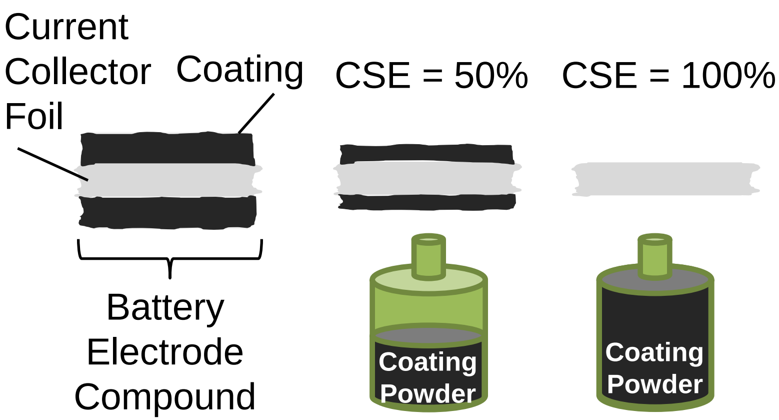
$$\text{CSE} = \frac{\textit{mass of separated component}}{\textit{initial mass of component}} = \frac{\textit{mass of separated coating}}{\textit{initial mass of coating}}$$

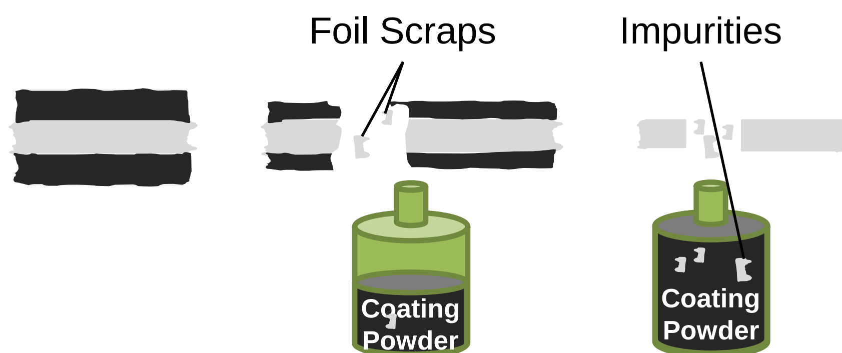
Impurities of Component A

$$= \frac{\textit{mass of component A}}{\textit{mass of product}}$$

$$= \frac{\textit{mass of metal impurities}}{\textit{mass of separtated coating powder}}$$

- important for hydrometallurgical process
- determined via Atomic Absorbtion Spectroscopy of leach liquor





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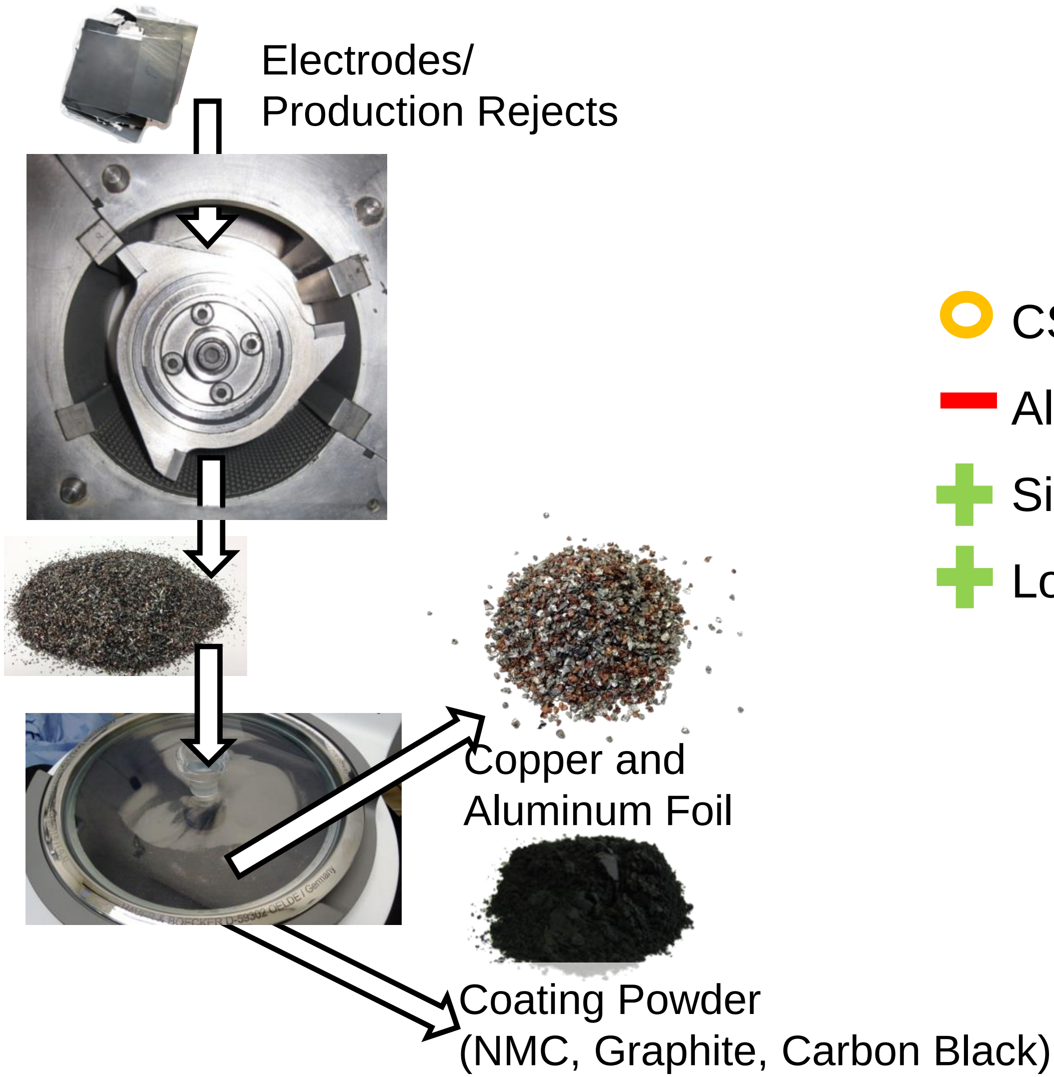
First Solution: Cutting Mill and Sieving



- ○ CSE 80 - 95 % of Active Material
- − Al/Cu Impurities 1 - 5 wt.-%
- + Simple
- + Low Investments

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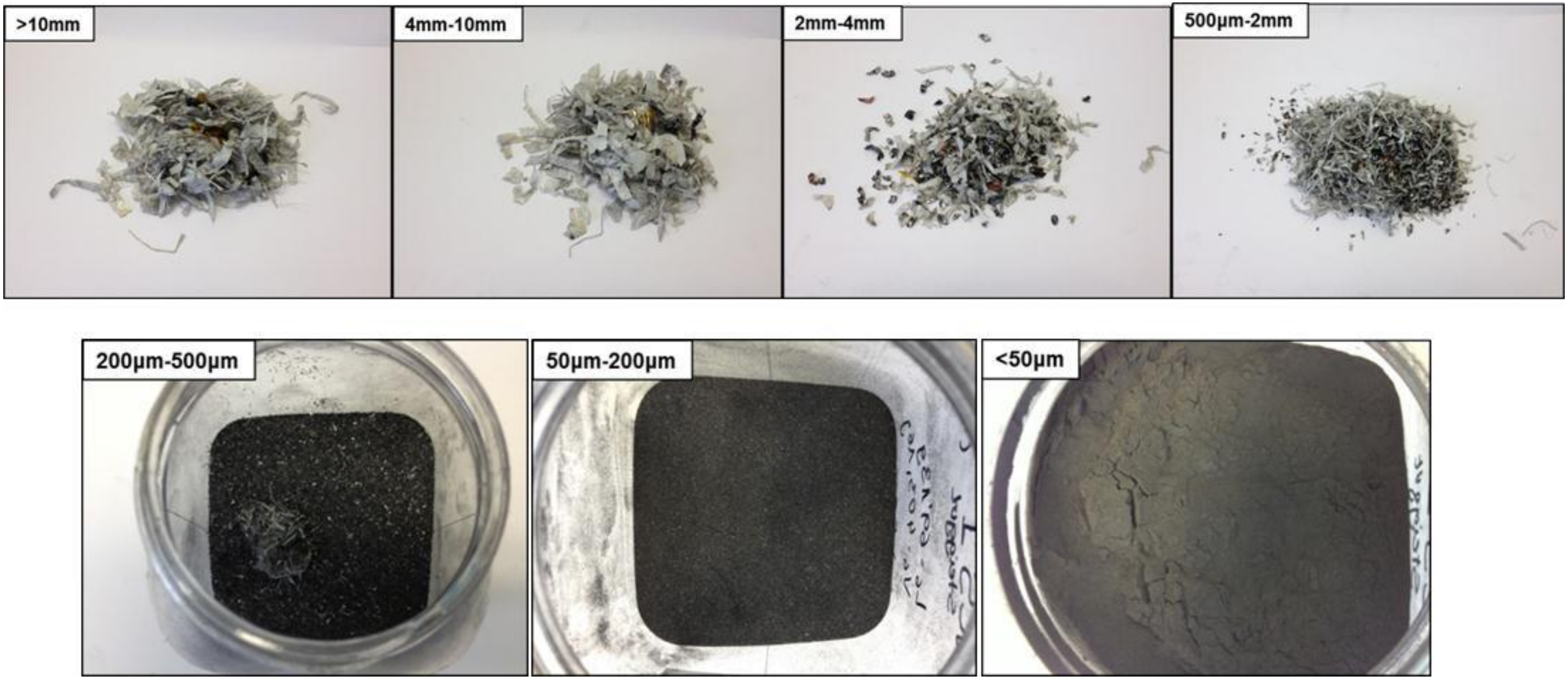
Separation results after sifting and sieving



Reference: TU Braunschweig and Lion Engineering GmbH

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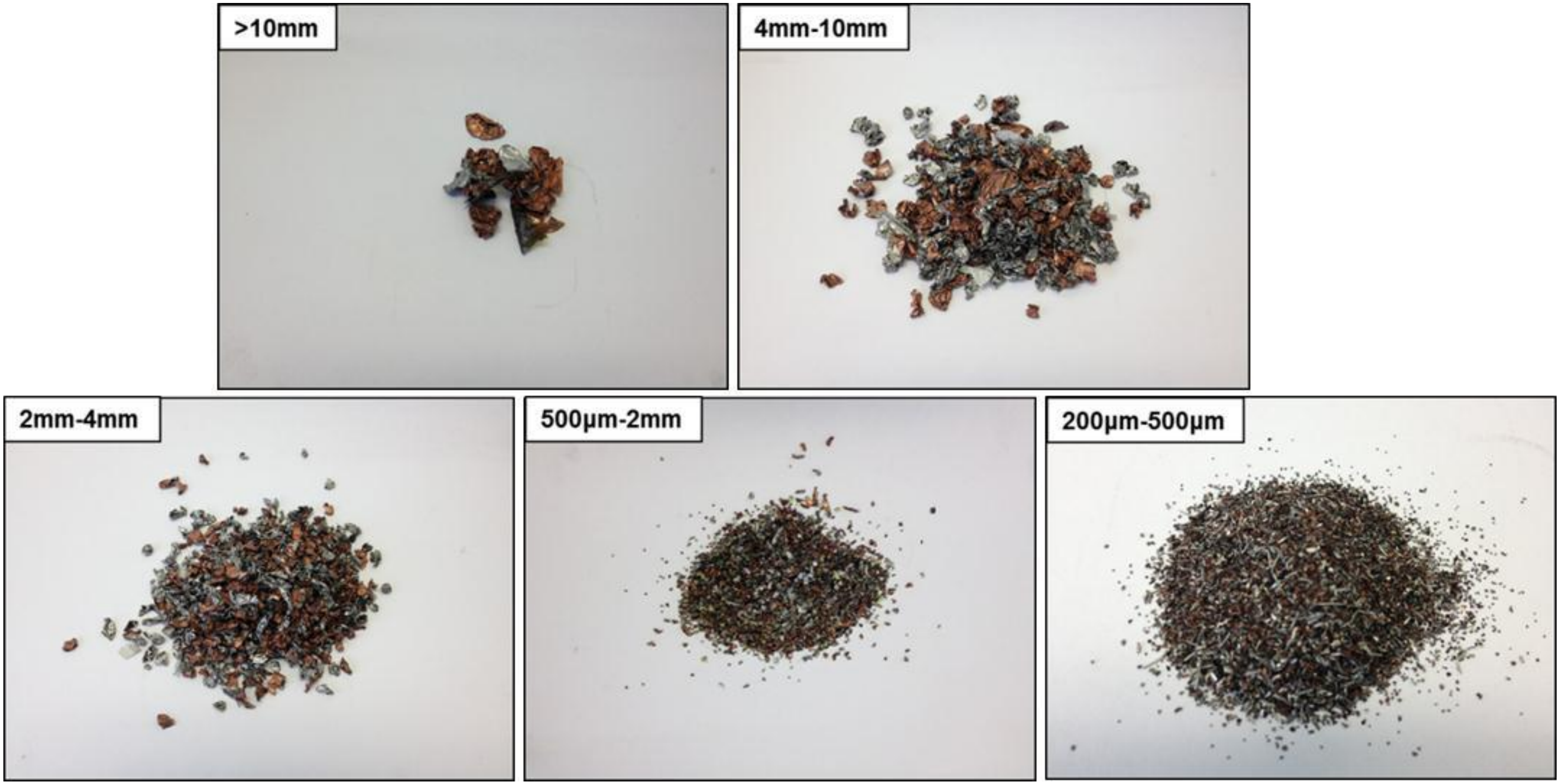

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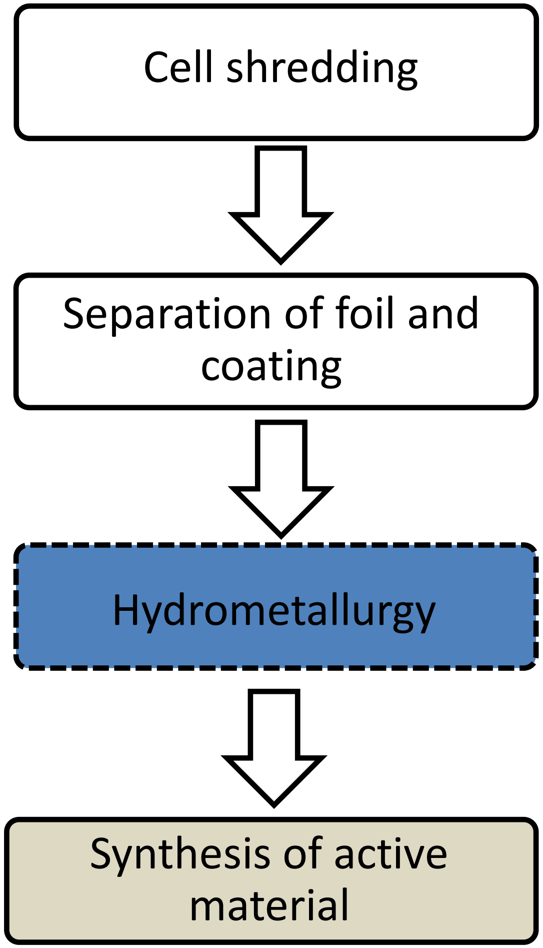
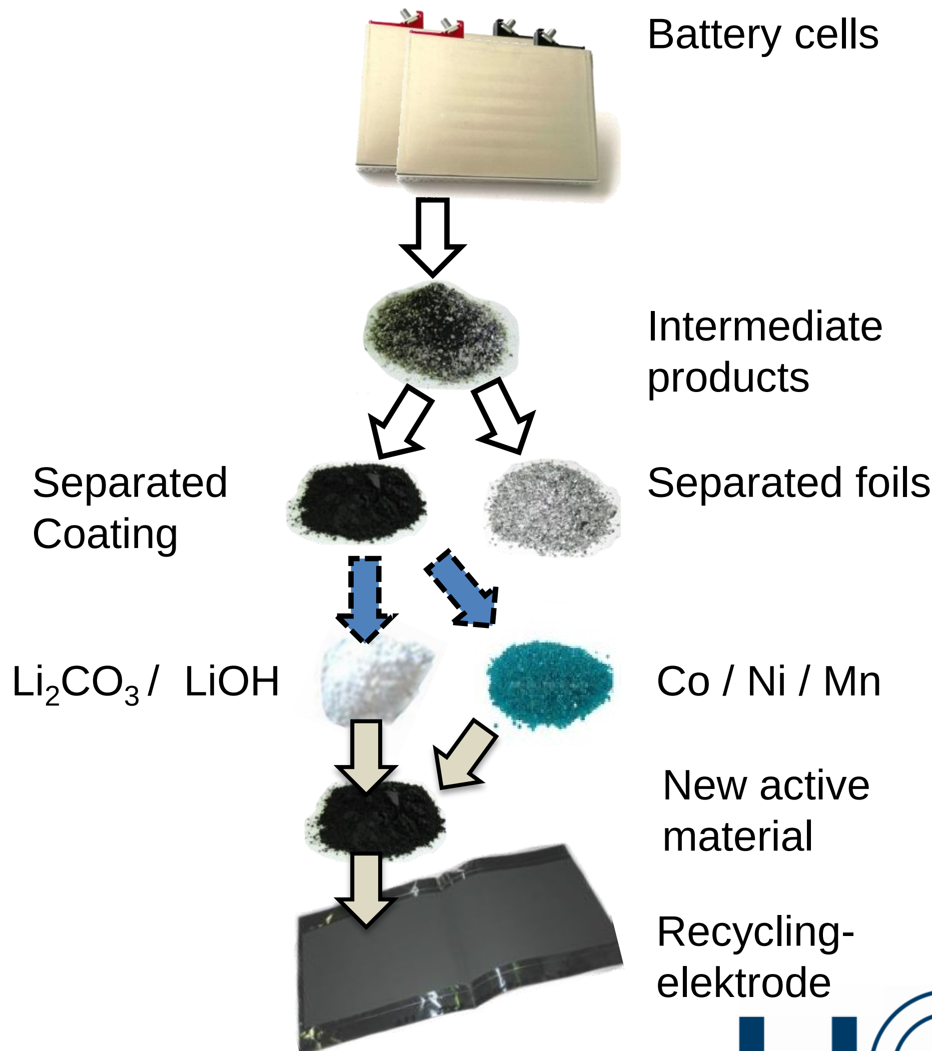
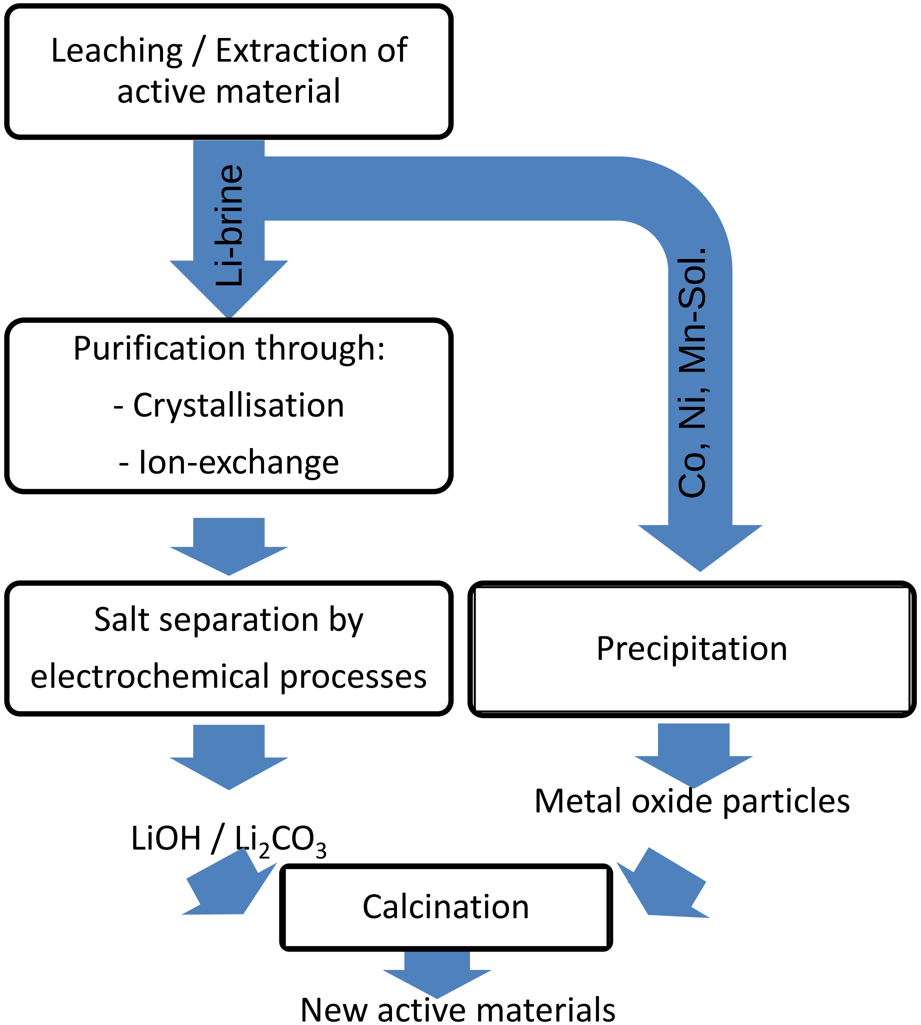




Reference: [TU Braunschweig]

Hydrometallurgical process



Hydrometallurgical lithium extraction

recycling yield:

- 85 % of lithium from $LiFePO_4$
- 95 % of lithium from $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

Pilot plant for hydrometallurgical process
Source: Rockwood Lithium

Reference: TU Braunschweig

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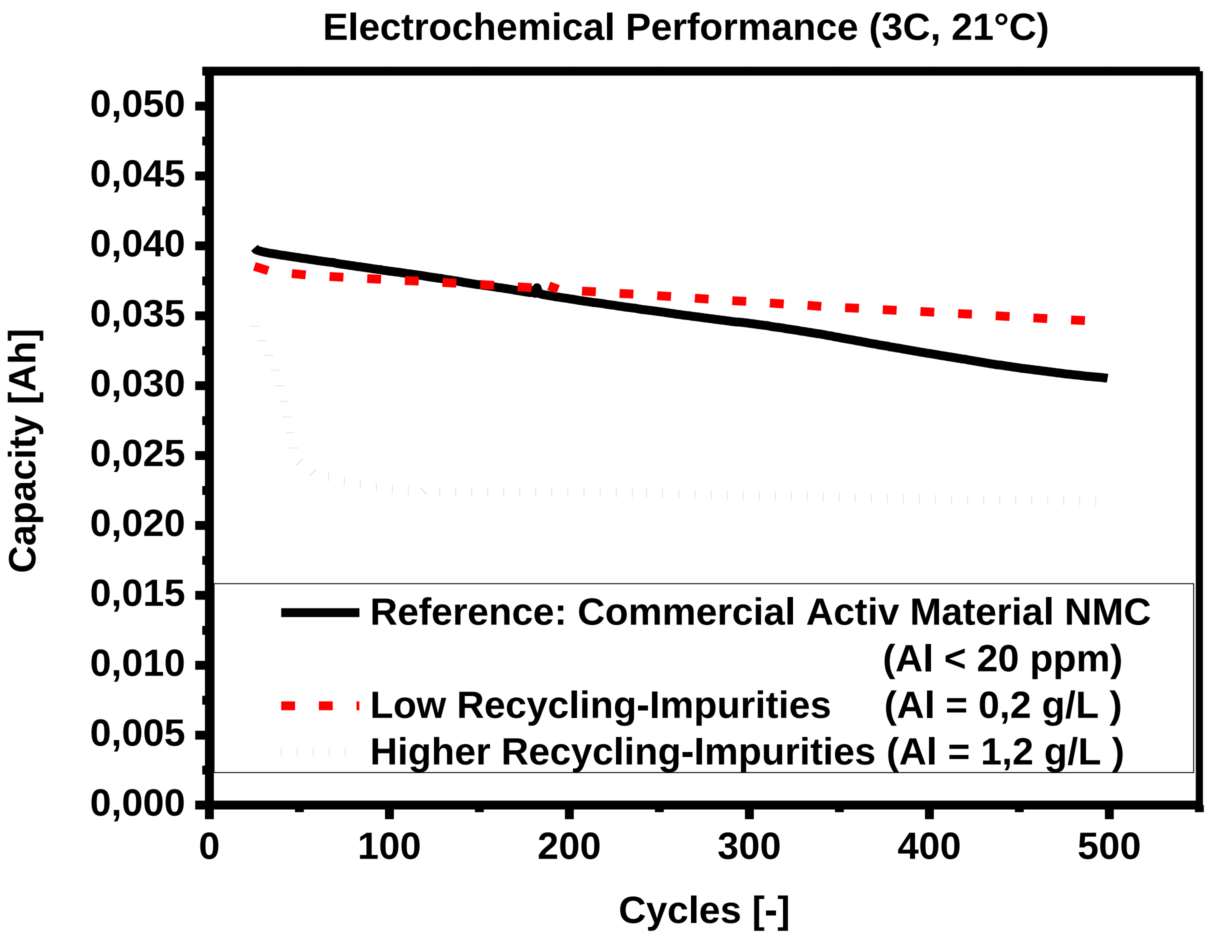
Influence of Impurities on the Re-Synthesis



Further information: Krüger, S.; Hanisch, C.; Nowak, S., Kwade, A.; Winter, M.: Effect of Impurities Caused by a Recycling Process on the Electrochemical Performance of $Li[Ni_{0.33}Co_{0.33}Mn_{0.33}]O_2$, Journal of Electroanalytical Chemistry, 2014

Reference: TU Braunschweig

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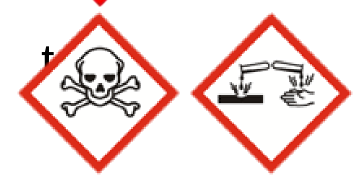
Dangers

- Decomposition of the binder **polyvinylidene fluoride** in case of fire
  - ➢ **Hydrogen Fluoride (HF)**

- **Cathodic Active Materials** contain nickel oxide → carcinogenic

- Risk of dust explosion
- Electrolyte solvents are inflammable

- Exothermic decomposition of conducting salt $LiPF_6$ t hydrogen fluoride



- Electrical hazard and reaction activation by short circuits

Reference: TU Braunschweig

Ba.Z.U.Ka.

Ba.Z.U.Ka. (BatterieZellen-UntersuchungsKammer

Battery**-S**ecurity-Test**-O**bject**-**to **O**perate**-G**as-**A**nalytics**):** system to analyze gases resulting from abuse tests quantitatively and qualitatively

Resulting gases during a nail-penetration-test with a NMC pouch cell in Ba.Z.U.Ka.

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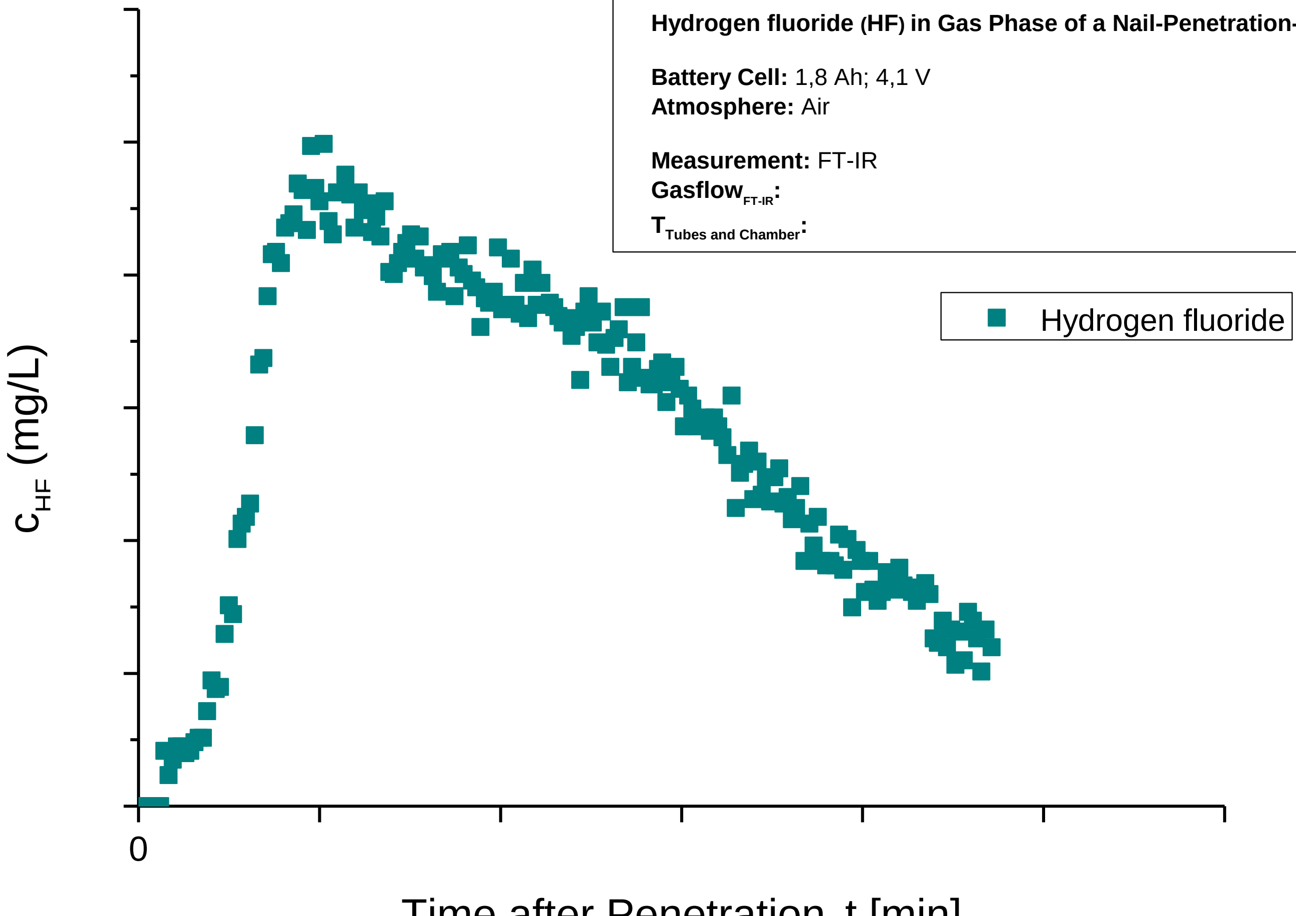
Nail-Penetration-Test of a Lithium-Ion Battery Cell

Hydrogen fluoride (HF) in Gas Phase of a Nail-Penetration-Test

Battery Cell: 1,8 Ah; 4,1 V
Atmosphere: Air

Measurement: FT-IR
Gasflow$_{FT-IR}$:
T$_{Tubes\ and\ Chamber}$:

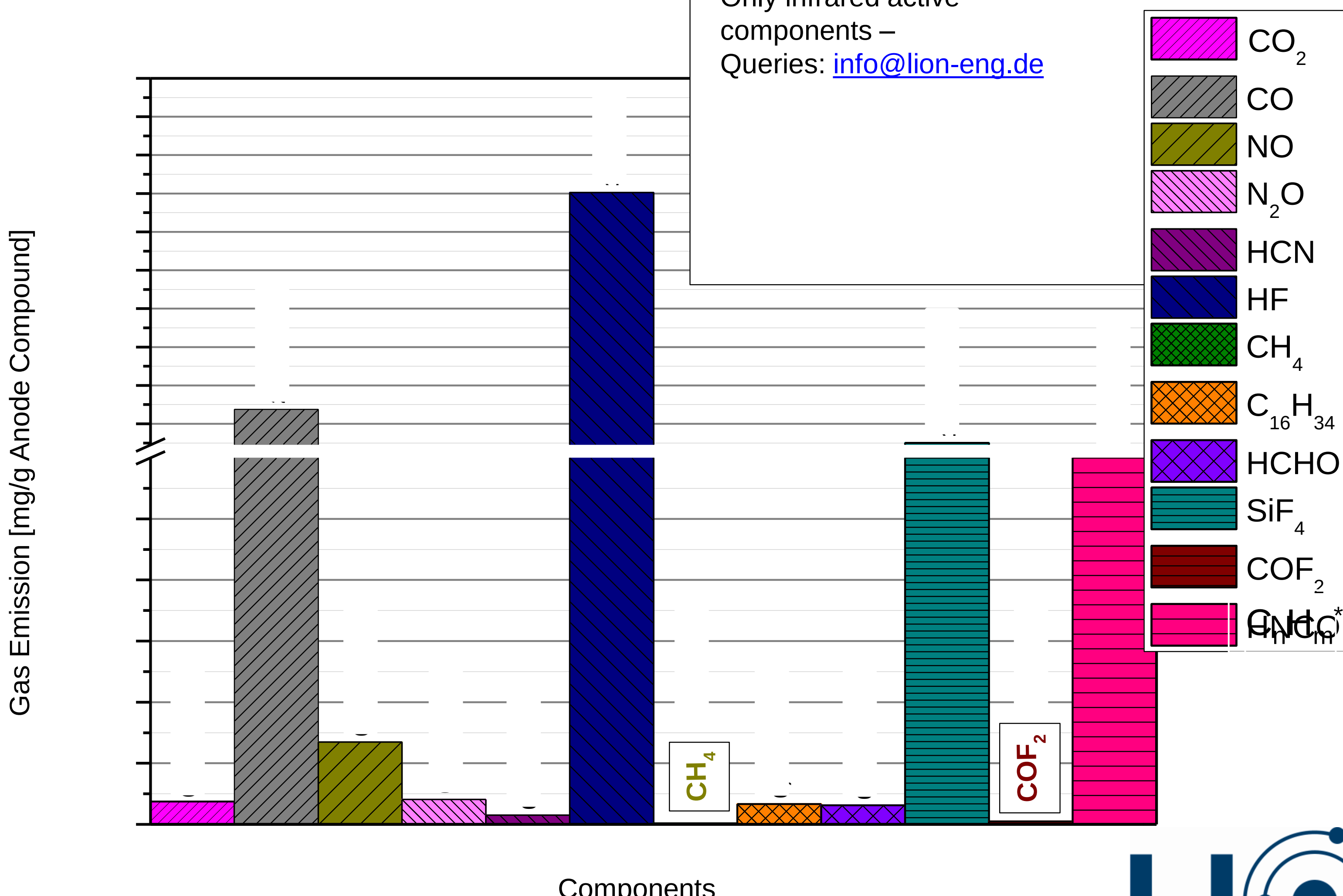


(with continuous Gasflow N_2 (   )

Reference: [TU Braunschweig]() and [Lion Engineering GmbH]()   Queries: [info@lion-eng.de]()

If an electrode burns: Infrared Spectroscopy

Only infrared active components –
Queries: info@lion-eng.de



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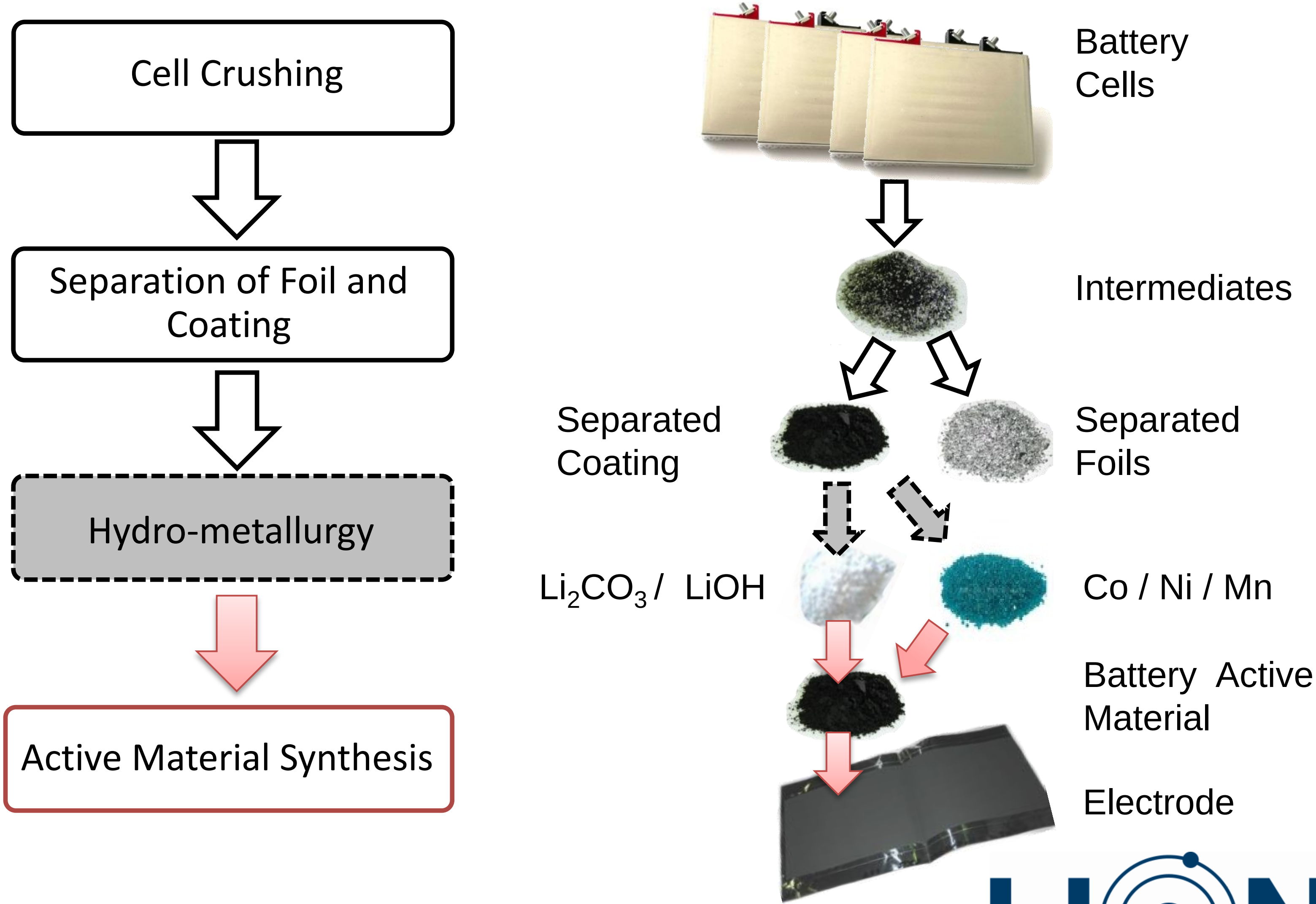
Separation of Active Materials from LIB Cells



First Solution: Cutting Mill and Sieving

- ○ CSE 80 - 95 % of Active Material
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- + Simple
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Facts, which led to a new process

1. **Binder polyvinylidene fluoride (PVDF)**
   - **a) adhesion** between **coating and current collector foil**
   - **b) cohesion** between electrode **coating particles**
   - **c) lower decomposition temperature** than other components

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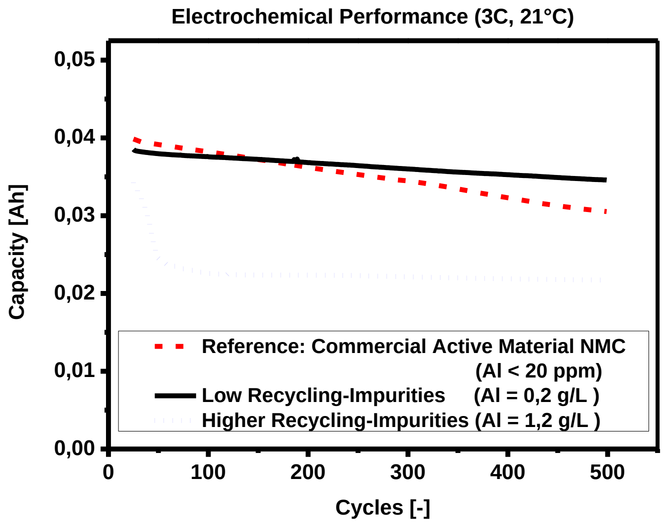
2. **High educt purity** for **synthesis battery grade active material**



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3. **Mechanical separation** of electrodes
   - a) **coating agglomerate** diameters up to **250 µm**
   - b) **foil scraps** of **50-200 µm**

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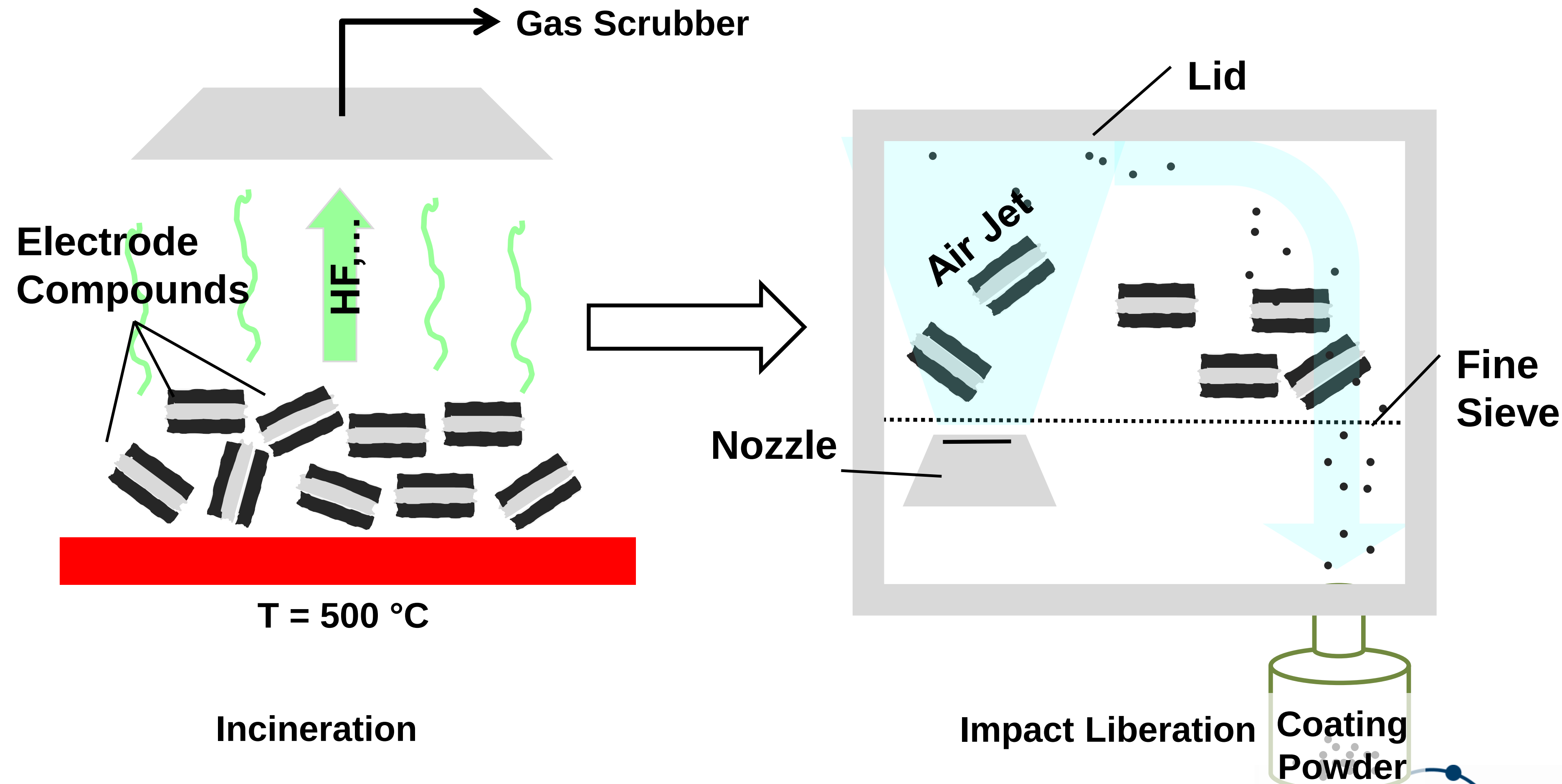
4. **Fine sieving reduces impurities**

5. **Impact stress** transforms kinetic energy into dispersing energy
   - a) **loosen coatings** from their substrate
   - b) **break agglomerates**

Adhesion Neutralization via Incineration and Impact Liberation (ANVIIL)



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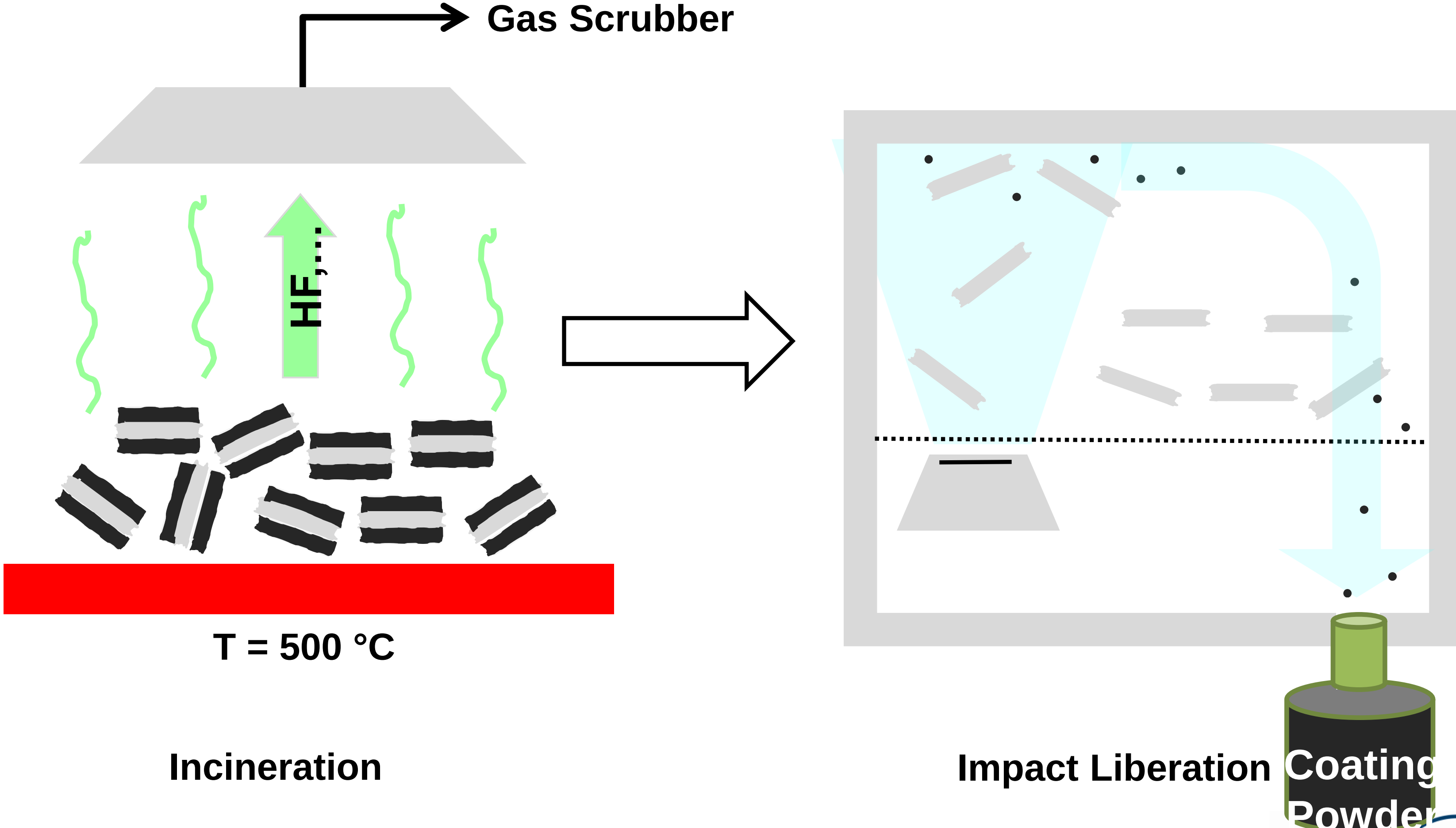
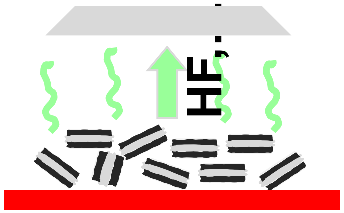


Conclusion

- High Compound Separation Efficiency > 99%
- Aluminum Impurities < 0.1 wt.-%
- Incineration Gases have to be dealt with
- Results of the LCA of the Öko-Institut e.V. are published



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TRUSD (The Reliable Universal Secure Database)

- **Oracle based database and logistics solution for lithium-ion battery systems:**

  - Tracking of the systems and its components within the recycling path
  - Generation of dispatch notes with characteristics

  - Condition validation according to VDA standards

  - Materials management
    - Where is which amount?
    - Verification of disposal

  - Monitoring of materials behaviour in the process
    - Recycling quotas
    - Consistent and enforced data entry for process steps by different stakeholders
    - Easy tracing of products and samples
    - Better analysis/comprehension of the process steps
    - Replicable process evaluation on reliable data base
    - Good overview

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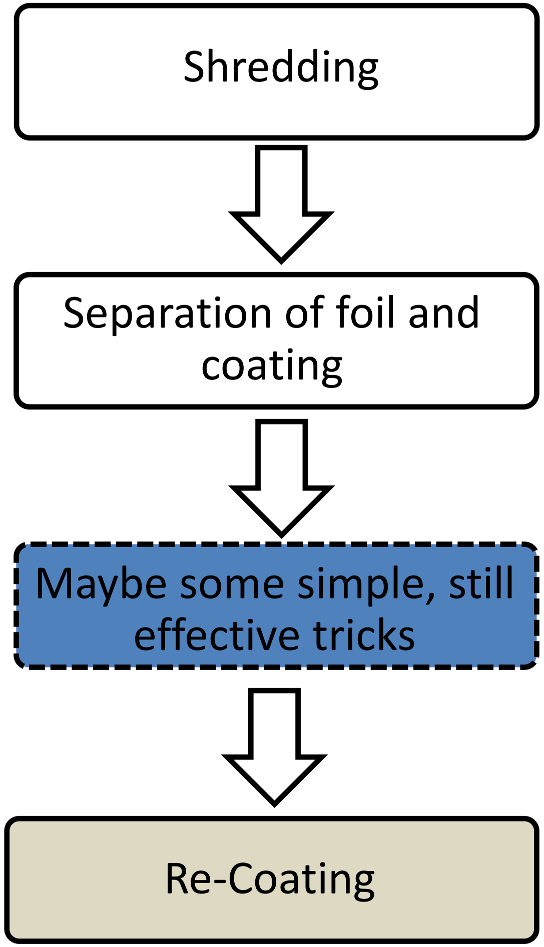
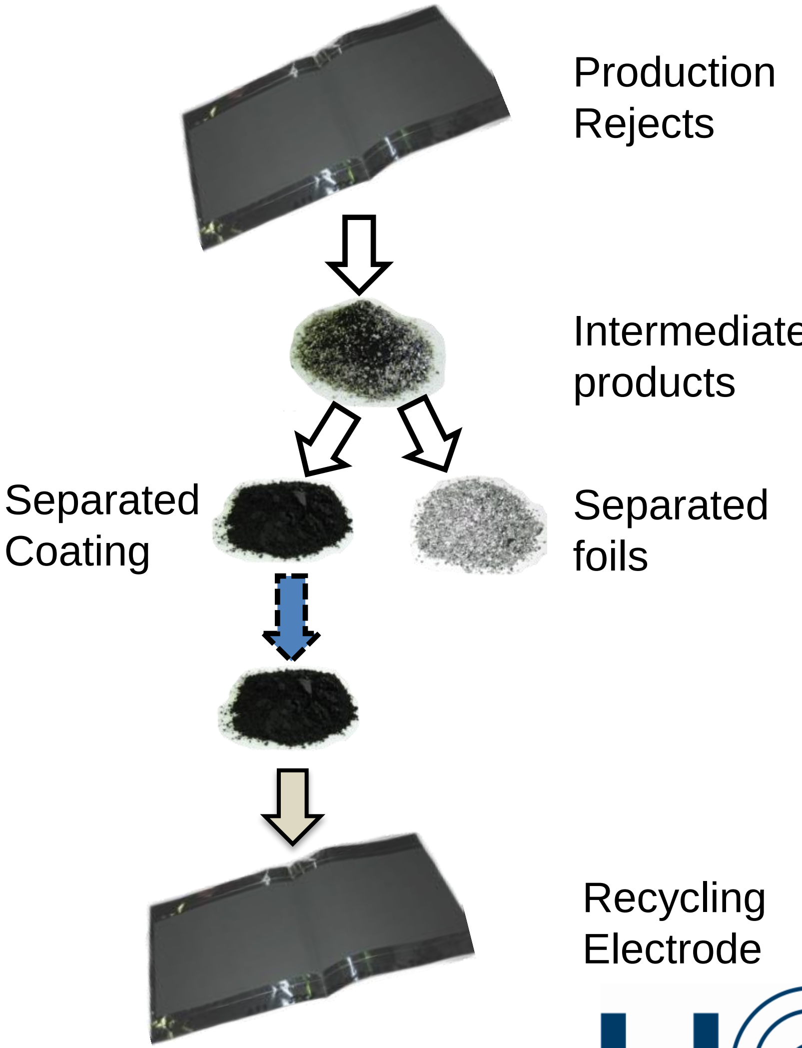
Recycling of Production Rejects





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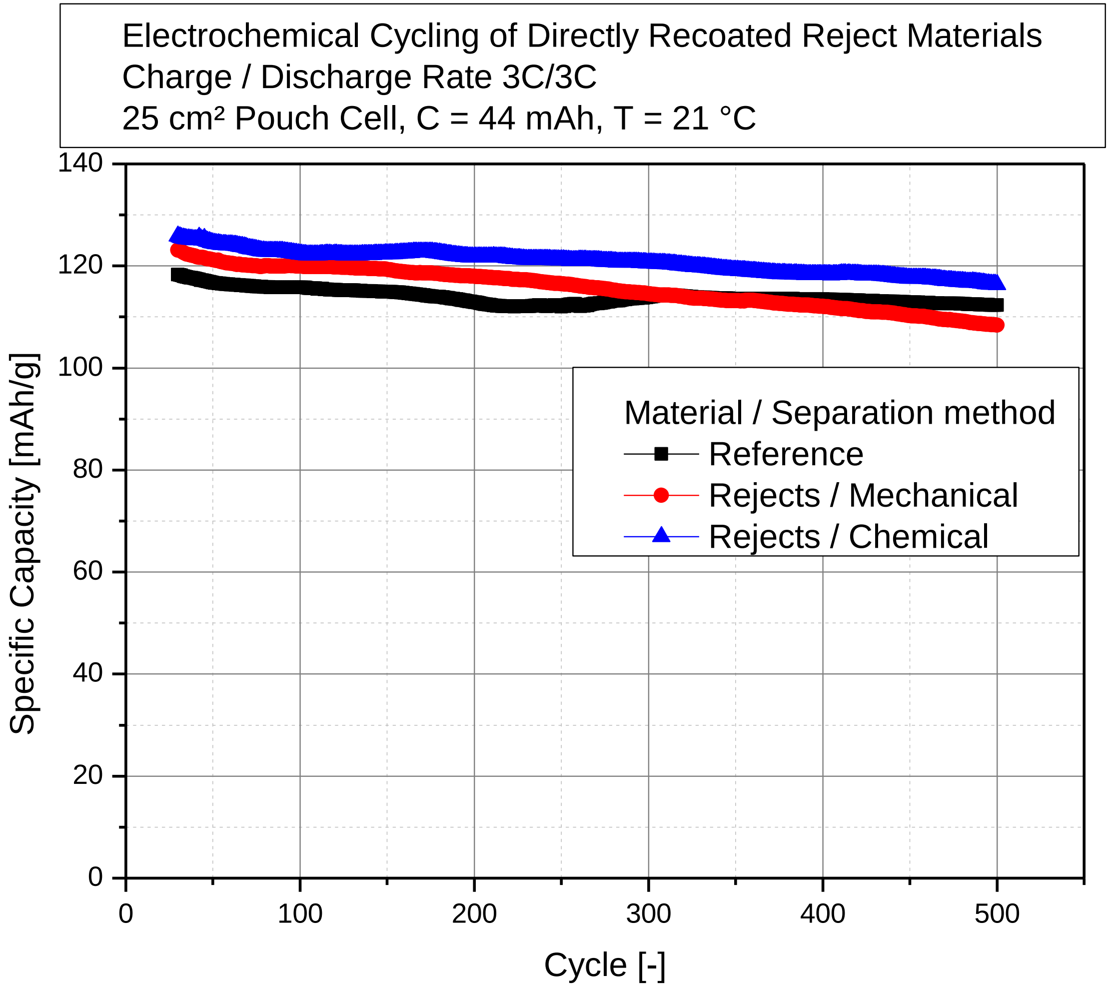
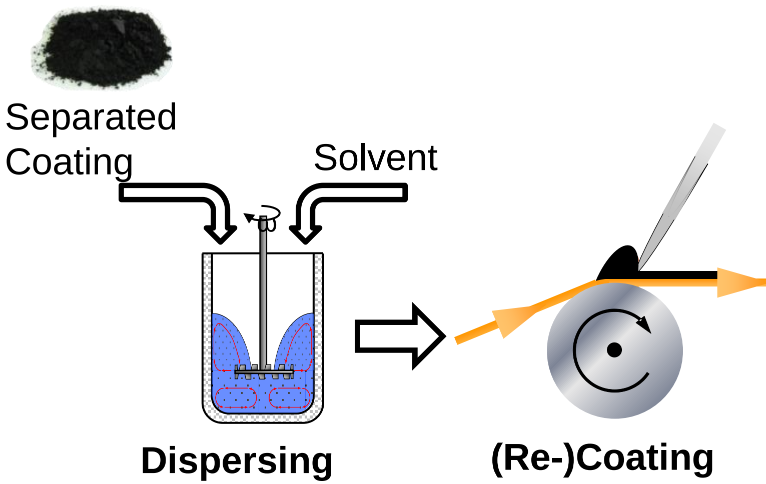
Recycling of Production Scraps/Rejects



Further information:
In-Production Recycling of Active Materials from Lithium-Ion Battery Scraps
in ECS Transactions 64(22): 131-145 · April 2015



Reference: TU Braunschweig and Lion Engineering GmbH

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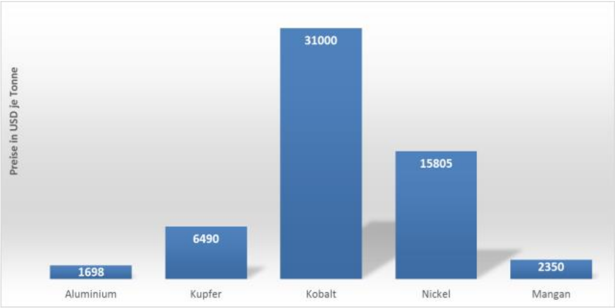
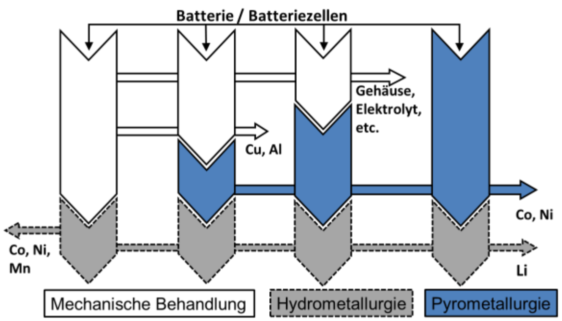
Conclusion

- Metallurgical Recycling of spent batteries is feasible to regain Co and Ni
  - Future battery materials will be an economical challenge for the recycling process (reduction of Co/Ni in Battery Active Materials)



- Increasing of Recycling Yield possible by Combination of different unit operations → payoff of higher process costs? info@lion-eng.de !



- Challenges:
  - Hydrogen fluoride and other components
  - Purity of regained materials

Further information: **Recycling of Lithium-Ion Batteries**
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Handbook of Clean Energy Systems - Volume 5 Energy Storage, 2015 edited by Jinyue Yan, Luisa F. Cabeza, Ramteen Sioshansi, 01/2015: chapter 27: pages 2865-2888; John Wiley & Sons, Ltd.., ISBN: 978-1-118-38858-7

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Thank You!

Further questions?

Christian Hanisch

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