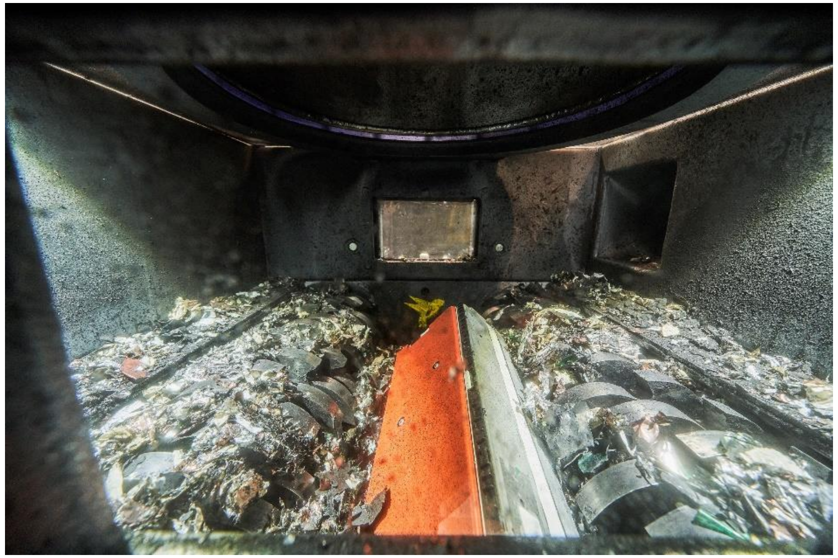
Technische Universität Braunschweig

BATTERY LABFACTORY BRAUNSCHWEIG

iPAT Institut für Partikeltechnik



Comminution and classification as important processes for the circular production of lithium batteries

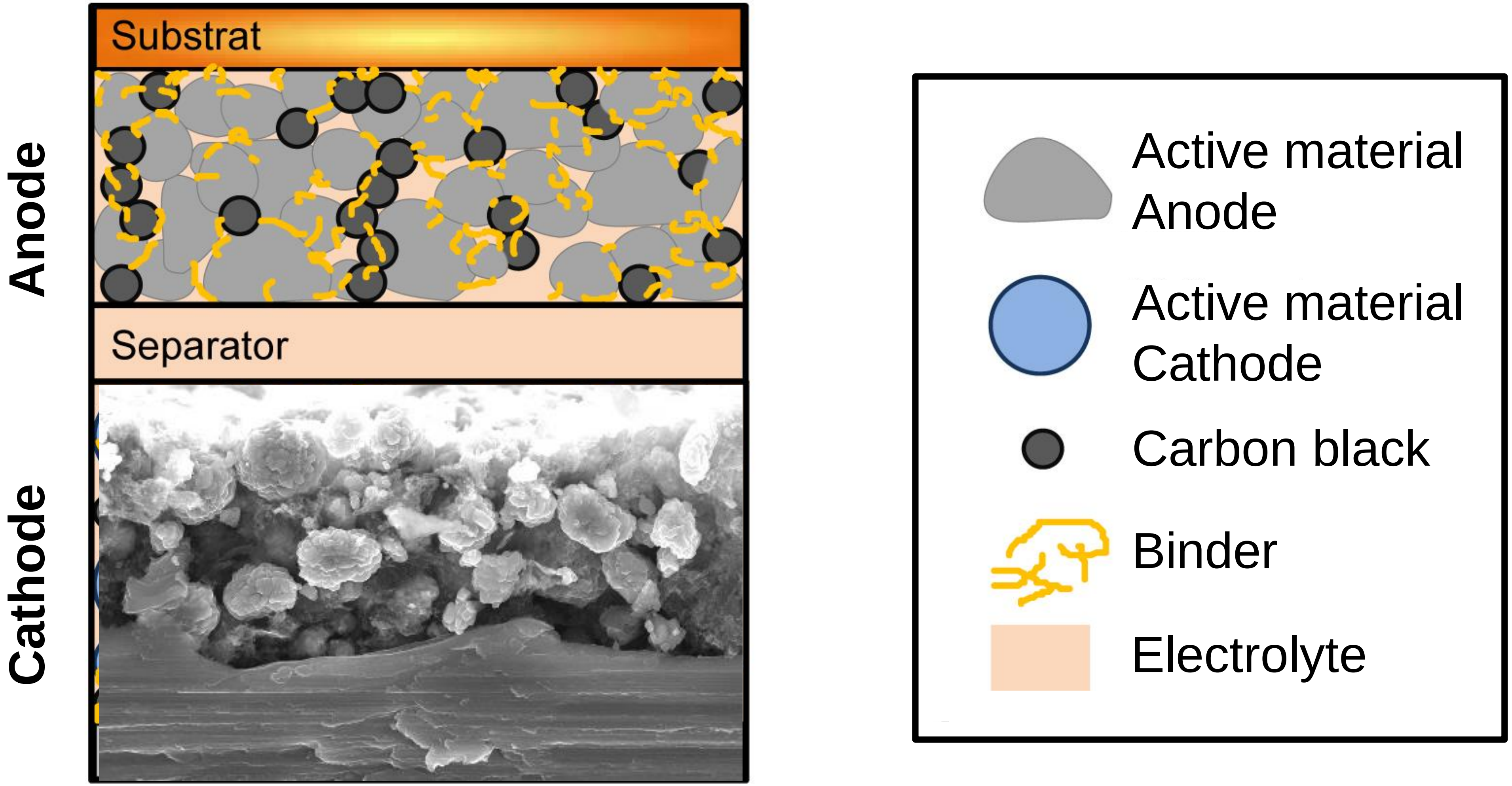
Arno Kwade, Steffen Fischer, Dennis Beusen, Marcella Horst, Marcel Möller, Peter Michalowski

Institute for Particle Technolgy & Battery LabFactory Braunschweig

Content

Content

Components of LiBs



Components and function of Lithium-ion battery

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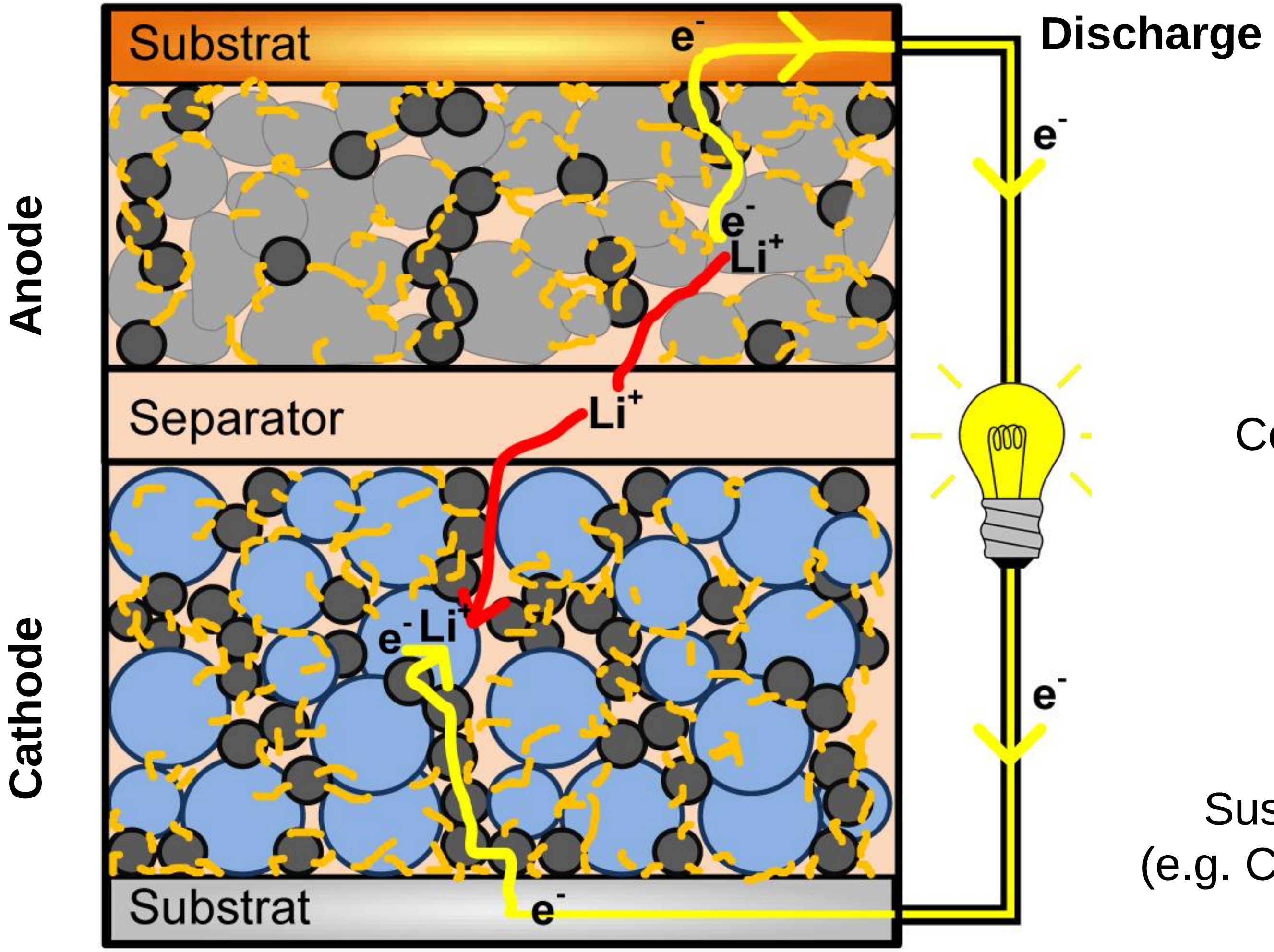
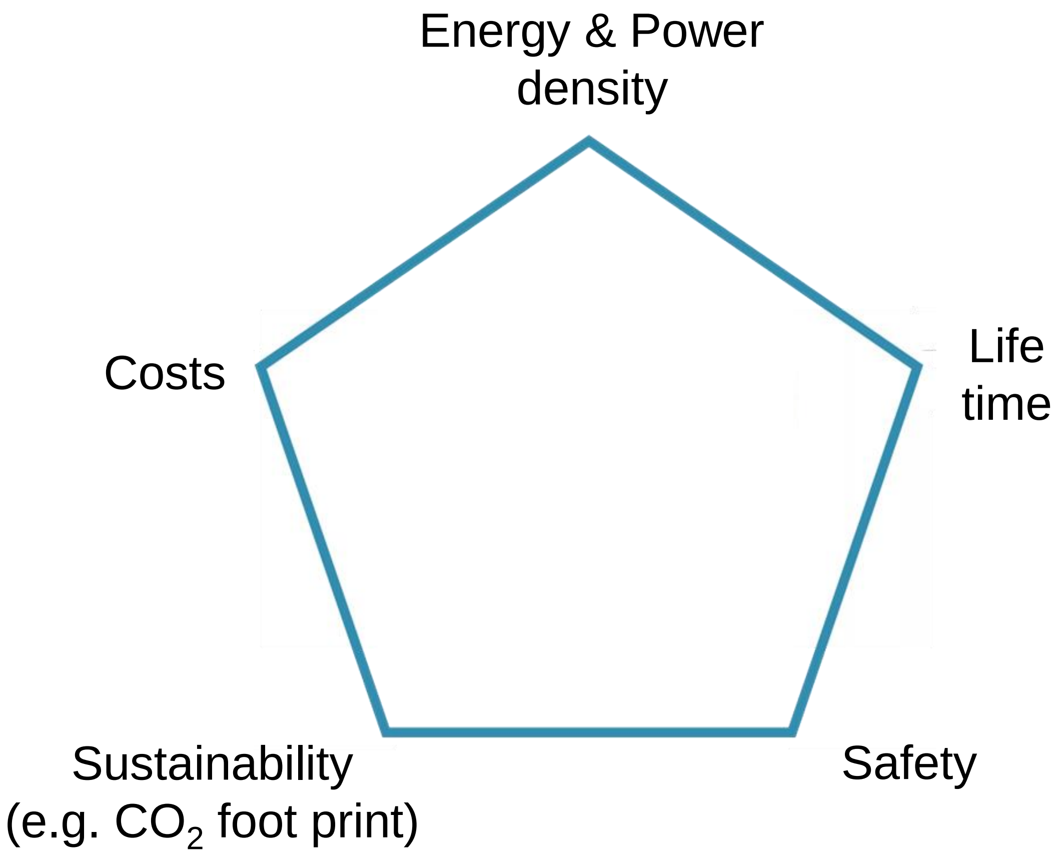
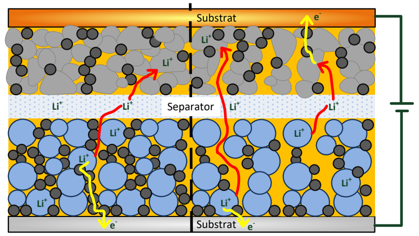




Technology Trends

Diversification of cell chemistry and cell design

Lithium-Ion



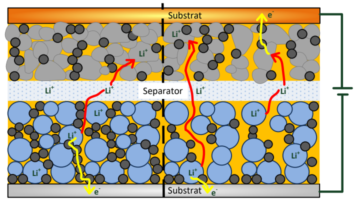
NCM622/NCM811/
NCA vs. Graphite

Material,
Electrode and
cell design
improvement

Maximizing cell performance

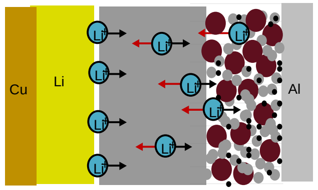
Minimizing cost/ ecological impact

Lithium-Ion



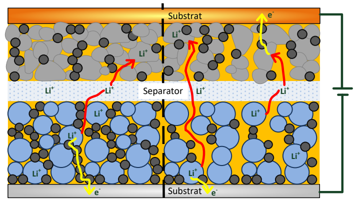
NCM9.5.5 vs Si/C

Solid State



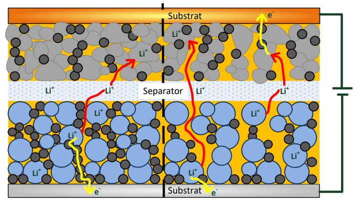
NCM9.5.5 vs. Li

Lithium-Ion



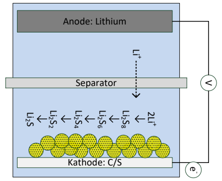
NCM307 vs Si/C

Lithium-Ion



LFP/LMO vs Graphit
Sodium-Ion-Batteries

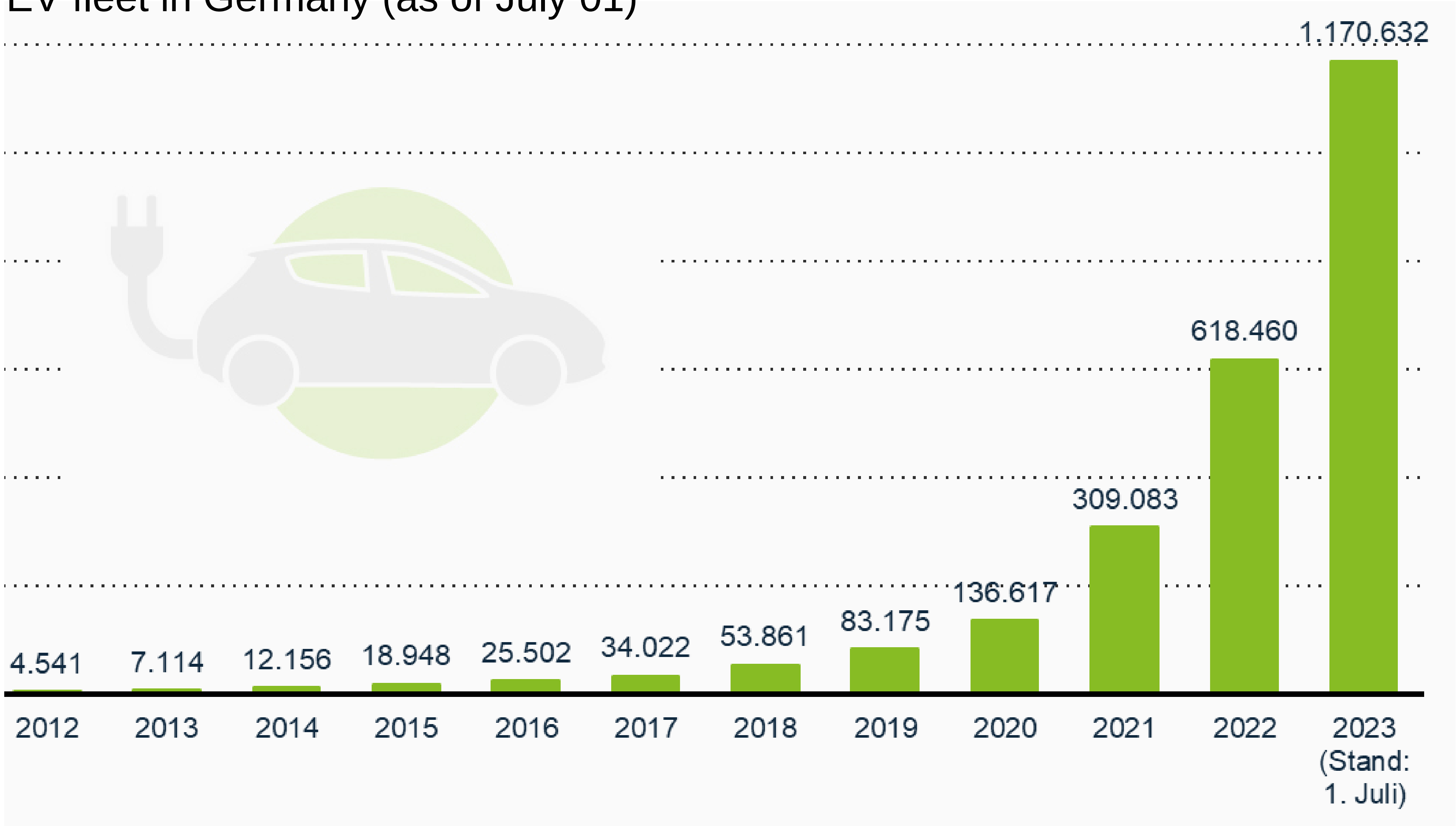
LiS



S-C vs. Li

Battery as a key technology for electromobility

EV fleet in Germany (as of July 01)



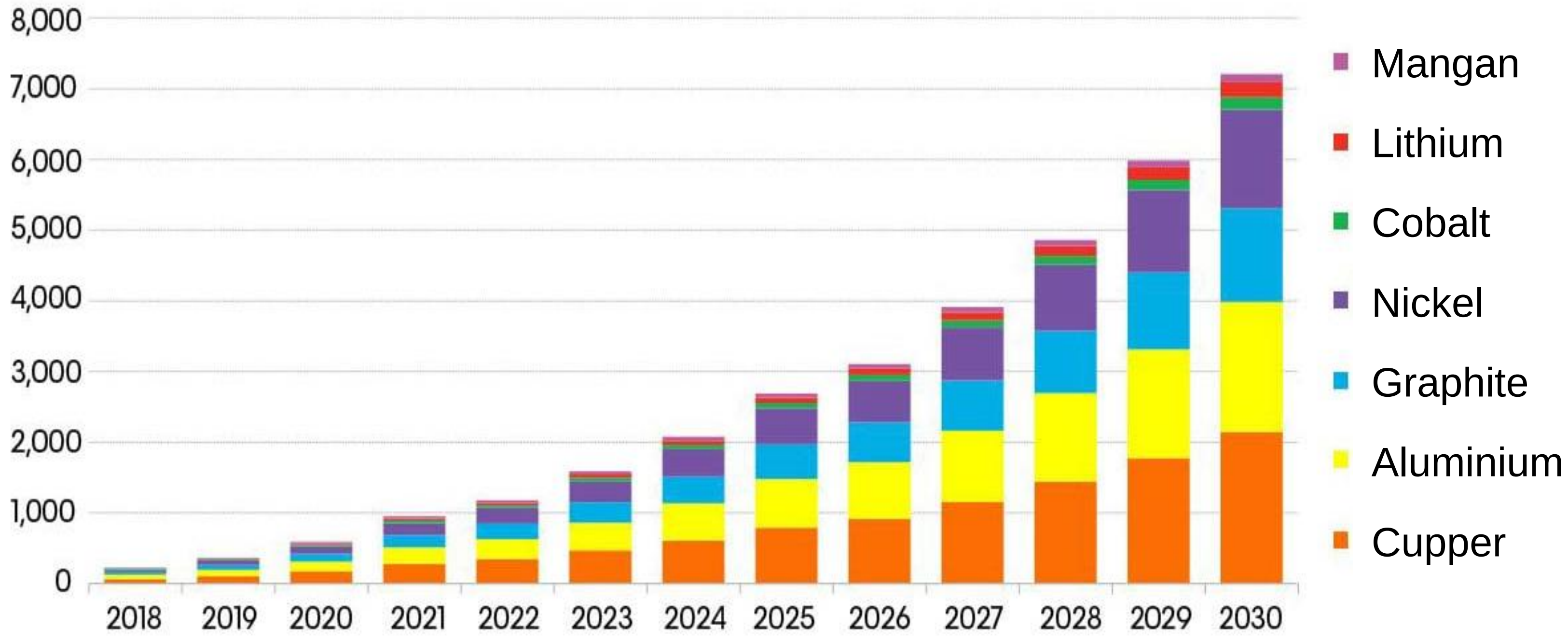
Quelle(n): KBA statista

„ Seven to ten million electric vehicles are to be registered in Germany by 2030, according to the target set by the German government.“

Quelle: https://www.bundesregierung.de/breg-de/themen/klimaschutz/verkehr-1672896

Demand on raw materials for electric vehicles

Metric tons x 10^3



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.

- Sharp increase in material demand for cell production
- CO_2-impact of materials has to be minimized
- Social aspects of raw materials have to be taken into account

Motivation
Sustainability and circular economy

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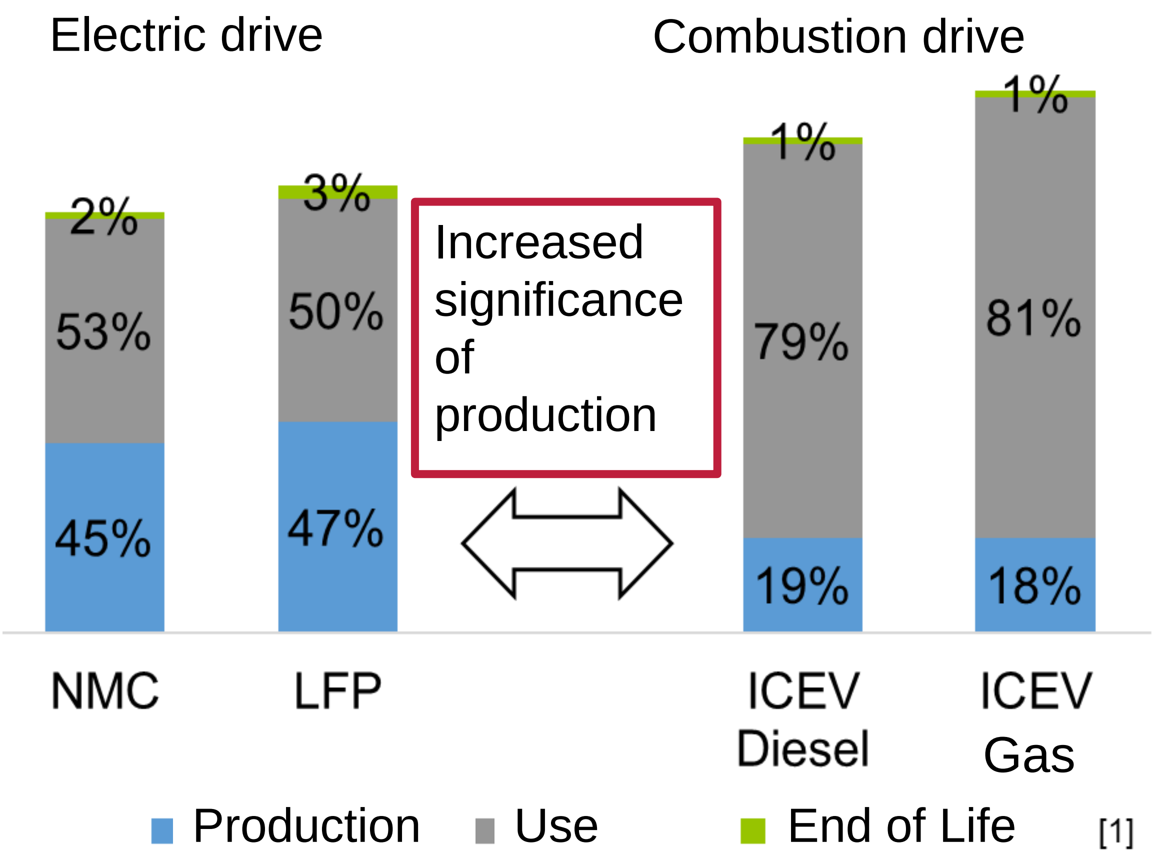
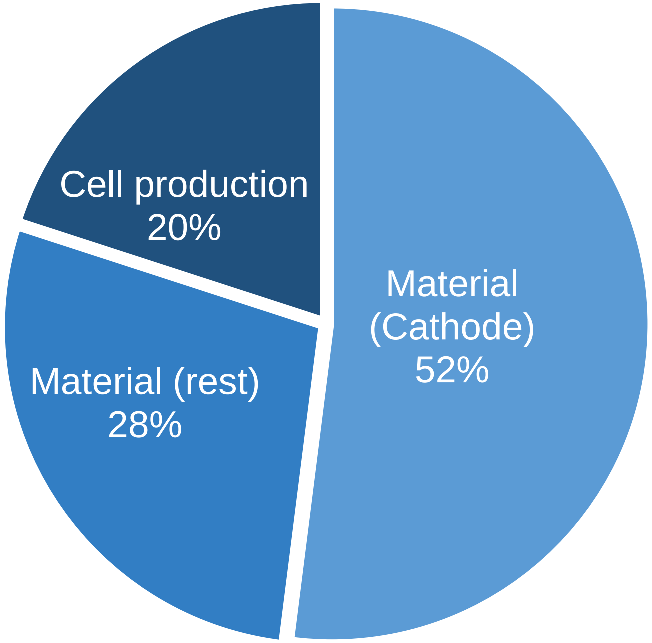
Comparison of greenhouse gas potentials



[1]

Cradle-to-Gate CO_2-eq Emissions



- Materials are responsible for around 80 % of the average CO2 emissions of an EV battery,
- with 10 % scrap, share of cell production rises to 28 % [2]

Efficient use of materials and energy crucial in production

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[1] Basierend auf Daten von Ciez R E, Whitacre J F (2019) Examining different recycling processes for lithium-ion batteries. *Nature Sustainability*. 2(2):148–156.

[2] von Drachenfels, N., Husmann, J., Khalid, U., Cerdas, F., & Herrmann, C. (2022). LCA of the Battery Cell Production: Using a Modular Material and Energy Flow Model to Assess Product and Process Innovations. *Energy Technology*.

Content

1. Introduction into LiBs and their sustainability
2. Closed-loop Circular Production
3. Introduction into Battery Lab Factory Braunschweig
4. Recycling Technologies
5. Sustainable Electrode and cell production
6. Conclusion and outlook

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

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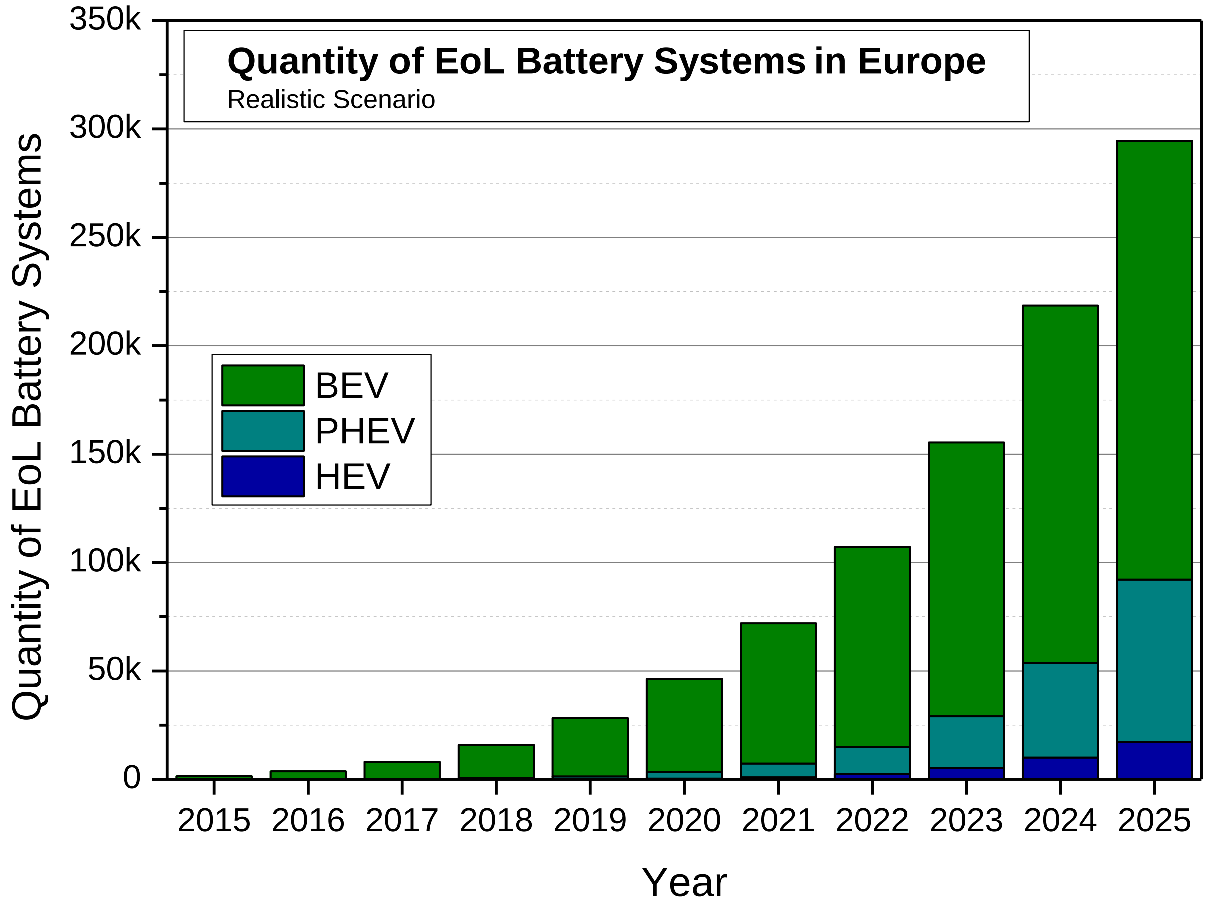

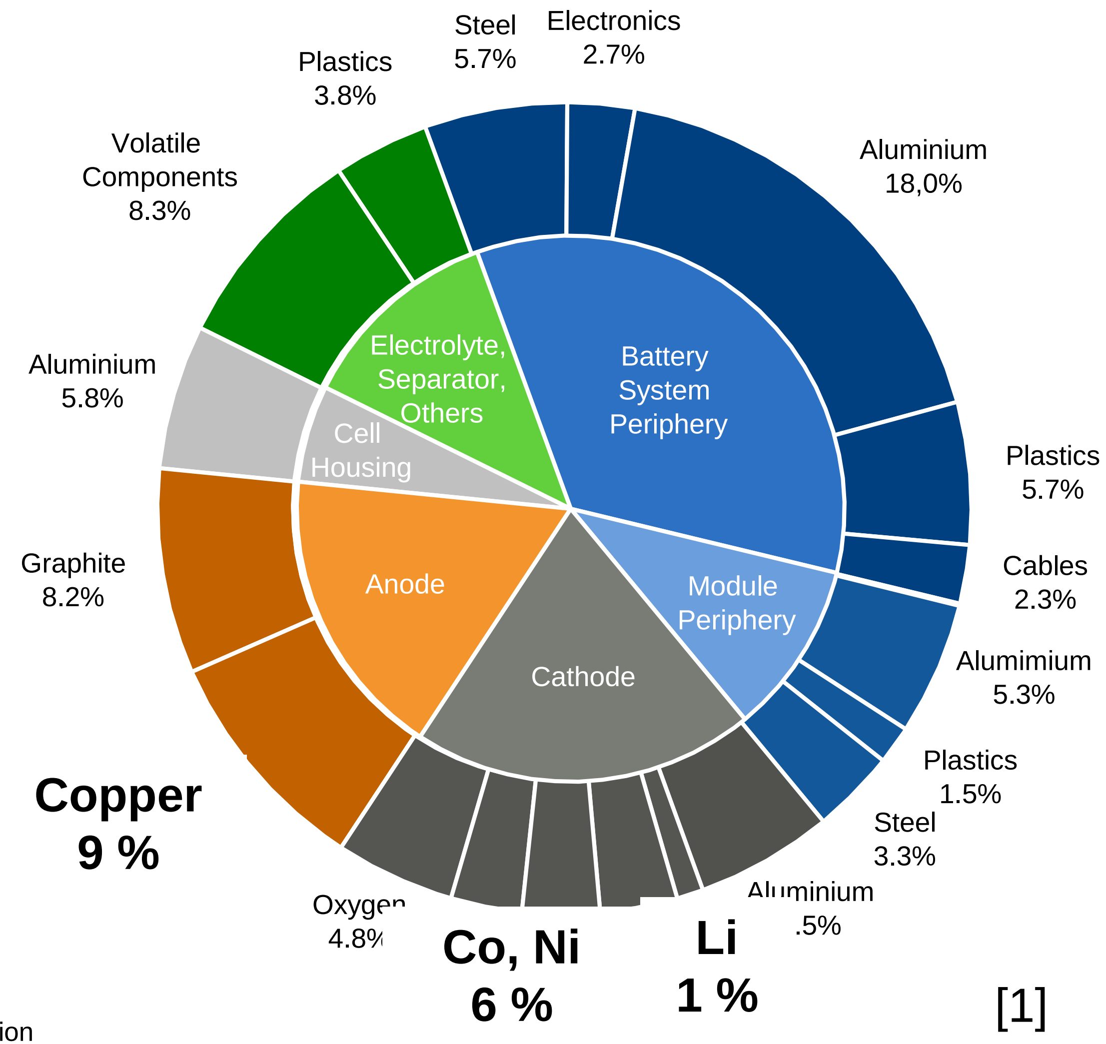

[1]

Source: Institute of Automotive Management and Industrial Production

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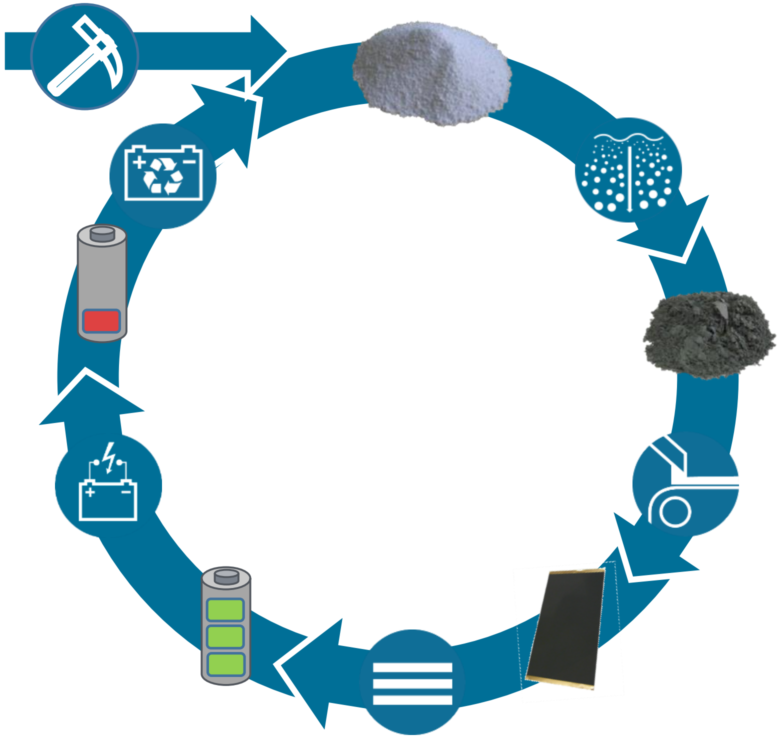
[1] according to: https://iopscience.iop.org/article/10.1149/2.0271701jes

Measures to reach a sustainable battery cell

Sustainable, energy efficient raw material processing

Sustainable active and passive material synthesis

Energy efficient recycling processes

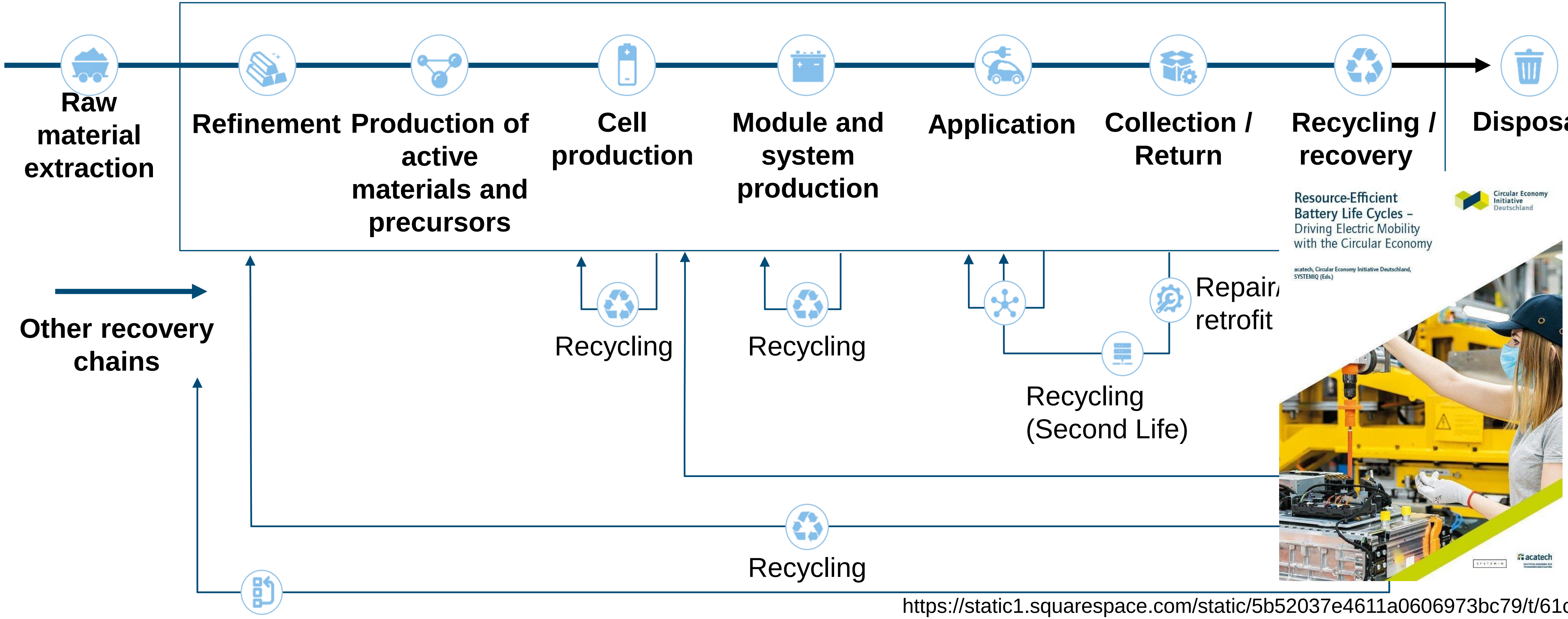


Closed material cycles

Energy efficient and robust electrode and cell production processes

Sustainable cell design

Circular Economy Initiative Germany
Central recommendations for action



https://static1.squarespace.com/static/5b52037e4611a0606973bc79/t/61c1e856a32b9841b83e0034/1640097893046/TB_Gesamtbericht+EN_DOI.pdf

Circular Economy Initiative Deutschland (Ed.): Resource-Efficient Battery Life Cycles – Driving Electric Mobility with the Circular Economy, *Kwade, A. & Hagelüken, C. et. al., acatech/SYSTEMIQ, Munich/London 2020. DOI: https://doi.org/10.48669/ceid_2021-2

Recycling – Circular battery economy concepts

Recycling Rates

Circular Economy Initiative Deutschland

EU battery regulation (**since 17.8.23**)

Material	Recommended Recovery rates*		EU battery regulation	
	2025 – binding	2030 – to be aspired to***, ****	31.12.25/ 31.12.27	31.12.30/ 31.12.31
Total battery**	60 %	70 %	65 %	70%
Lithium	50 %	85 %	50 %	80 %
Cobalt	85 %	90 %	90 %	95 %
Nickel	85 %	90 %	90 %	95 %
Copper	85 %	90 %	90 %	95 %
Steel	90 %	95 %	-	-
Aluminum (without Al foil)	90 %	95 %	-	-

Regulation (EU) 2023/1542 of the European Parliament and of the Council of 12 July 2023 concerning batteries and waste batteries, amending Directive 2008/98/EC and Regulation (EU) 2019/1020 and repealing Directive 2006/66/EC (Text with EEA relevance)

www.circular-economy-initiative.de

https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32023R1542

Content

Recycling Technologies

Unit Operations

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Deactivation

- Full discharge and short circuit
- Treatment in salt solution
- Freezing of electrolyte

Drying/Pyrolysis

- Thermal treatment
- Deactivation and treatment of black mass
- Removal or at least disintegration of electrolyte, binder and polymers

Mechanical Processing

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

Pyrometallurgy

Smelting of

- Battery Moduls
- Electrode Scraps
- Active Material Powder

→ Regaining of Co, Ni, Cu

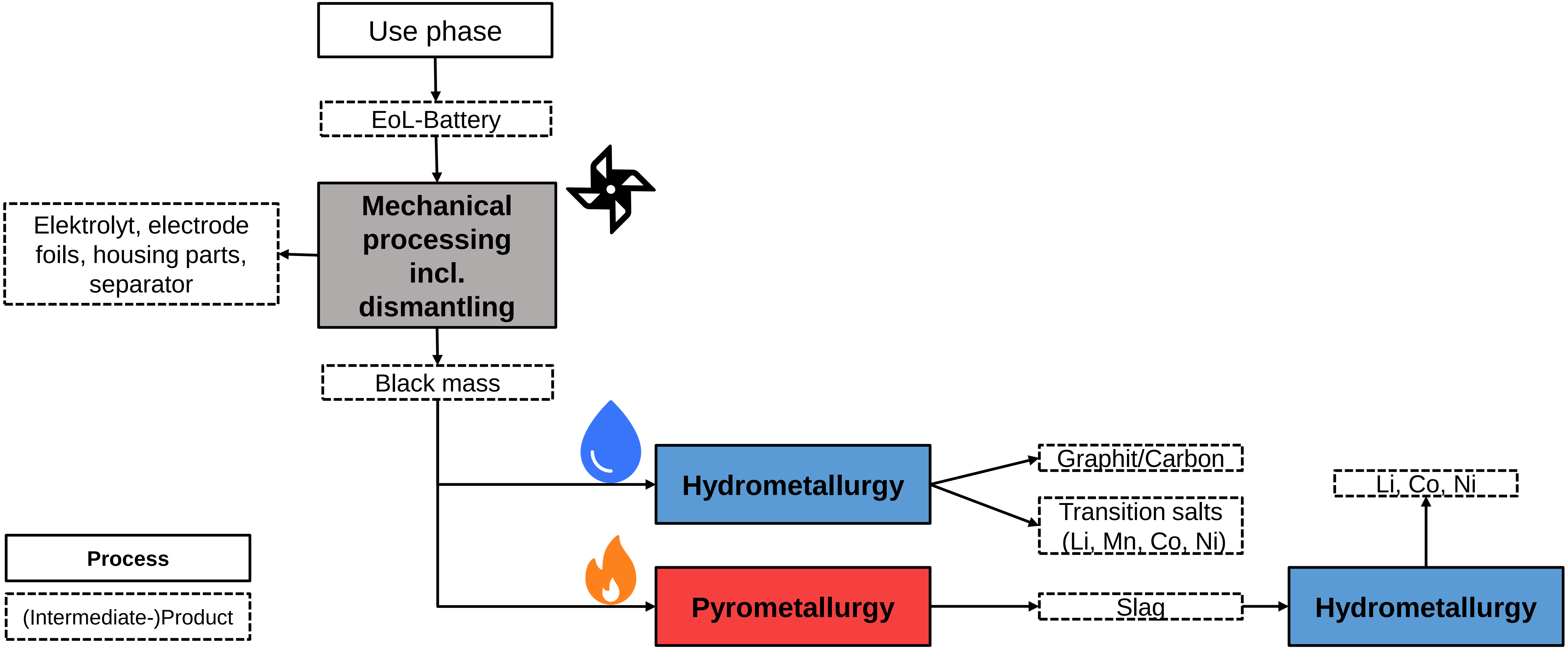
Hydrometallurgy

Chemical Processes

- Leaching
- Extraction
- Cristallisation
- Precipitation

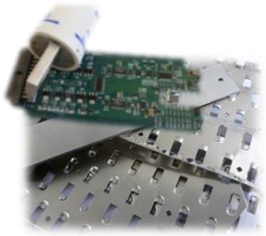
→ Regaining of Metals Co, Ni, Li from separated powders or slag

Recycling Technologies
Future closed material cylces



Mechanical Recycling
LithoRec

Discharge → Disassembly → Crushing → Drying → Mixing



Periphery

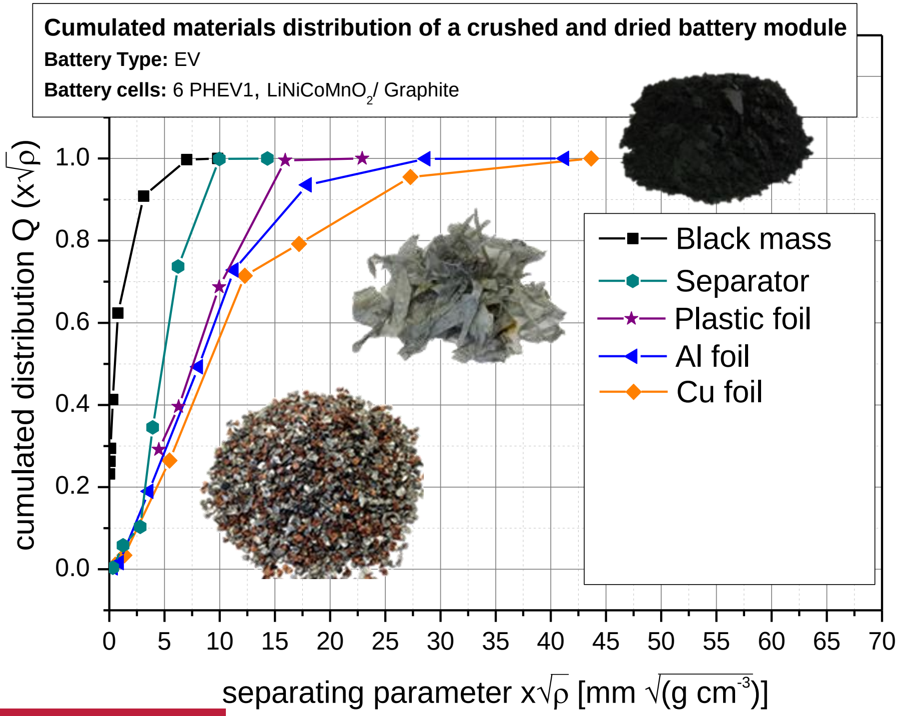
LithoRec II

https://www.erneuerbar-mobil.de/sites/default/files/2017-01/Abschlussbericht_LithoRec_II_20170116.pdf

A. Kwade, J. Diekmann: Recycling of Lithium-Ion Batteries – The Lithorec Way. Springer, 2018

Mechanical Recycling
LithoRec

Discharge | Disassembly | Crushing | Drying | Mixing | 1st Classification

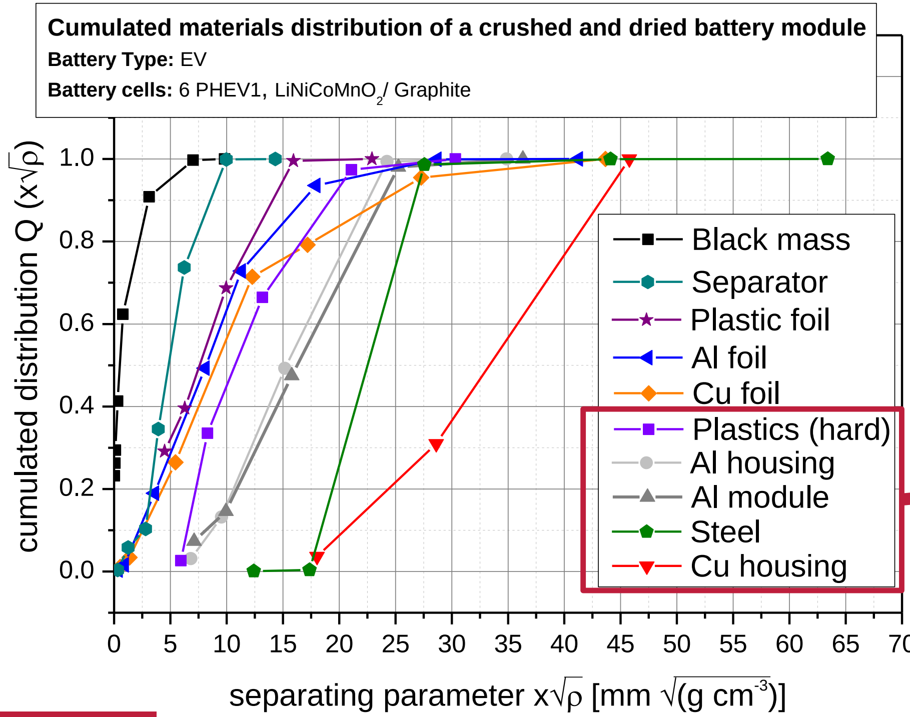


Zig-Zag-Classifier

Mechanical Recycling

LithoRec

Institut für Partikeltechnik



Shredded material (heavy fraction)

Zig-Zag-Classifier

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https://iopscience.iop.org/article/10.1149/2.0271701jes

A. Kwade, J. Diekmann: Recycling of Lithium-Ion Batteries – The Lithorec Way. Springer, 2018

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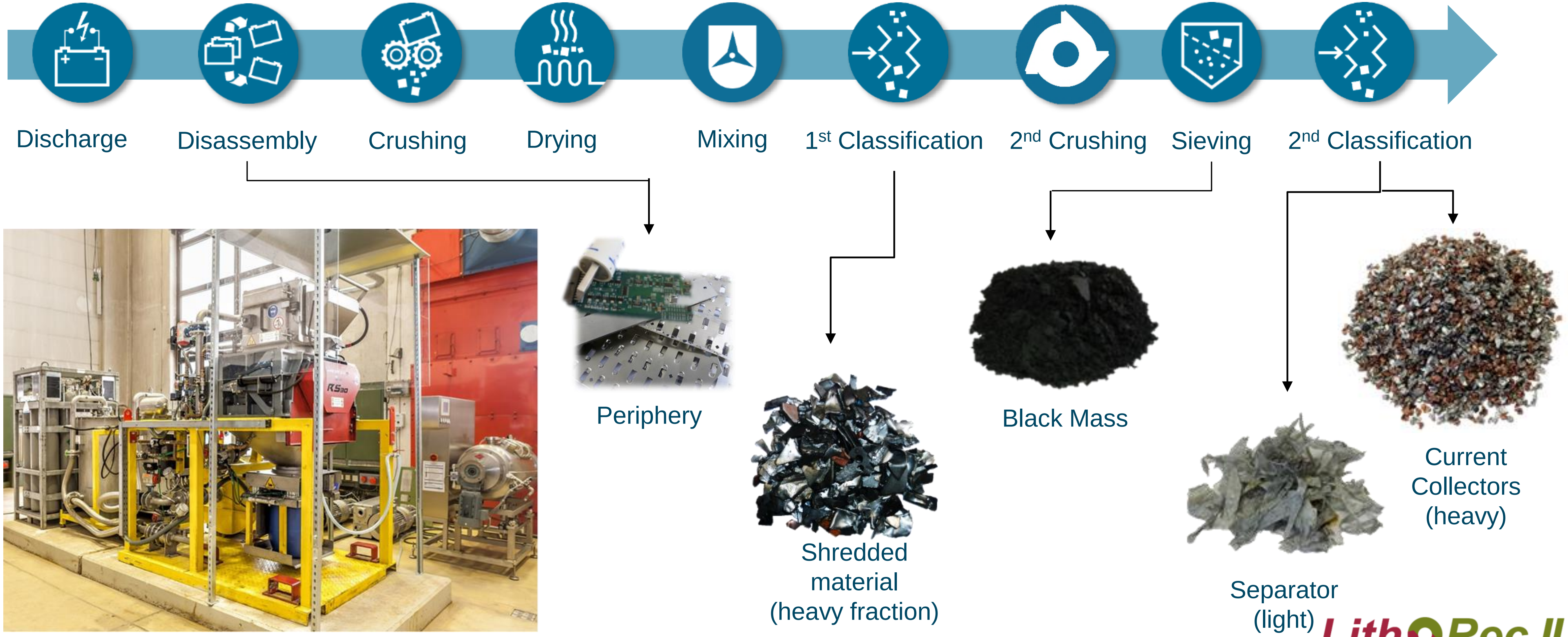
Mechanical Recycling

LithoRec

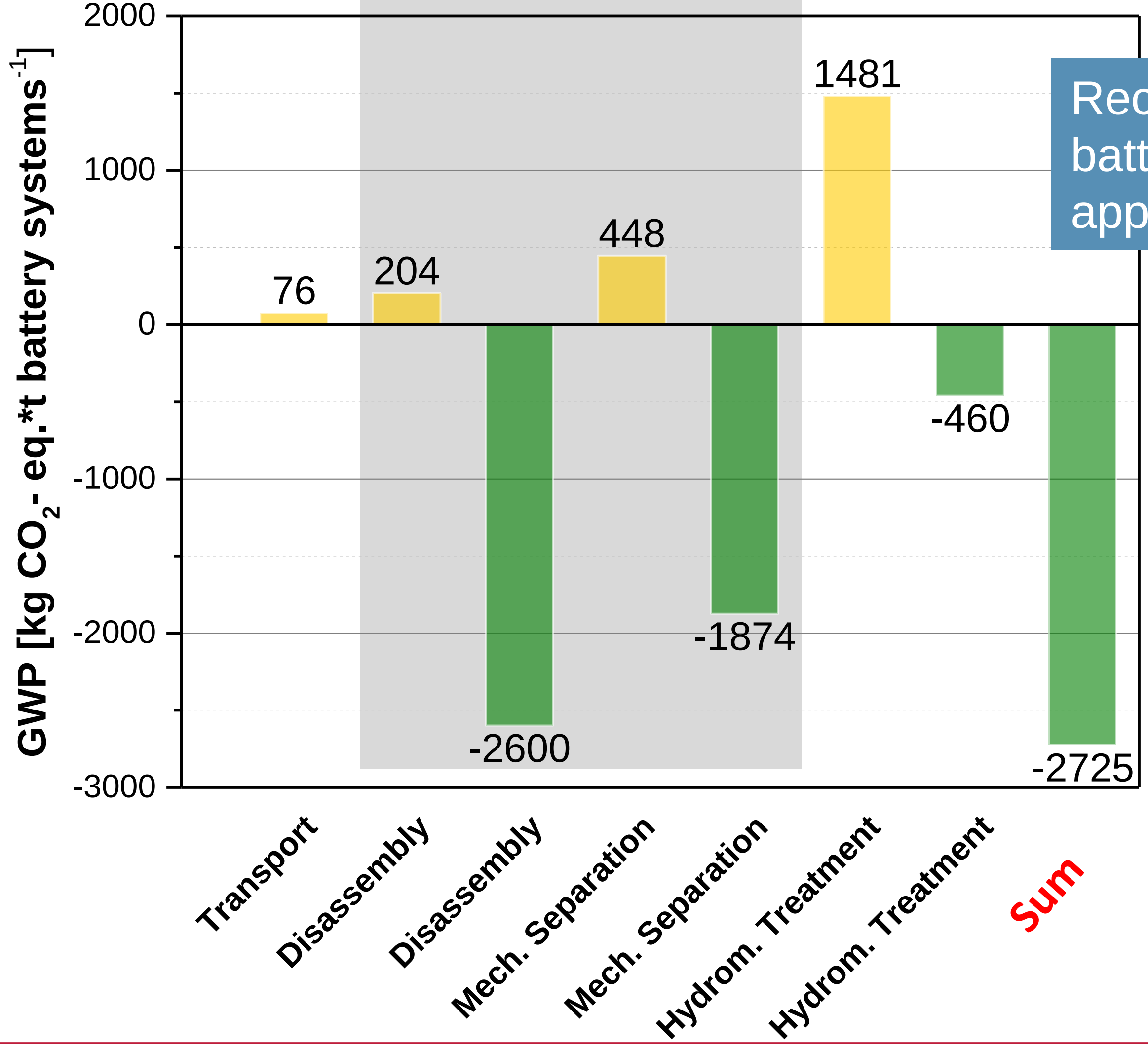


https://iopscience.iop.org/article/10.1149/2.0271701jes

A. Kwade, J. Diekmann: Recycling of Lithium-Ion Batteries – The Lithorec Way. Springer, 2018

Recycling Technologies

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

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

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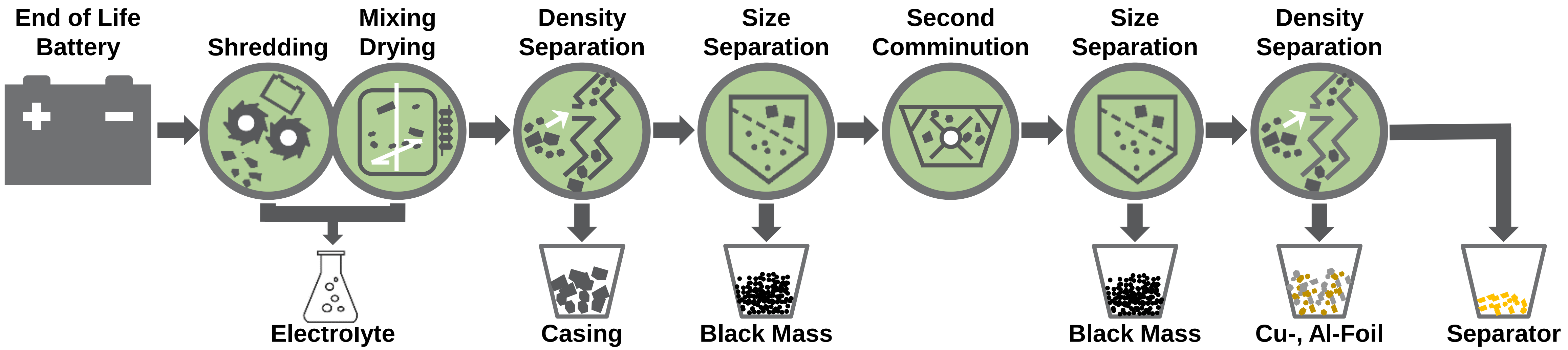
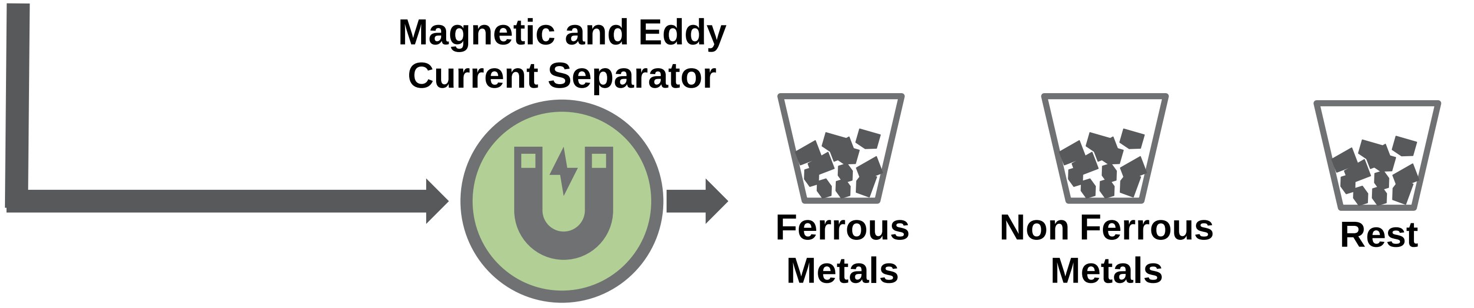
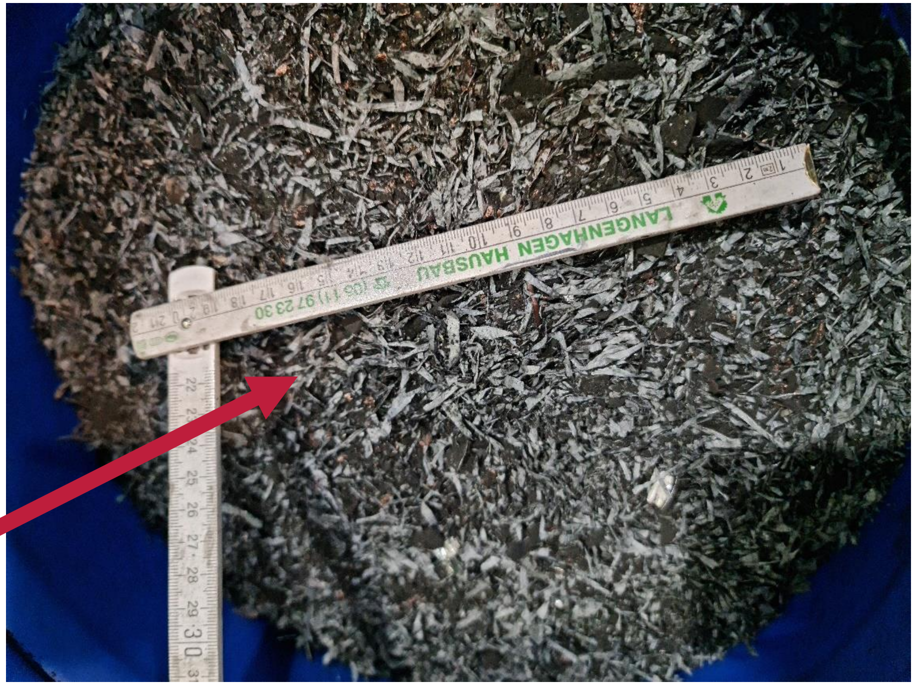
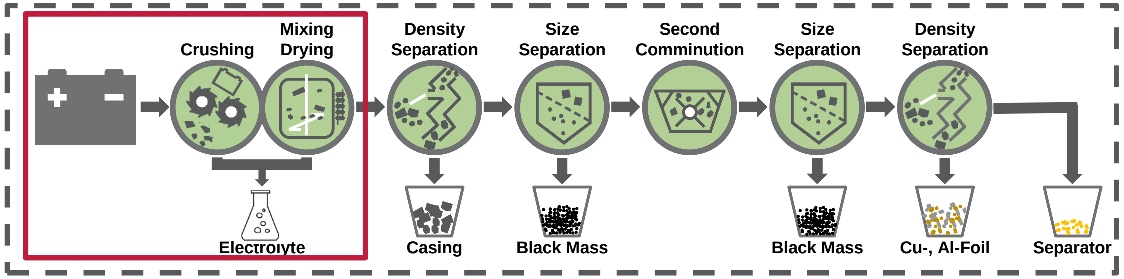
Mechanical Recycling
Pilot Plant Process Chain





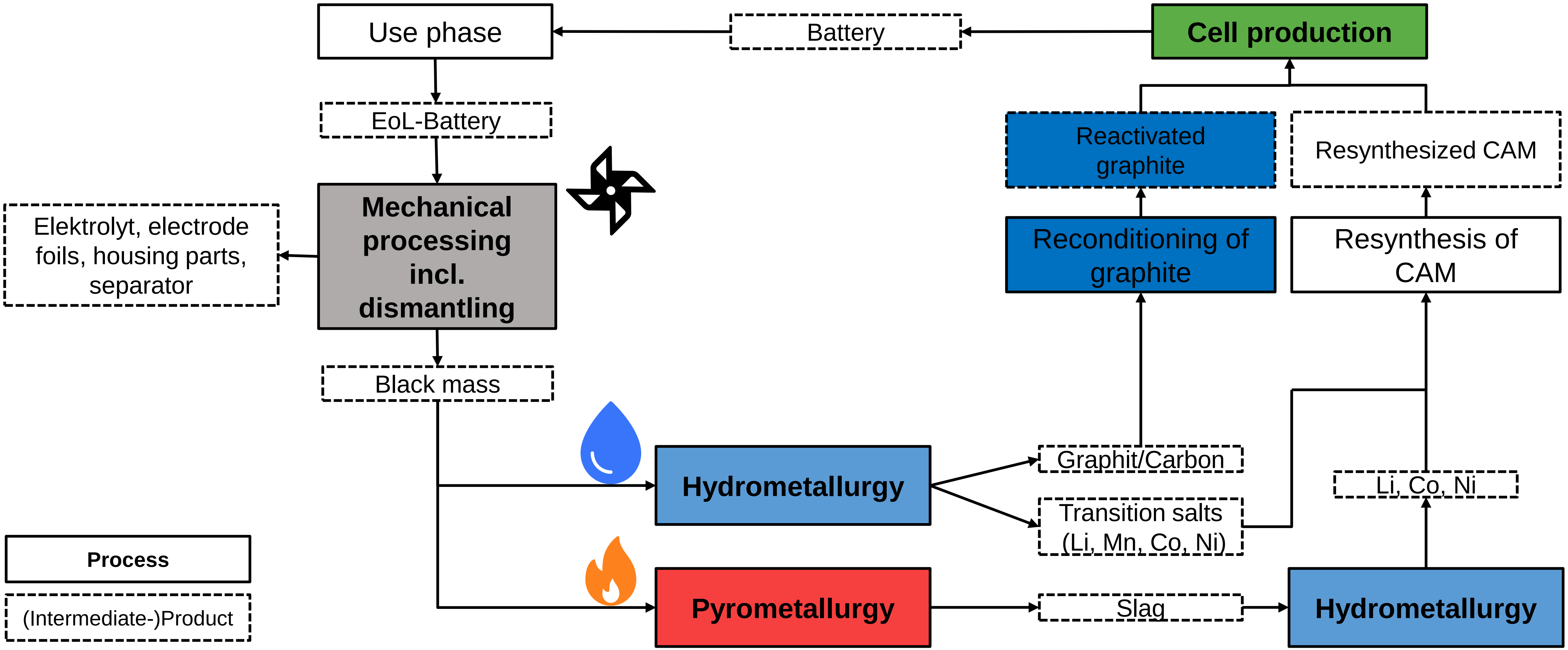
Mechanical Recycling
Shredder-Dryer-Combination





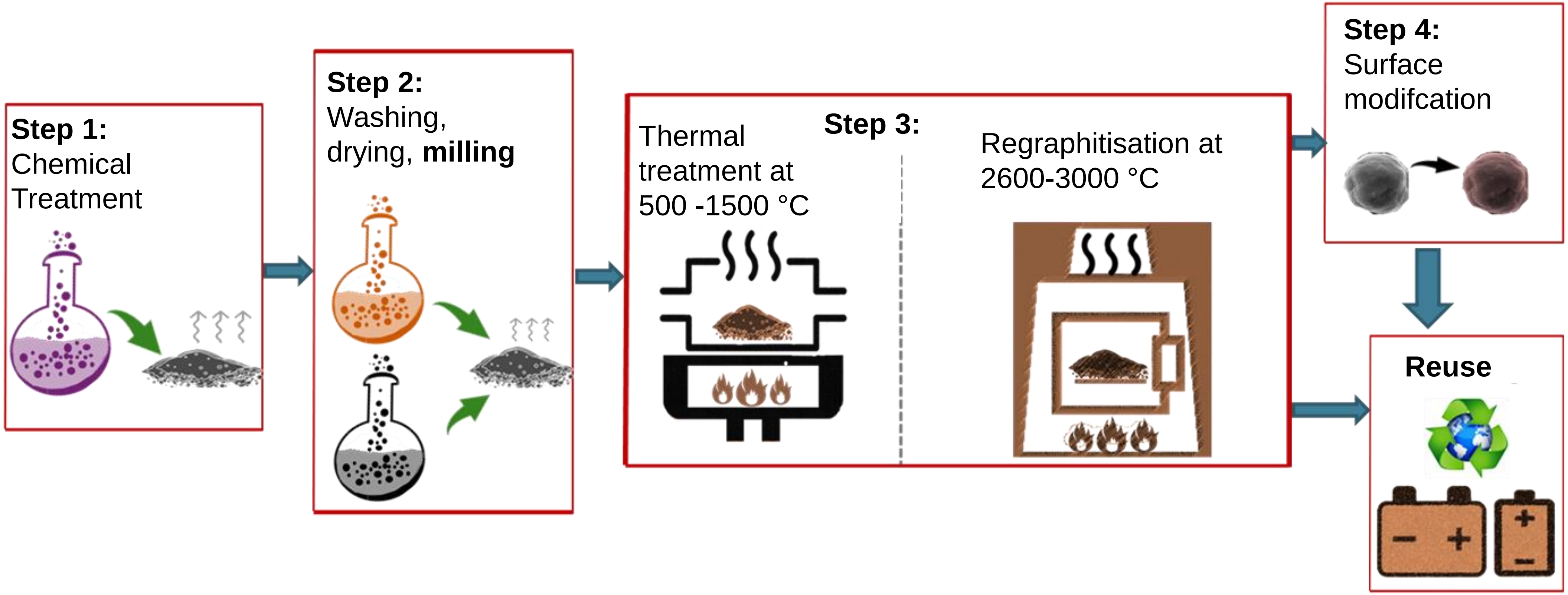
Circular battery cell production

Future closed material cylces



Recycling Technologies
Reconditioning of graphite

- Large-scale recycling processes use graphite as a reducing agent in the thermal recycling of transition metals
- So far no industrially established processes for reconditioning graphite known

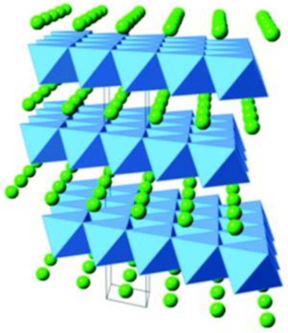


https://iopscience.iop.org/article/10.1149/2.0271701jes

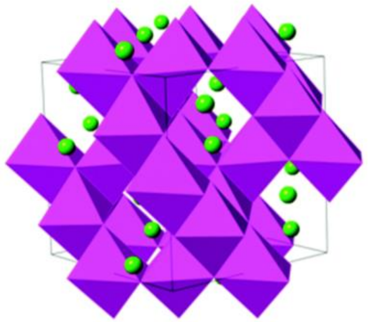
Content

Active materials for the cathode

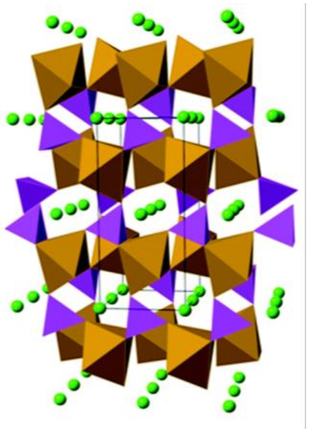
- **Lithium metal oxides** with morphology of **layered oxide**
  - $LiCoO_2$
  - $LiNMO_2$ (N, M = Ni, Co, Mn in different amounts N + M = 1)
    - e.g. **$LiNiMnCoO_2$** (NMC 111, NMC 622, NMC 811)
    - e.g. **$LiNiCoAlO_2$** (NCA)



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

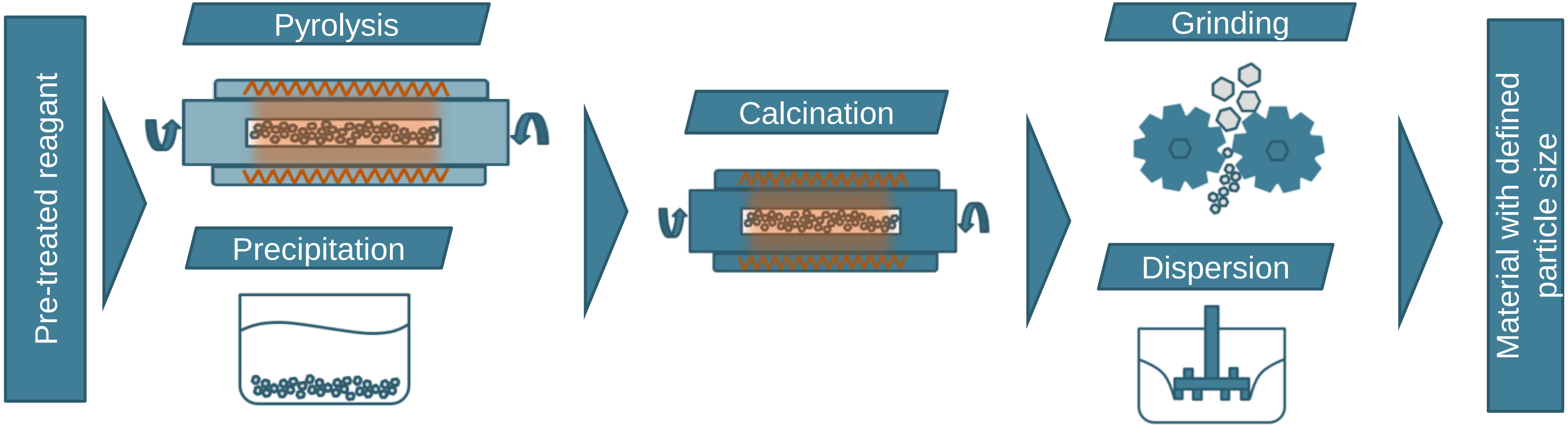


- **Lithium metal phosphates**
  - $LiMPO_4$ (M = Fe, Co, Ni, Mn) e.g. **$LiFePO_4$**

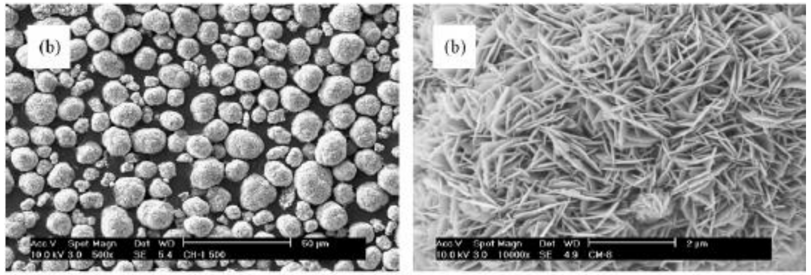


https://www.sciencedirect.com/science/article/pii/S1369702114004118?via%3Dihub

Synthesis of cathode active material

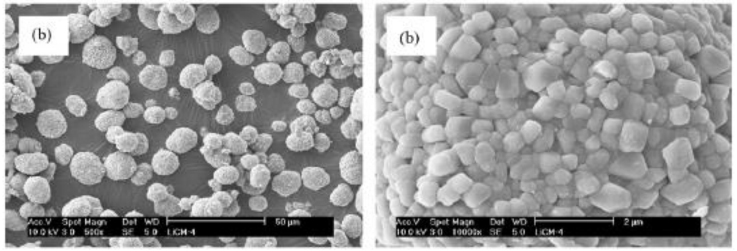


NMC Precursor after precipitation



[1]

NMC after calcination



[1]

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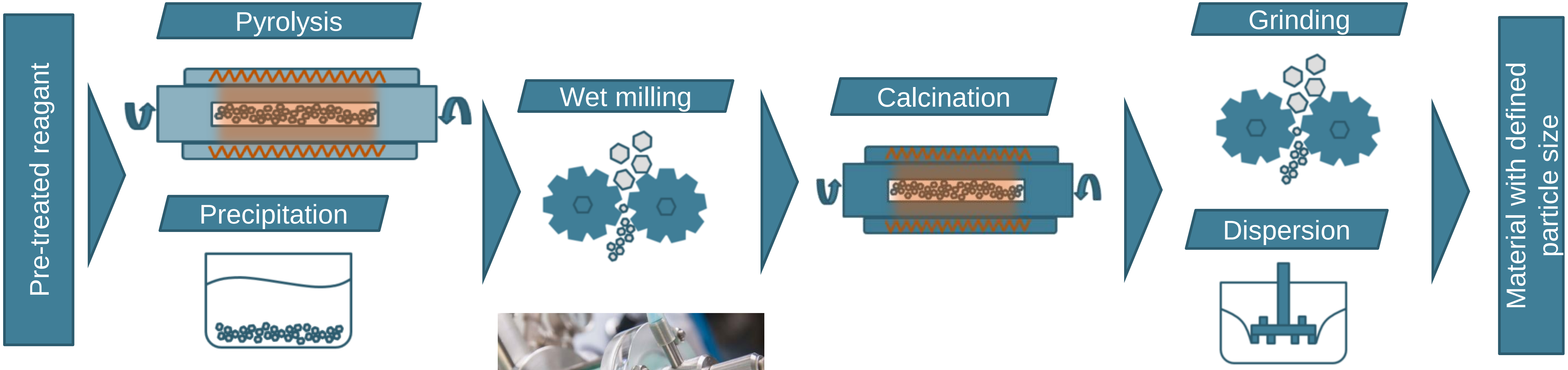
[1] K.K. Cheralathan et al. / Journal of Power Sources *195 (2010) 1486–1494*

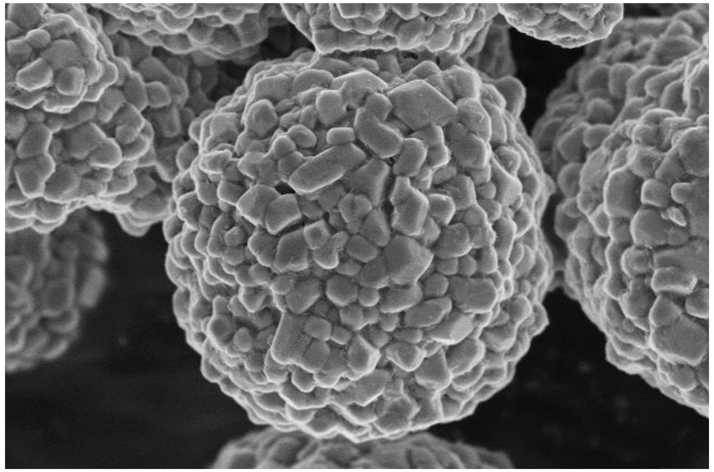
Optional milling of precursor



[1] K.K. Cheralathan et al. / Journal of Power Sources *195 (2010) 1486–1494*

Cathode material finishing
Application of classifier mills

- Gentle grinding → just de-aggregation, without particle damage
- Steep particle size distribution
- Avoidance of metal contamination with ceramic execution
- Prevention of moisture absorption in the process with closed loop system
- Applicable products (x_{50} around 10 µm):
  Lithium Cobalt Oxide (LCO)
  Lithium NiCoAl Oxide (NCA)
  Lithium NiCoMn Oxide (NCM)
  Lithium Manganese Oxide (LMO)



Classifier mill

Source: HOSOKAWA ALPINE

Typical anode materials

Material	Energy density	Power density	Stability	Safety	Costs
Synthetic graphite	+	○	+	+	+
Natural graphite	+	○	+	+	++
Amorphous carbon / Hard Carbon	-	+	-	+	-
LTO $Li_4Ti_5O_{12}$	--	++	++	++	
Si	++	+	--		
Li-metal	++	-	--	--	

http://www.fvee.de/fileadmin/publikationen/Workshopbaende/ws2010-1/ws2010-1_07_WohlfahrtMehrens.pdf)

Processing and spherodization of natural graphite

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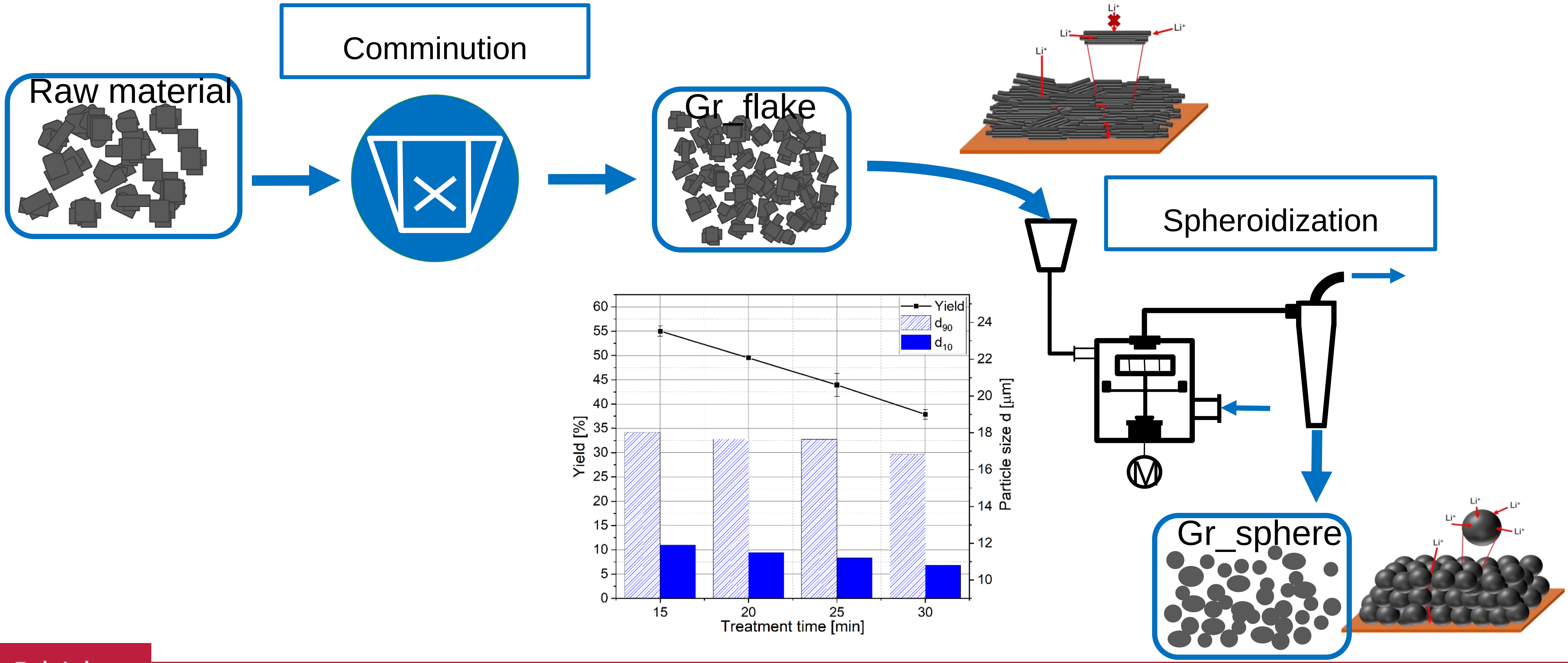

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Fischer, S.; Doose, S.; Müller, J.; Höfels, C.; Kwade, A. Impact of Spheroidization of Natural Graphite on Fast-Charging Capability of Anodes for LIB. *Batteries* **2023**, *9*, 305.

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Results of the spheroidization process

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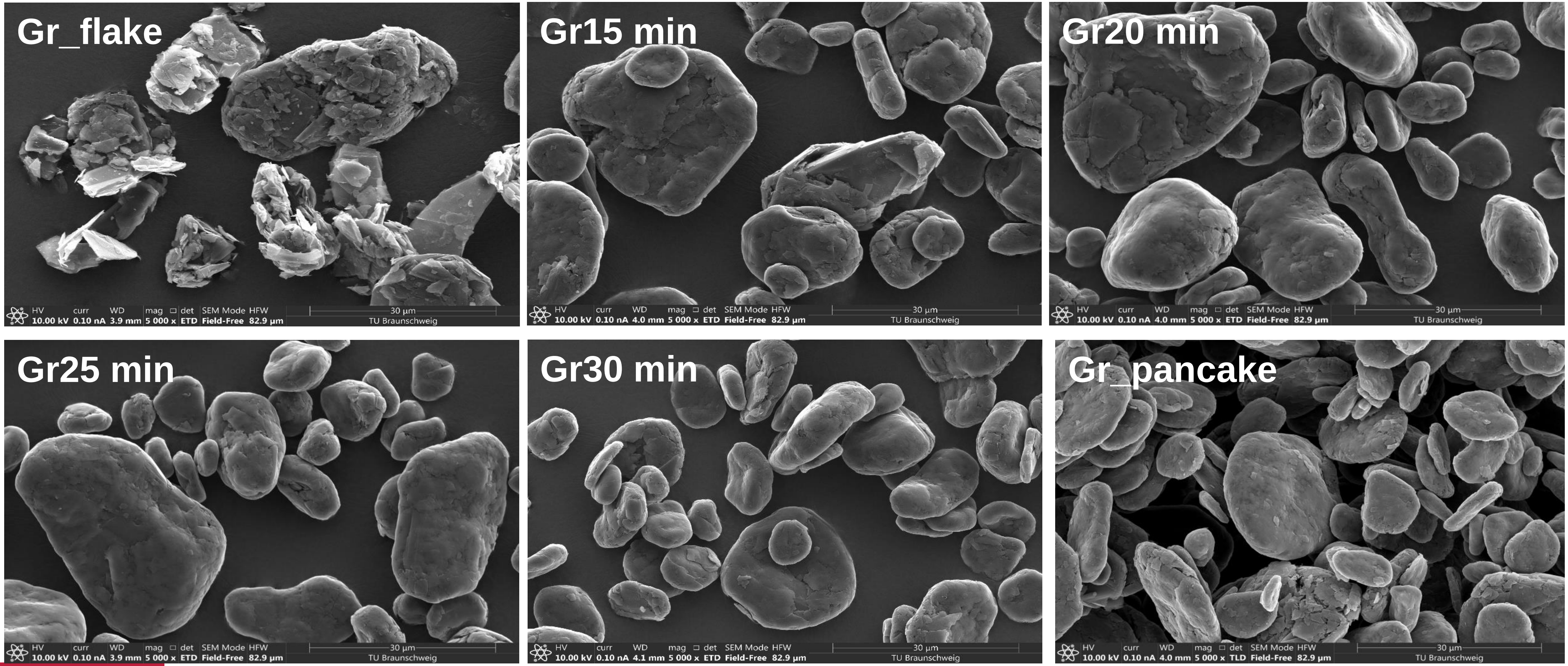

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Fischer, S.; Doose, S.; Müller, J.; Höfels, C.; Kwade, A. Impact of Spheroidization of Natural Graphite on Fast-Charging Capability of Anodes for LIB. *Batteries* **2023**, *9*, 305.

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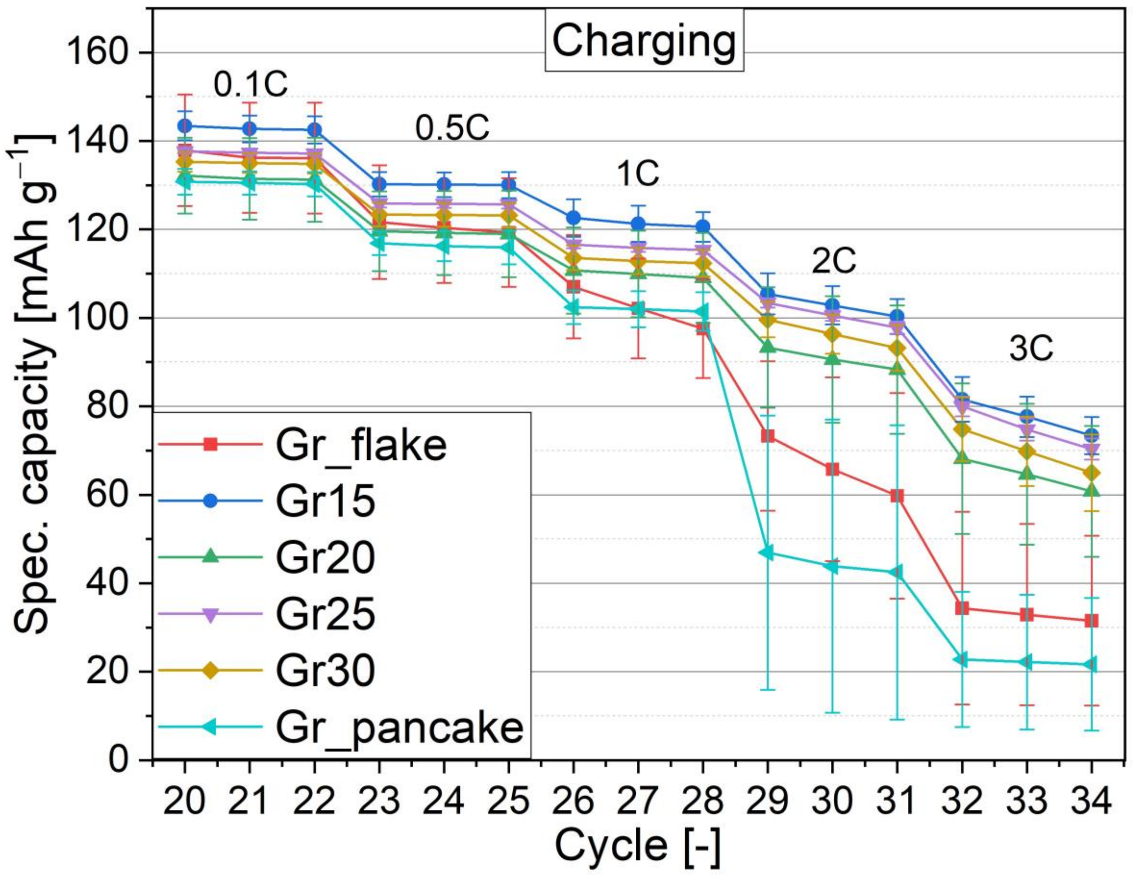
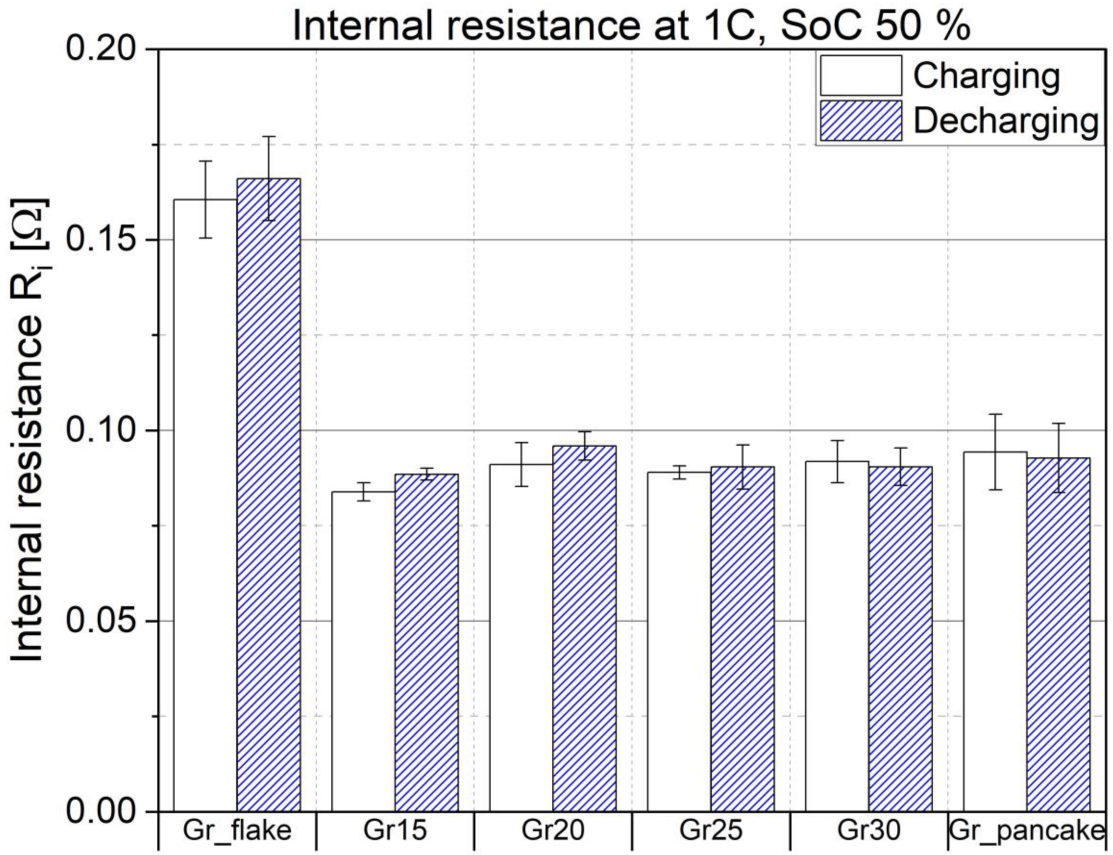
Cycling tests of spheroidized graphite anodes

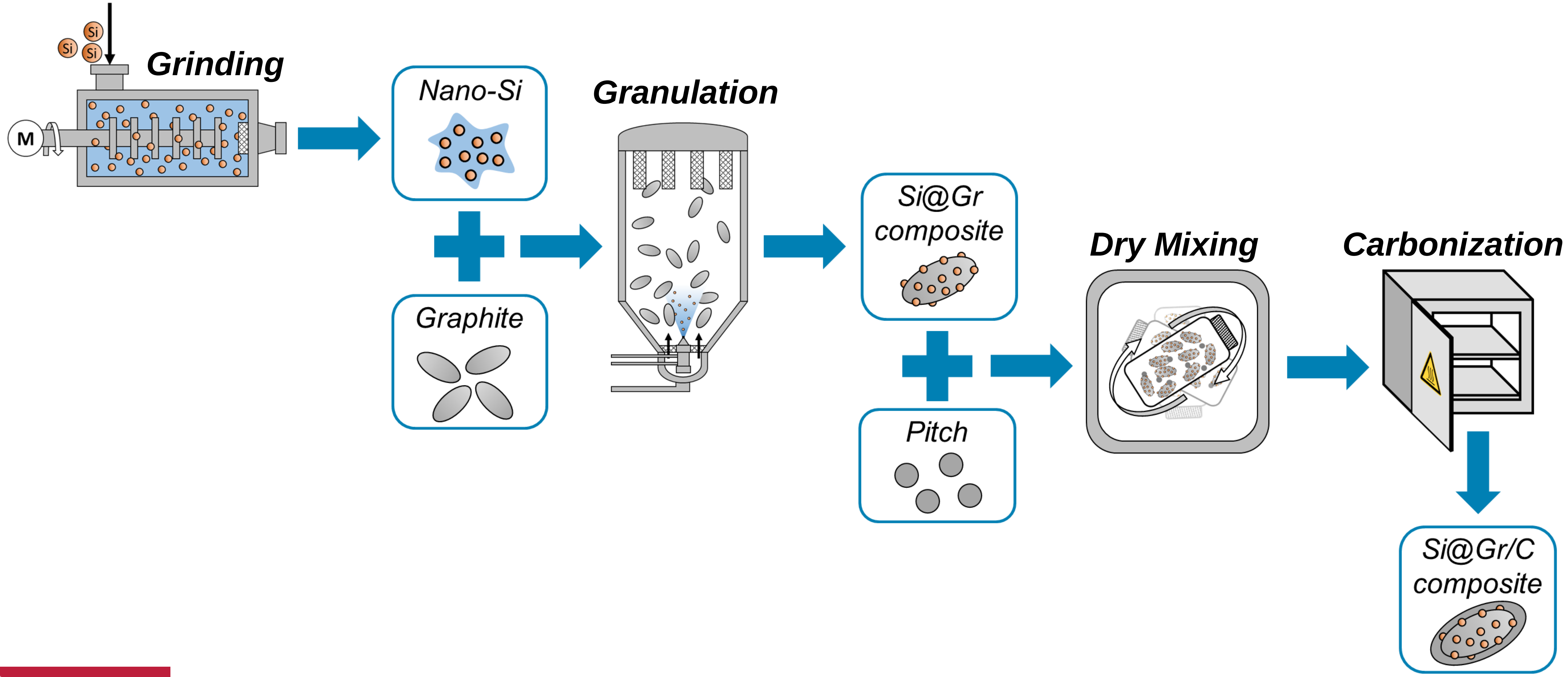




→ Improved electrochemical performance of spheroidized graphite pouch cells

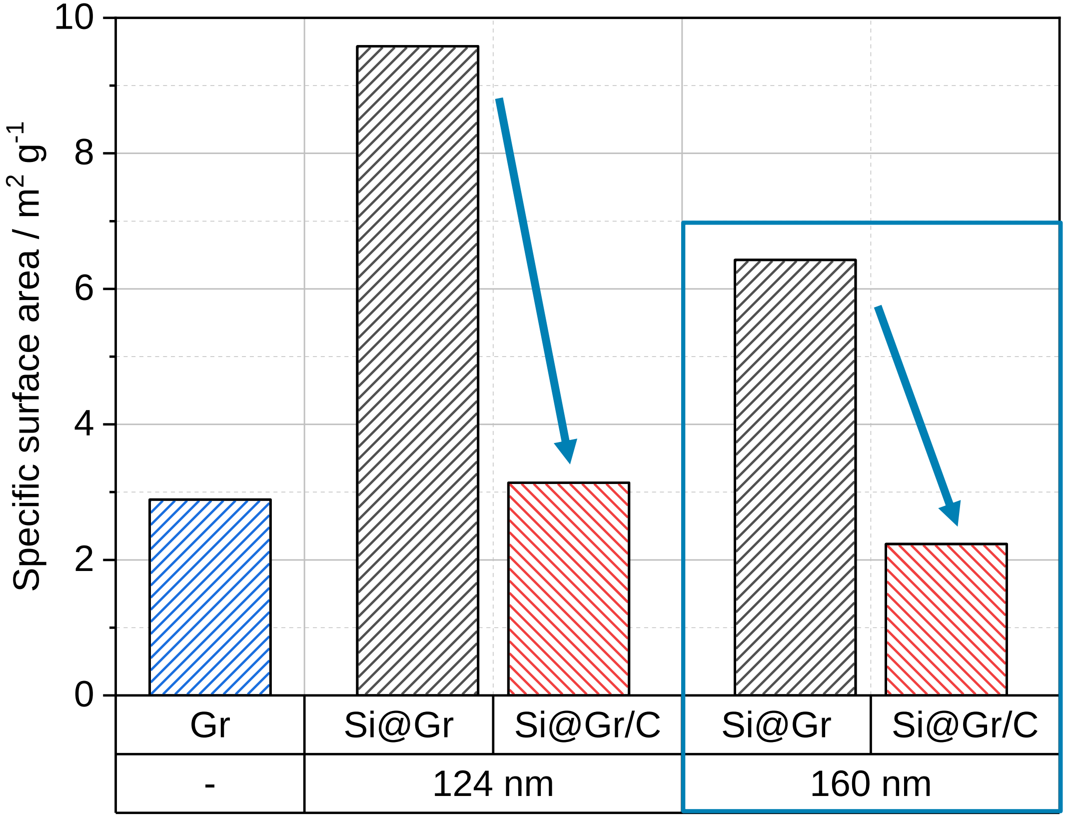
Fischer, S.; Doose, S.; Müller, J.; Höfels, C.; Kwade, A. Impact of Spheroidization of Natural Graphite on Fast-Charging Capability of Anodes for LIB. *Batteries* **2023**, *9*, 305.

Methodology
Preparation of Si@Gr/C composites

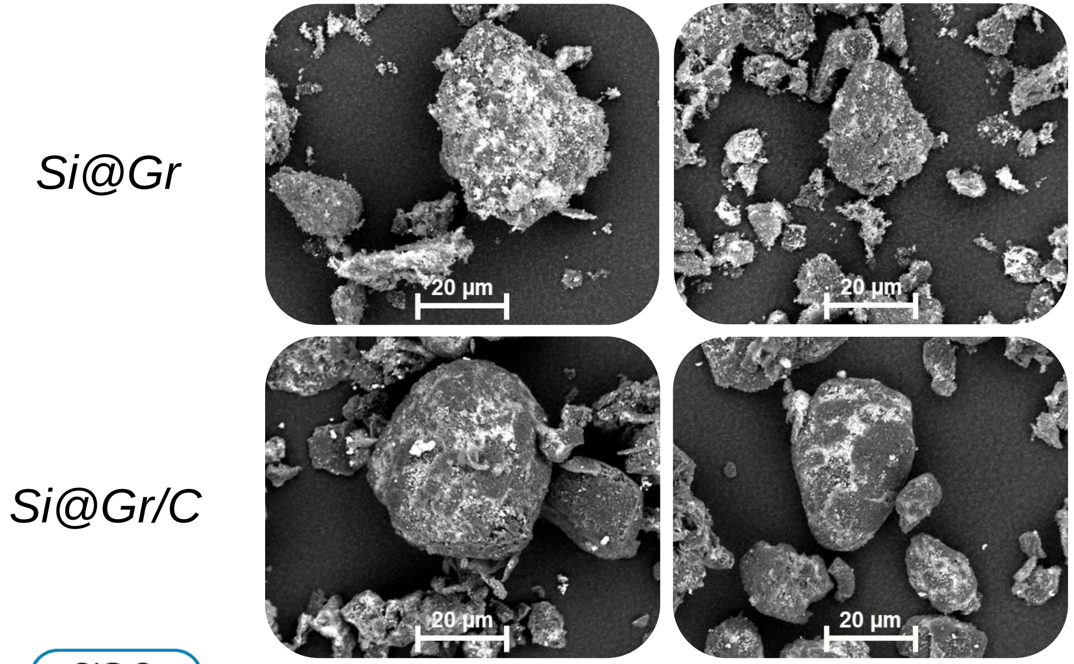


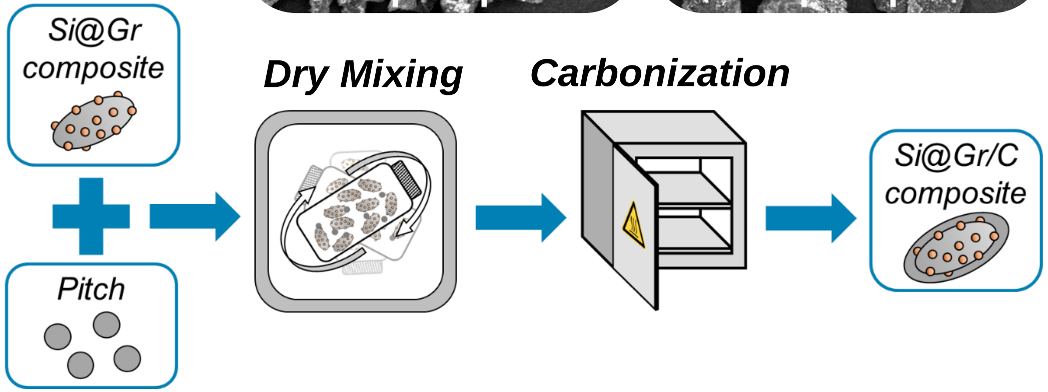
10.14356/kona.2023006
https://www.sciencedirect.com/science/article/pii/S0378775322009788 ;
https://www.mdpi.com/2313-0105/9/7/377

Preparation of Si@Gr/C composites
Specific surface area – Pitch coating



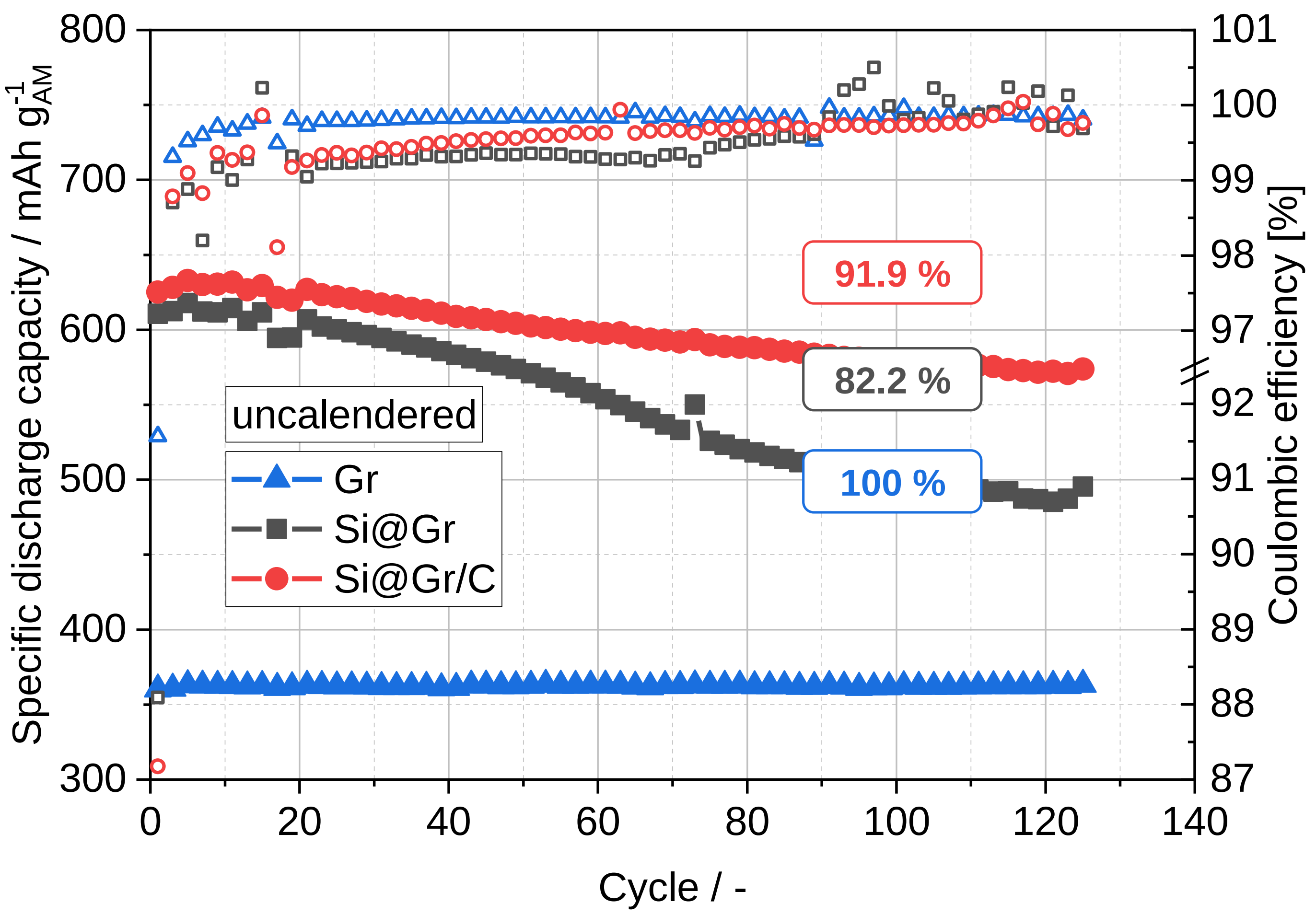
- Pitch coating decreases specific surface area





Electrochemical performance

Influcence of pitch coating (*Gr vs. Si@Gr vs. Si@Gr/C*)



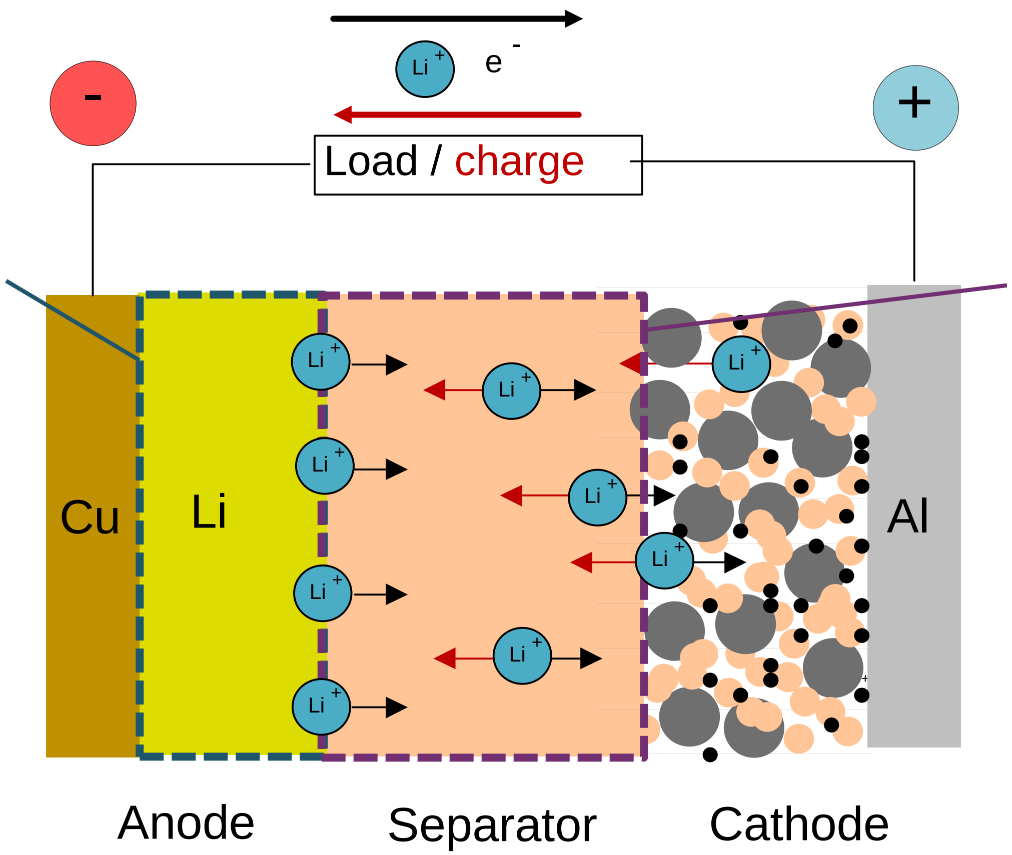
Cycling protocoll

Half-cell cycled against Li-Ref.

Lithiation:	0.1C CCCV
Delithiation:	0.3C CC
Voltage window:	0.01 - 0.9 V

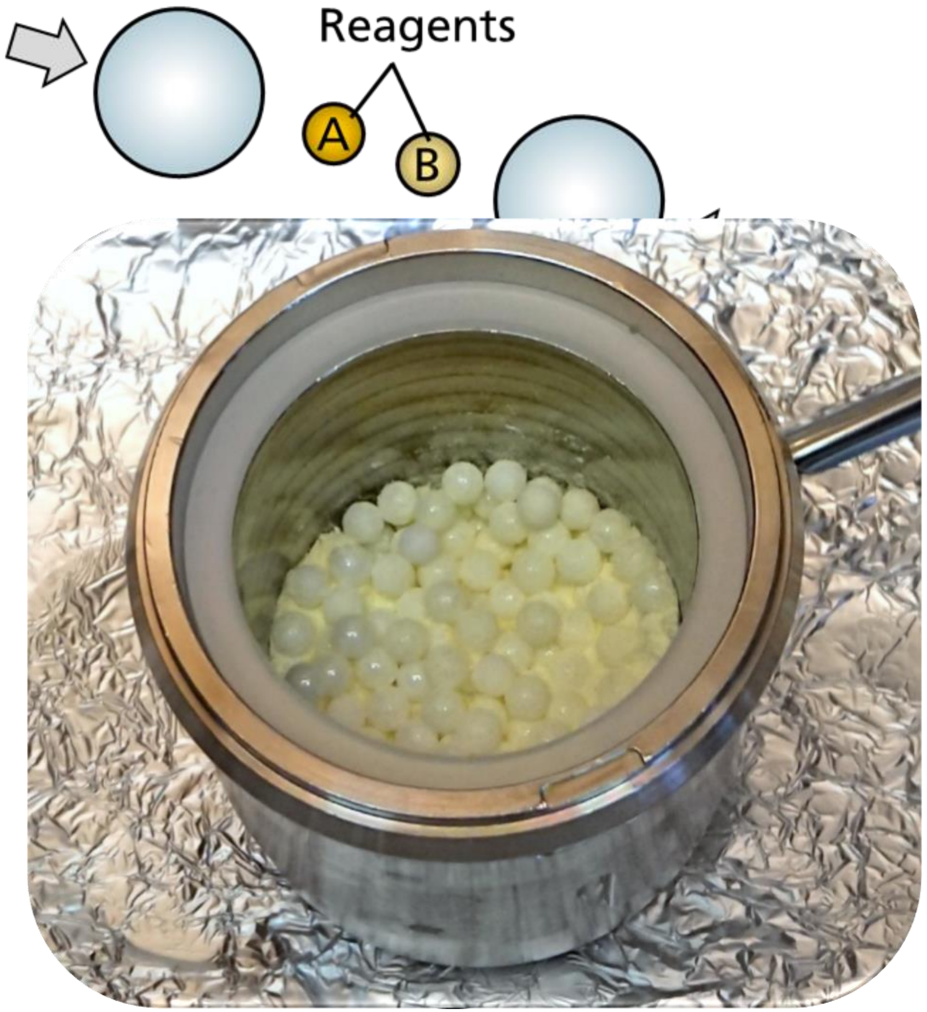
Solid electrolytes for solid state batteries

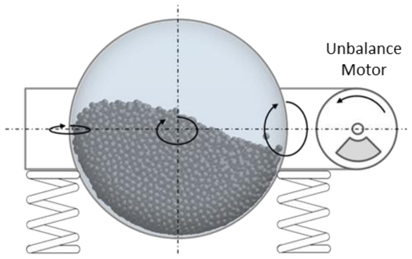
- Within lithium ion solid state batteries
  - the graphite or graphite/Si anode is replaced by a **lithium foil** or other lithium structure
  - the polymer separator is replaced by a very **dense layer of solid particles**
  - the liquid electrolyte is replaced by a **solid particulate electrolyte**
- Three different solid electrolytes and combinations of them are investigated
  - Oxides (e.g. LATP, LLZO)
  - Sulfides (e.g. Thiophospates)
  - Polymers (e.g. PEO)

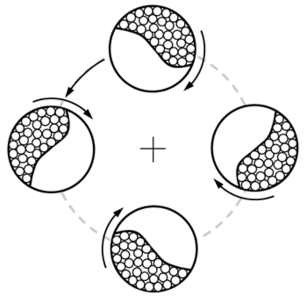


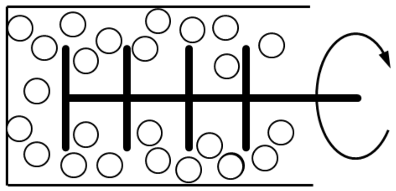
Solid electrolyte

- Stoichiometrical formulation of reagents
  - Sulfides: e.g. $xLi_2S + xP_2S_5 \rightarrow Li_xP_xS_x$
  - Oxides: e.g. LLZO, activation by ball milling + calcination
- Chemical reactions are inititated by kinetic energy of media-particle collision events
- Synthesis can be performed under dry or wet conditions







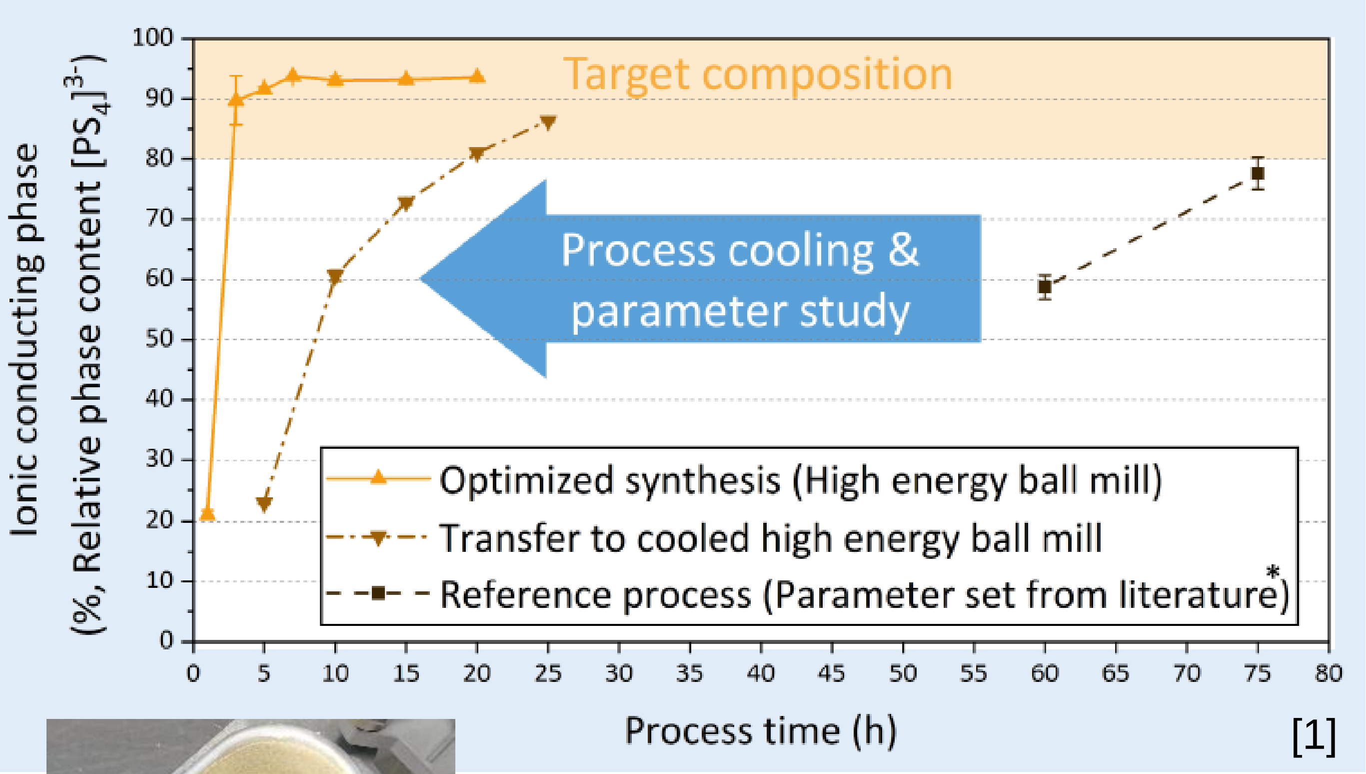


Development of a Scalable Synthesis Route for Sulfide SE

iPAT Institut für Partikeltechnik

Mechanochemical synthesis in high-energy ball mills

- Characterization of synthesis progress by Raman spectroscopy
- Process parameters (rotational speed, grinding media size) strongly influence process yield and product structure
- Reduction of process time from > 75 h to < 5 h by process cooling and parameter optimization
- Transfer of process to scalable and continuous ball mill



[1]

[1]

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[1] Hofer, M. Grube, M., Michalowski, P. Zellmer, S. Kwade, A., Effect of process parameters on the mechanochemical synthesis of Li3PS4 in a high energy ball mill, 2022, Advanced powder technology, under review

[2] Schlem, R., … Kwade, A., Zeier, W., Energy Storage Materials for Solid State Batteries: Design by Mechanochemistry, 2021, Advanced Energy Materials, 11 (30)

BATTERY LABFACTORY BRAUNSCHWEIG

Content

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Process Chain Battery Cell Manufacturing

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Electrode-production

Material → Pretreatment and Mixing → Coating and Drying → Calendering

Cell-production

Cutting and Drying → Packaging → Contacting → Enclosure and Welding

Cell-conditioning

Filling → Formation and Ageing → Electrochemical Quality Control → Cells

Process chain of electrode production

Particle sizes
Electr. resistance

dry mixing → wet dispersing → coating and drying → calendering → Pouch cells

Particle size
Viscosity

Pore network structure
Electrical resistance
Adhesion force

Capacity
C-rate capability

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

Process chain of electrode production

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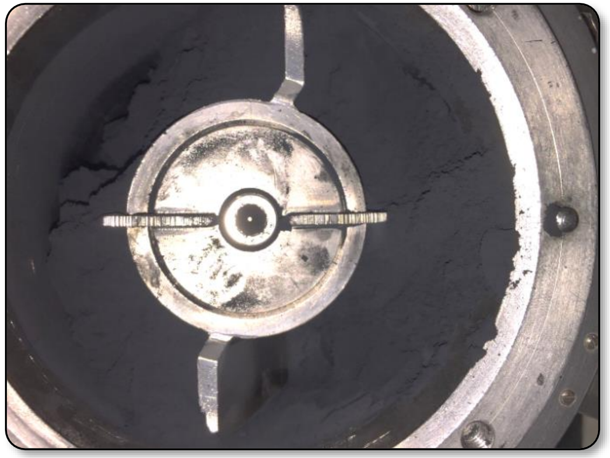
Dry mixing in electrode production

Raw materials:

- Active material
- Conductivity additive
- (binder)

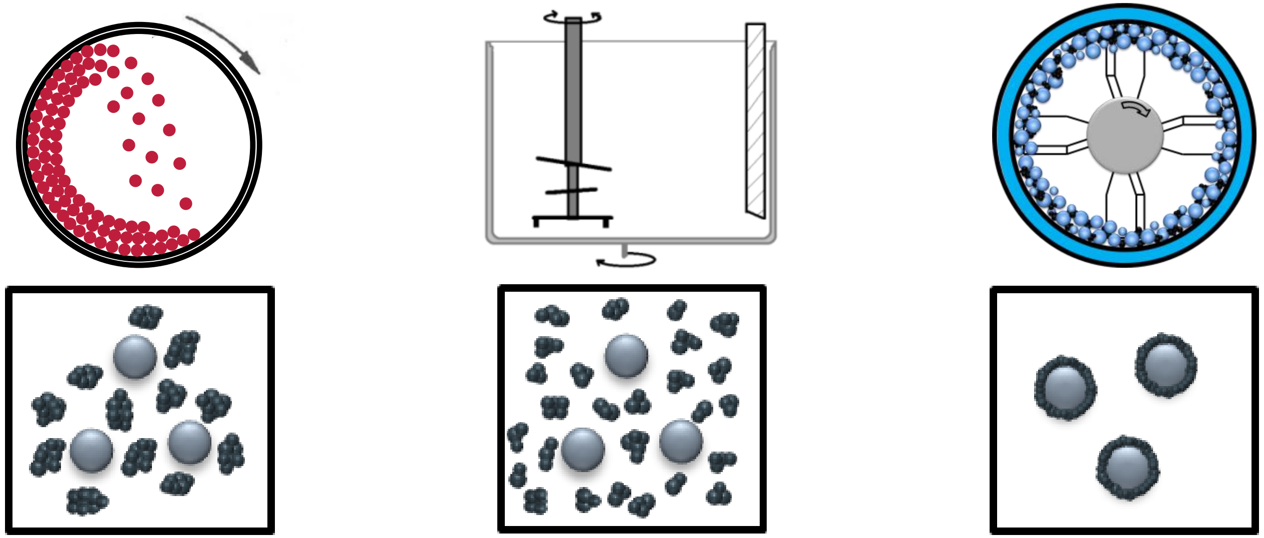
Product:

Dry powder mixture

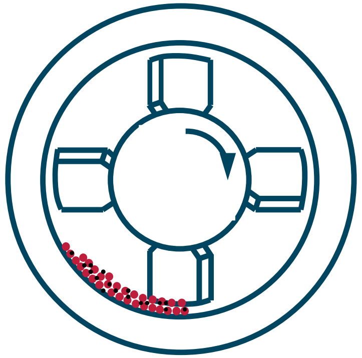


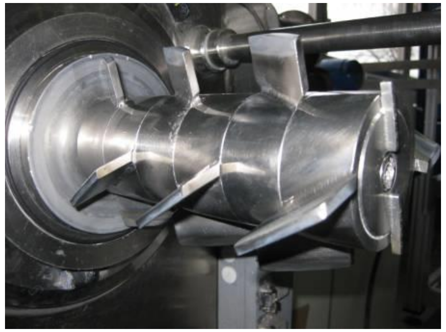
Target:

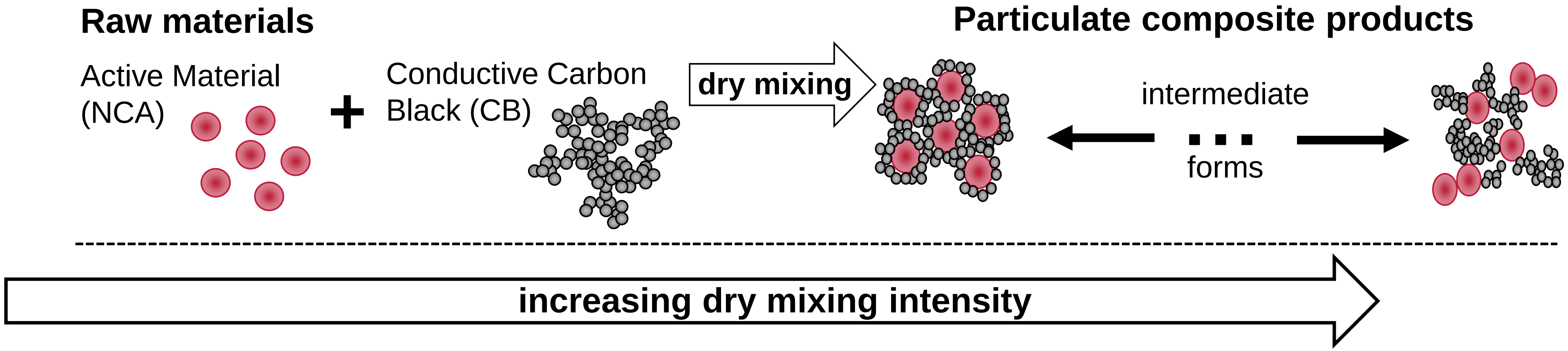
- Homogenization and structuring of active material and conductive carbon black as well as the carbon black-binder matrix (composite formation).
- Adjustment of the agglomerate size of conductive carbon black
- Influencing the pore structure

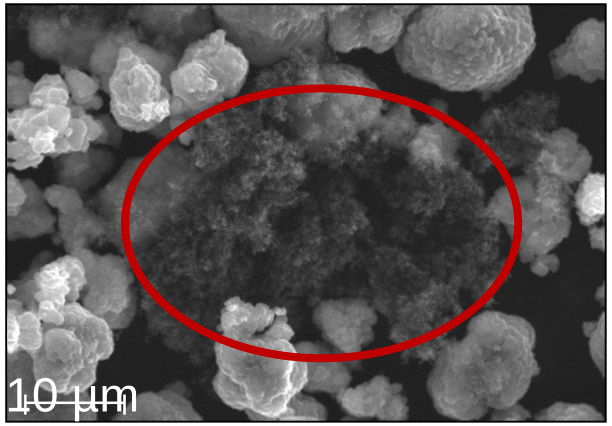


Dry Mixing Process
CB Agglomerate Size, Structure and Distribution



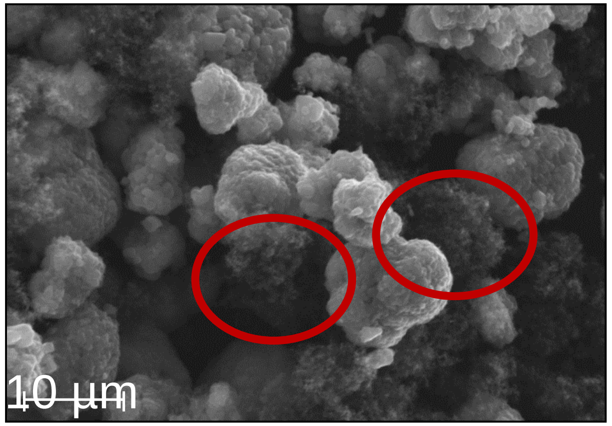






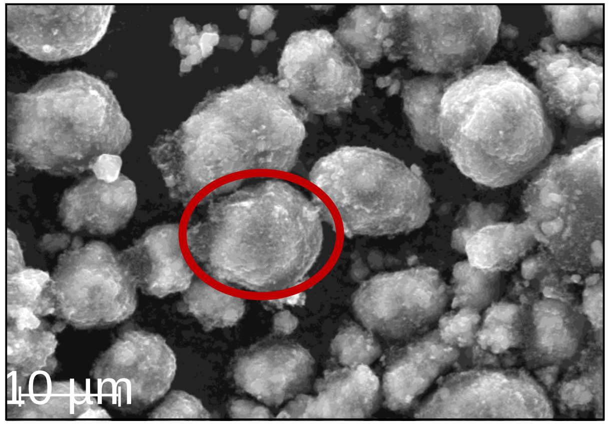
Rotary Drum Mixer

big CB agglomerates



Eirich Intensive Mixer / Planetray Mixer

small CB agglomerates



Nobilta – High Energy Mixing

CB attached to AM surfaces

H. Bockholt et. al. (2016) *Powder Technology* 297, pp. 266-274

Process chain of electrode production

Particle sizes
Electr. resistance

dry mixing → wet dispersing → coating and drying → calendering → Pouch cells

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Process chain of electrode production

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Particle sizes
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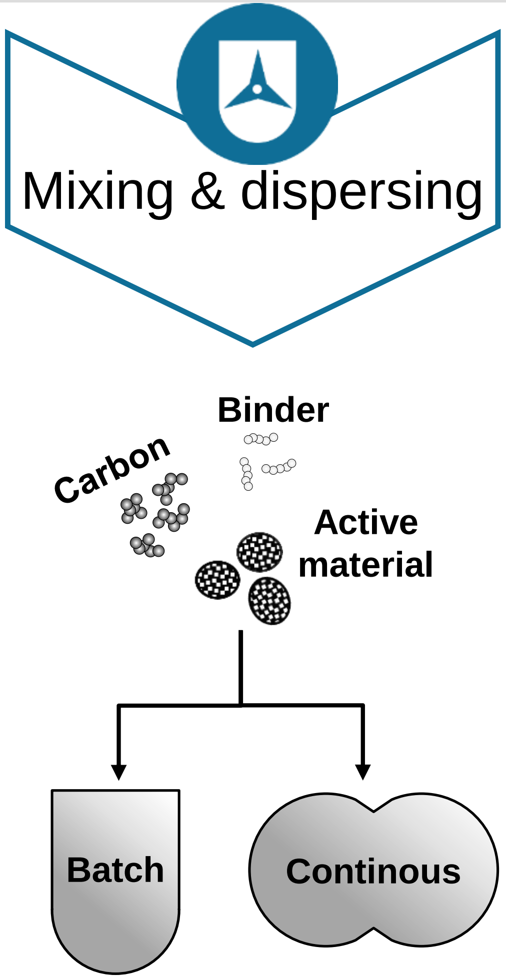
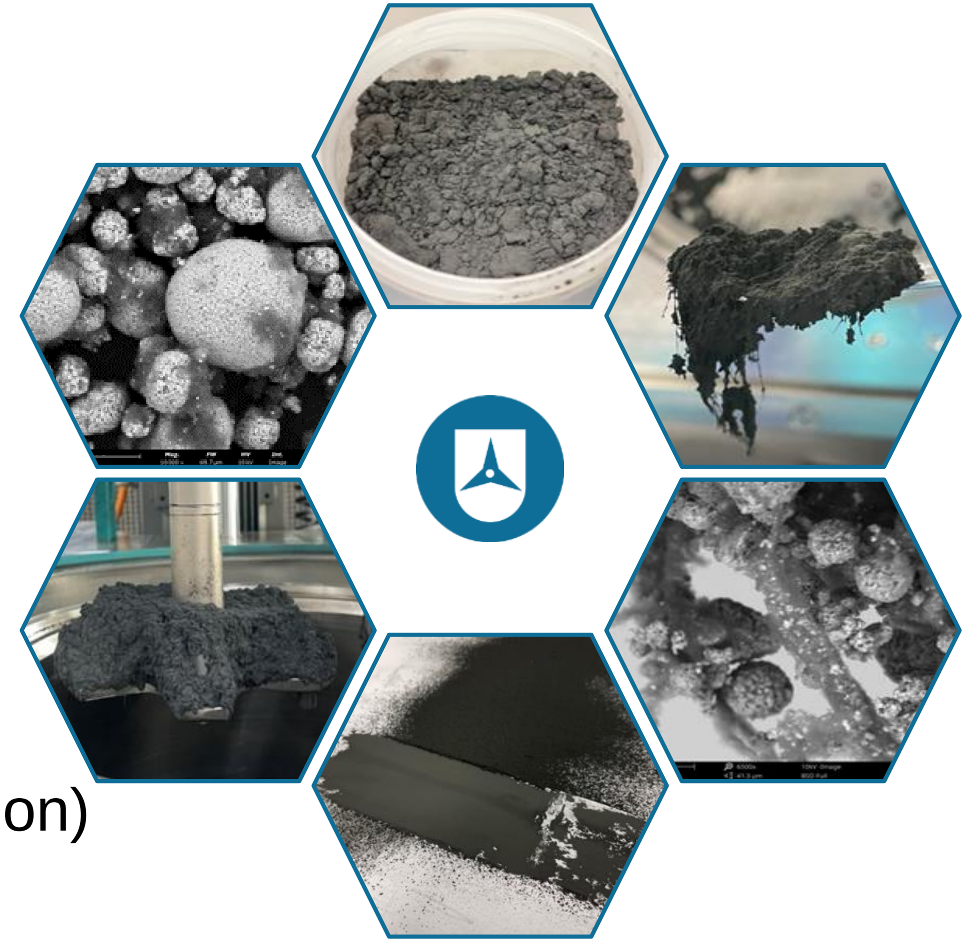
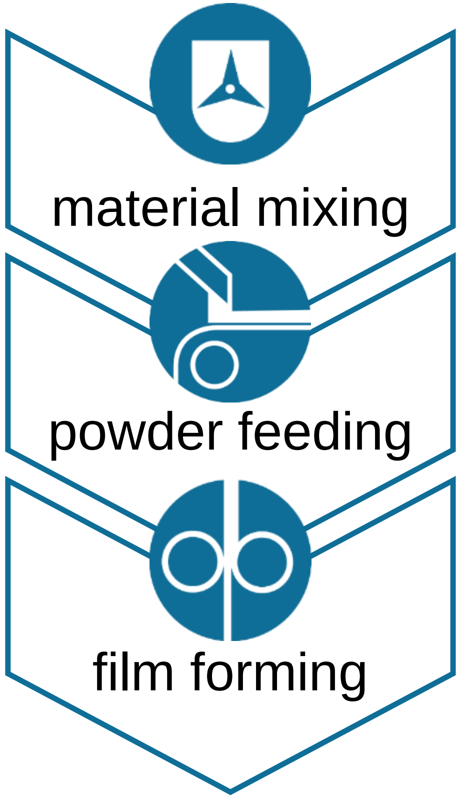
Powder mixing



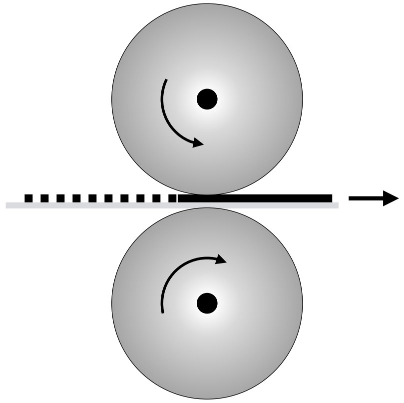
- Identifying and producing proper powder structures:
  - ➢ Homogeneity
  - ➢ Binder fibrillation/ dispersing
  - ➢ Carbon Black structuring
  - ➢ Agglomerate size
- Crucial effect on dry coating (powder application & film formation)



Continuous film forming, densification and lamination

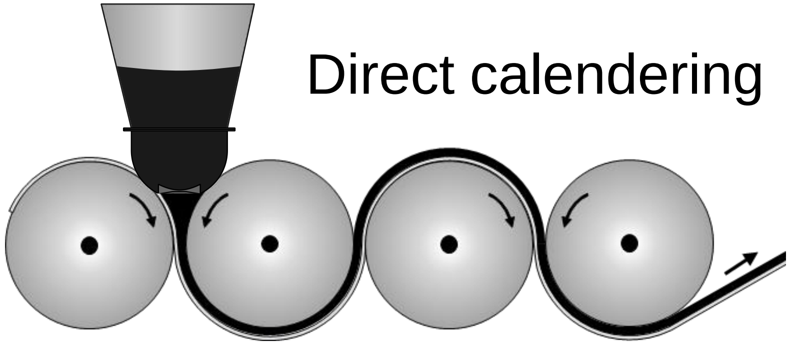


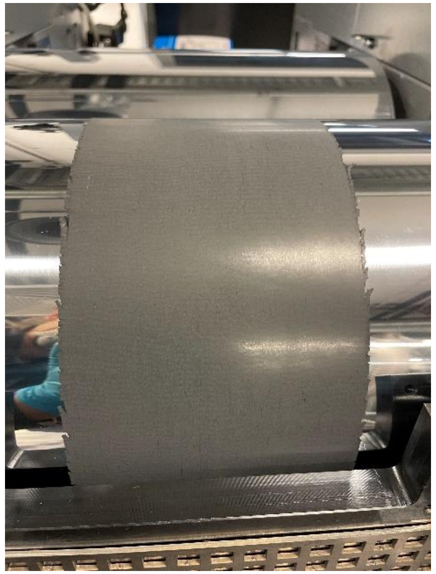
Two-roll calender

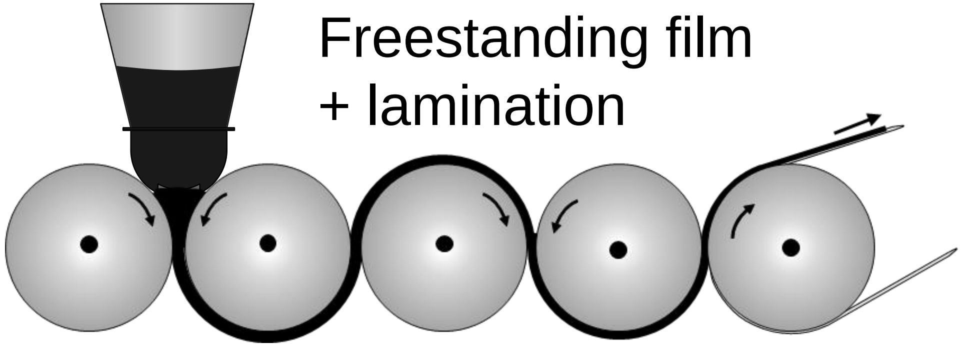


After pre-metered (sieve, chute, needle roller) application or electrostatic application

Multi-roll calender



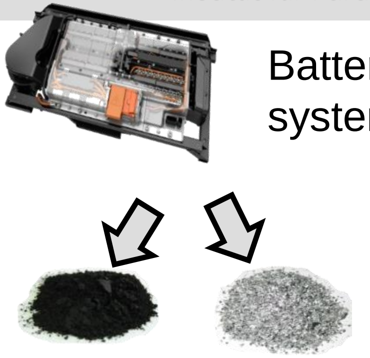




Content

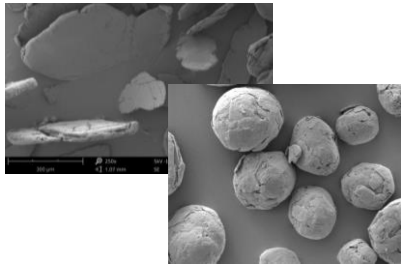
Conclusions

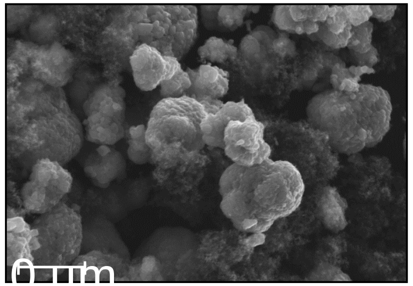
Future of milling and classification processes for energy storage materials



Battery system

- **Sustainable processes** are very important in minerals processing to fulfill environmental goals of car manufacturer (e.g. CO_2 footprint)
- In the future **recycling of production scrap and spent batteries** is very important to secure material delivery and close material cylce
- Milling processes are very important for **cathode and anode material production**, especially also regarding later electrochemical performance
- **Mechanchemical synthesis** has high potential in production of future energy storage materials like solid electrolytes and
- **Dispersing of conductivity additives** is very decisive for later battery performance - semi-continuous and continuous processes are the future
- **Mixing und dispersing** are crucial for dry electrode processing





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PhD-students and co-workers,

https://www.mdpi.com/2313-0105/9/7/377

… for your attention

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