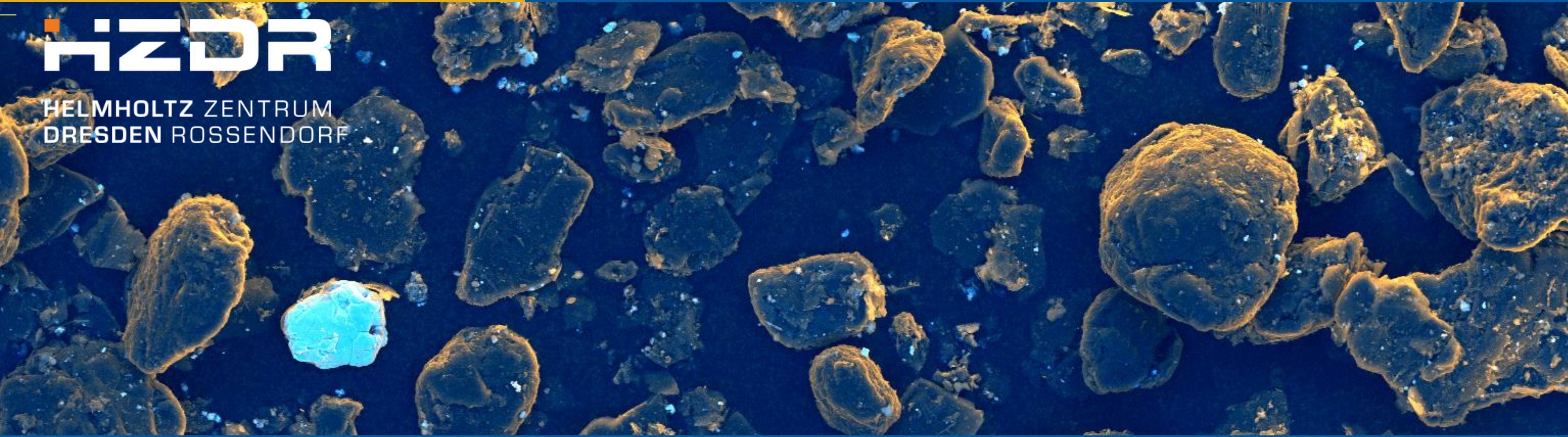


HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF

Recovery of spheroidized graphite from spent lithium ion batteries

Anna Vanderbruggen, Martin Rudolph

HELMHOLTZ INSTITUTE FREIBERG FOR RESOURCE TECHNOLOGY

Aalto University

MINERAL RECYCLING FORUM 2020
Pullman Hotel Aachen Quellenhof, 10-11 March 2020

Outline

1. *Motivation: Why recycling graphite?*
2. *Research and objectives*
3. *Black mass characterization*
4. *Flotation: separation graphite/metals*
5. *Results*
6. *Summary and outlooks*

B MeRang
Black Mass Recycling

HELMHOLTZ
RESEARCH FOR GRAND CHALLENGES

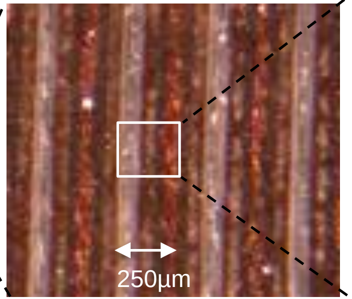
HiF HELMHOLTZ INSTITUTE FREIBERG FOR RESOURCE TECHNOLOGY

Motivation

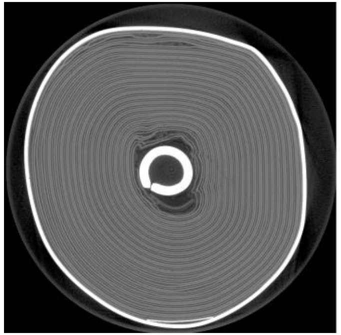
Pyrolysed battery Vertical cross section

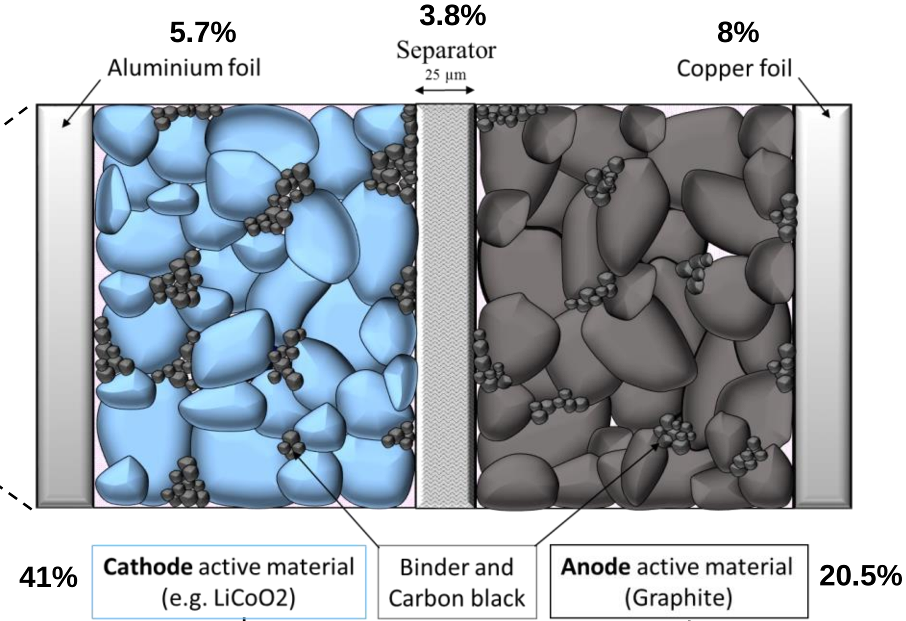
2 cm

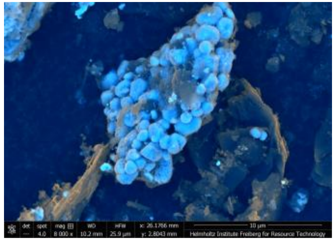
Zoom electrodes



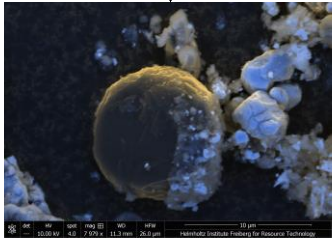
Horizontal cross section



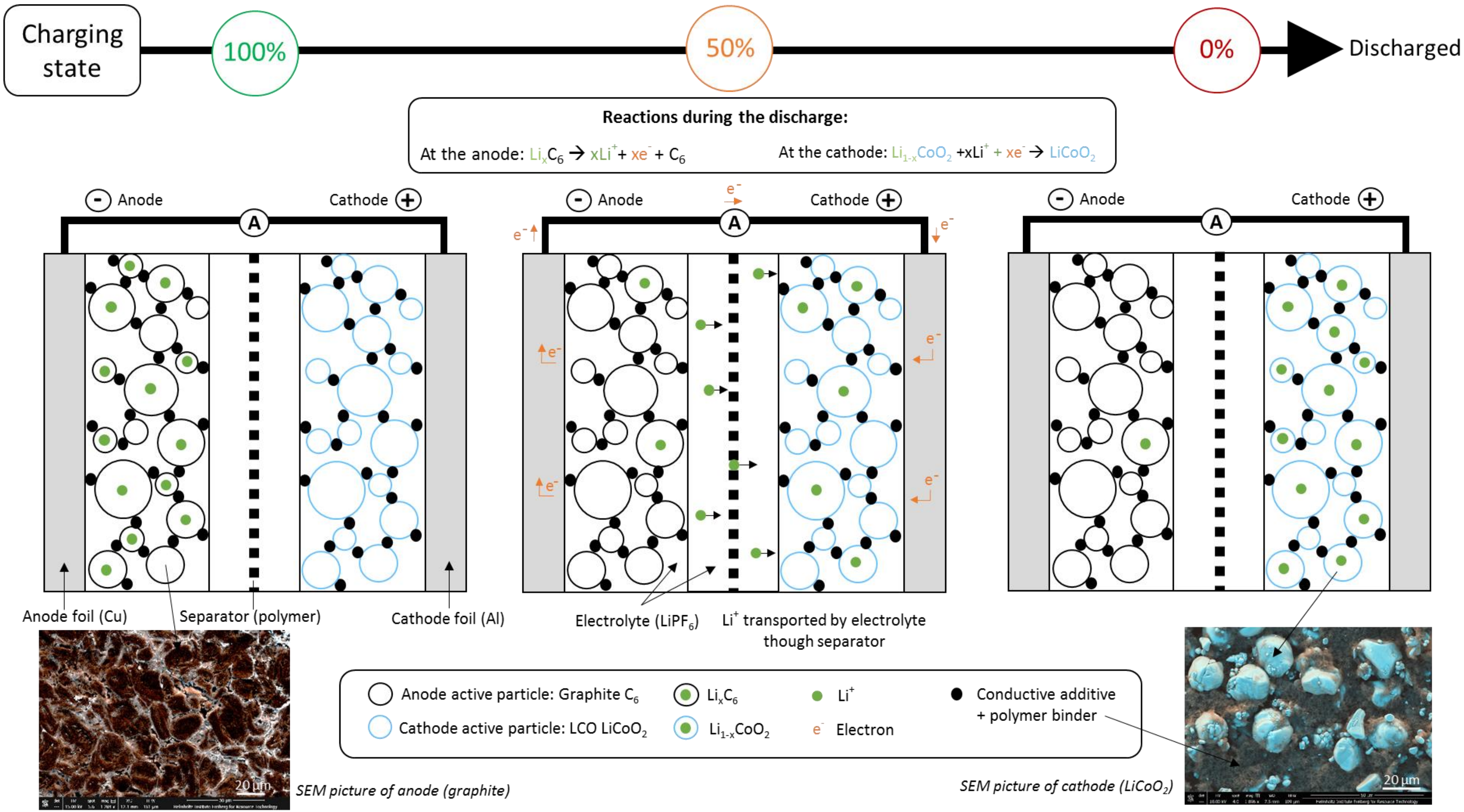




10 µm

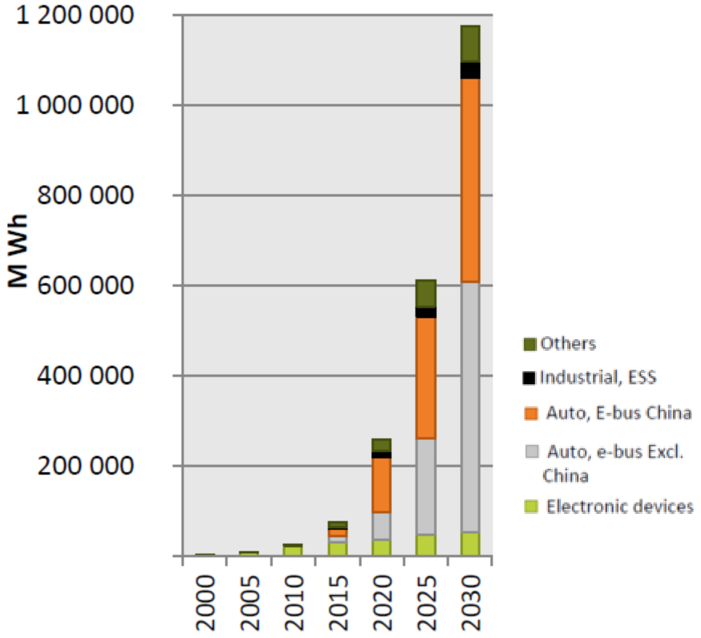


10 µm

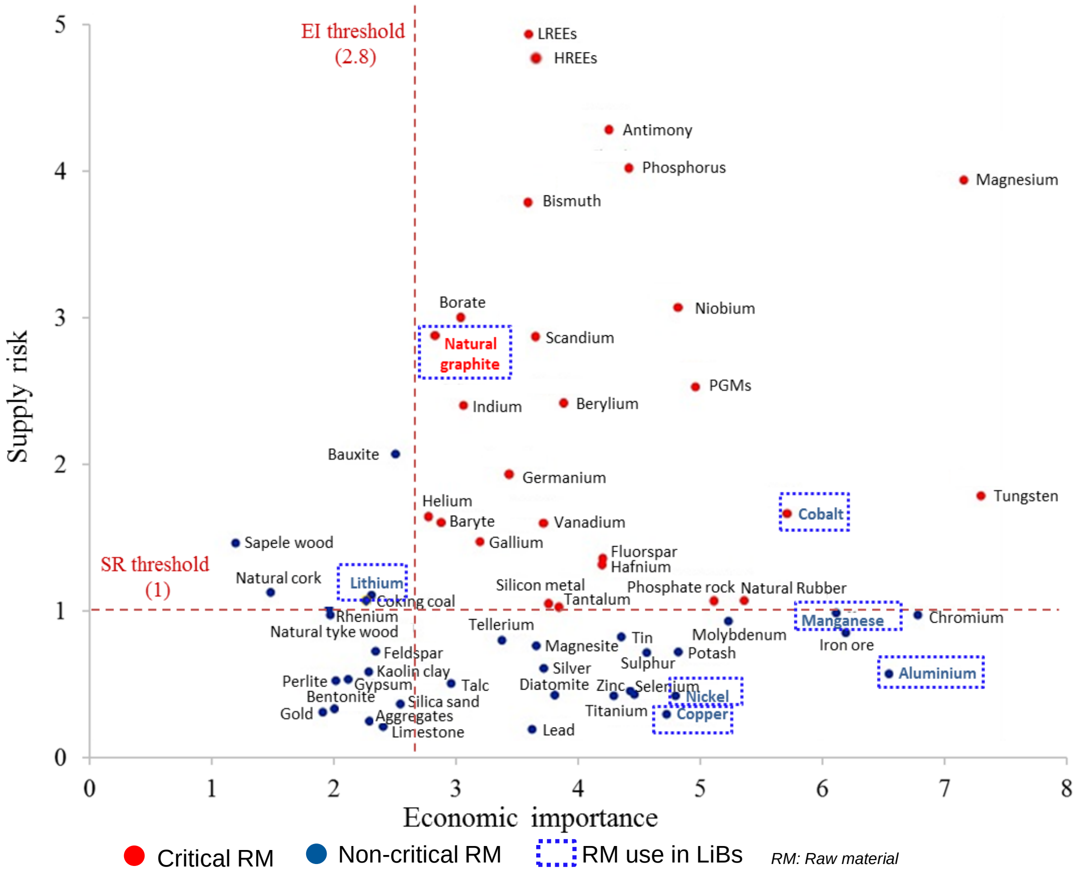

Charging state
100%
50%
0%
Discharged
Reactions during the discharge:
At the anode: LixC6 → xLi+ + xe- + C6
At the cathode: Li1-xCoO2 +xLi+ + xe- → LiCoO2
Anode
Cathode
A
e-
Anode foil (Cu)
Separator (polymer)
Cathode foil (Al)
Electrolyte (LiPF6)
Li+ transported by electrolyte though separator
Anode active particle: Graphite C6
Cathode active particle: LCO LiCoO2
LixC6
Li1-xCoO2
Li+
Electron
Conductive additive + polymer binder
20 µm
SEM picture of anode (graphite)
SEM picture of cathode (LiCoO2)

Motivation

Why recycle LiBs?



Li-ion battery sales, MWh, Worldwide, 2000-2030 (C. Pillot at ICBR 2019, AVICIENNE Energy)



Critical Raw Material CRM from European Commission (EC report, 2018)

Actual recycling processes

Company/Process	Capacity (t/y)	Technology	Main products	Graphite
Accurec GmbH	6 000	Pyro-dominant	Co alloy, Li_2CO_3	Not recovered
Akkuser Ltd	4 000	Pyro-dominant	Metal powder	Remain as fraction of the black mass
Sumitomo-Sony	150	Pyro-dominant	Co alloy, Co metal	Lost during calcination
Umicore	7 000	Pyro-dominant	Ni-Co alloy, $NiCo_3$, $NiSO_4$, $CoCO_3$, $CoSO_4$	Lost, used as a reduction agent
Duesenfeld	4000	Physical and Hydro	Organic carbonates, LiPF6, Fe metal, Cu metal, Al metal, graphite, cathode material	Aiming to recover for LiB purposes
Recupyl	110	Physical and Hydro	Li_2CO_3, Co metal	Filtered off in leaching step
OnTo	Nd	Physical and Hydro-dominant	NMC cathode active material	Aiming to recover for LiB purposes
TOXCO (Retriev)	4 500	Hydro-dominant	Li_2CO_3, mixed metal oxides	Recovered during filtration as MeO-graphite cake

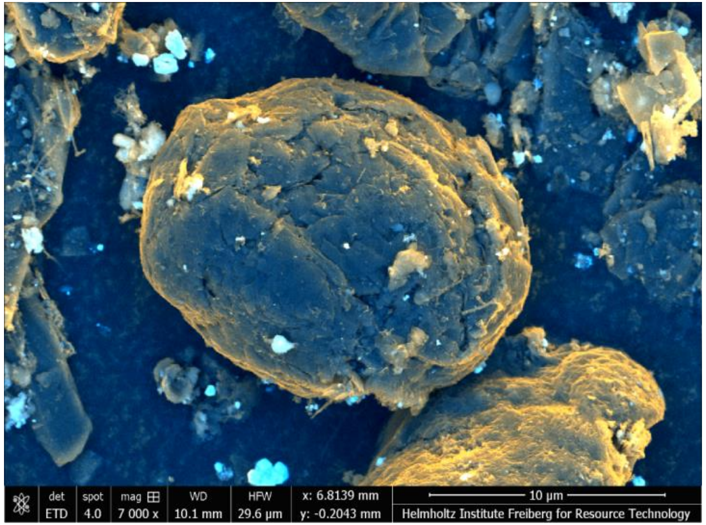
Summary of the actual major LiB recycling process, modified from (Liu et al., 2019) and (Velázquez-Martínez et al., 2019)

Motivation

Why recycle graphite?

- 15-20 wt. % of LiB is graphite
  Usually ending in the process waste!
- Graphite critical raw material in:
  - Europe
  - USA
  - Australia
- Flake graphite production:
  China 69% Europe 3%
- Increase recycling rate of LiB
  Directive 2006/66/EC: 50 wt.%

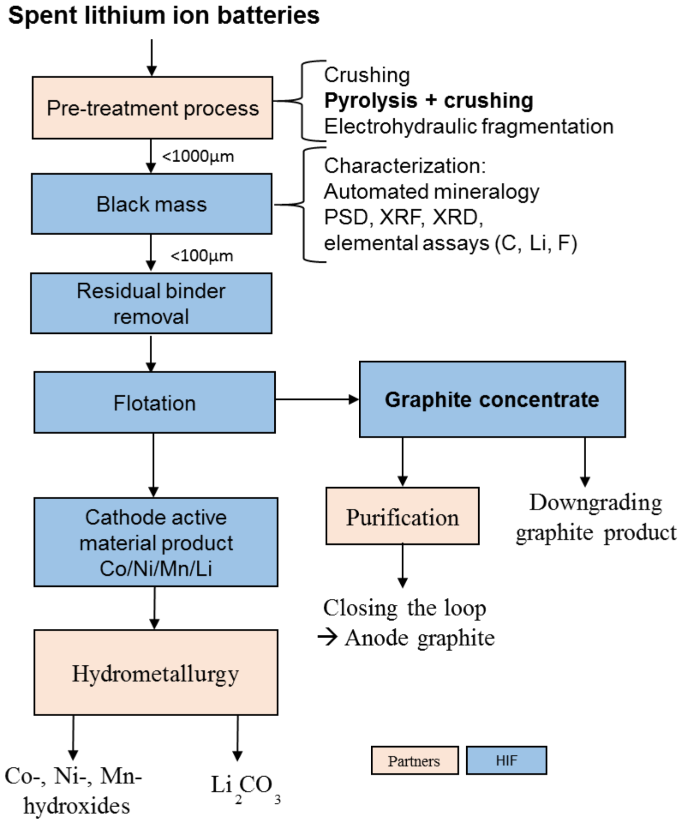
(Hatch, 2016;
Frey, 2018;
CRM reports, 2019)



Spheroidized graphite

- 9000-10000 $/t
- China: 90 % production

BooMeRang project



HELMHOLTZ
RESEARCH FOR GRAND CHALLENGES

BooMeRang
Black Mass Recycling

Research objectives:

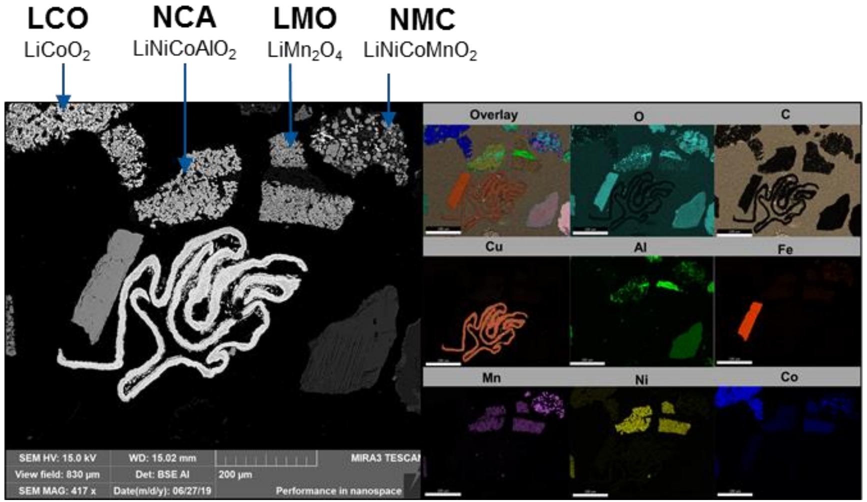
- ➢ Study the influence of different recycling pre-treatment on the electrode active material liberation
- ➢ Recovering spheroidized graphite by froth flotation

Fraunhofer IWKS
Fraunhofer Research Institution for Materials Recycling and Resource Strategies IWKS

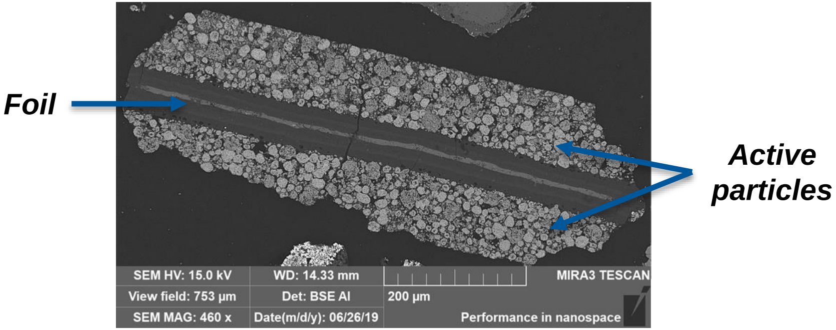
TECHNISCHE UNIVERSITÄT BERGAKADEMIE FREIBERG
Die Ressourcenuniversität. Seit 1765.

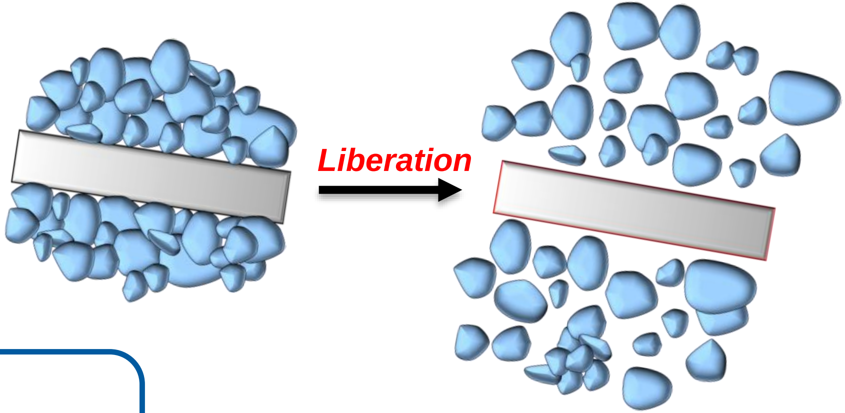
HIF HELMHOLTZ INSTITUTE FREIBERG FOR RESOURCE TECHNOLOGY

Characterization: Black mass



Elemental mapping of coarse fraction of the black mass with hypothesis for cathode active particle chemistry

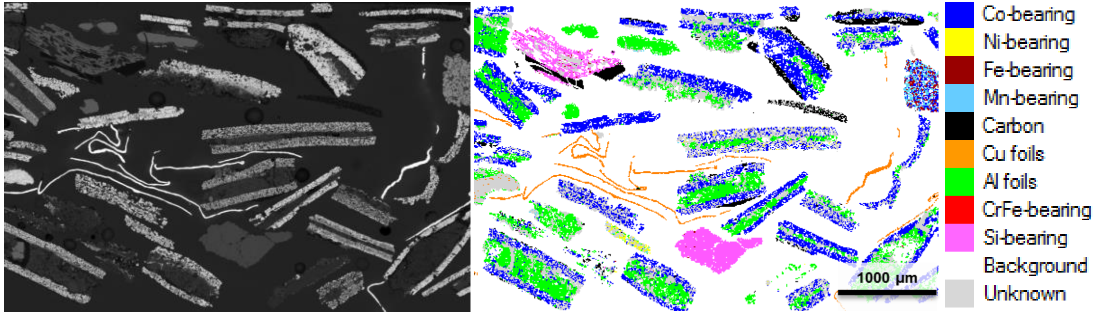




- ➢ Process able to deal with different battery chemistry
- ➢ Recycling efficiency depends on ***particle liberation***

Anna Vanderbruggen
Helmholtz Institute Freiberg for Resource Technology

Characterization: *Black mass coarse fraction*

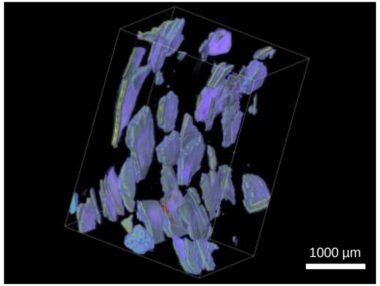


BSE image and processed MLA image of the > 500 µm fraction

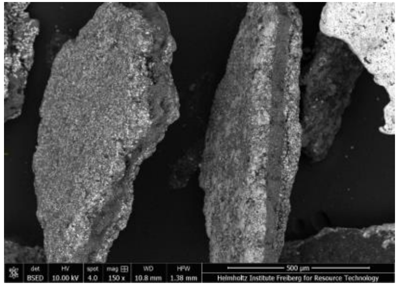
Automated mineralogy:
SEM (BSE images) + EDX analysis
Challenging for secondary material!

Estimation of the liberation degree:
- ➢ 35 wt. % of the aluminium foil
- ➢ 92 wt. % of the copper foils are liberated

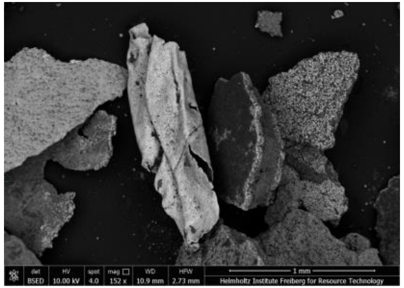
Able to understand and quantify the losses



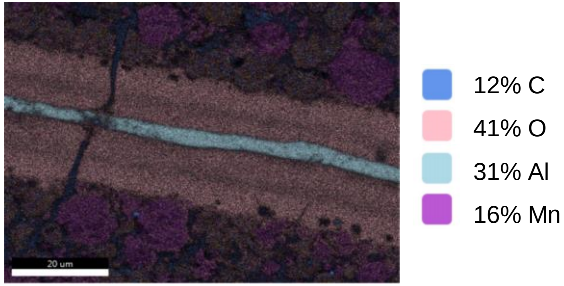
3D tomography on coarse particles



Unliberated cathode



Liberated Cu foil

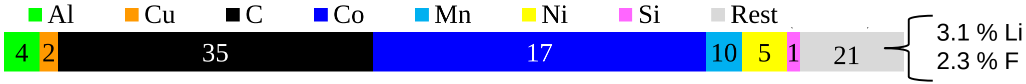


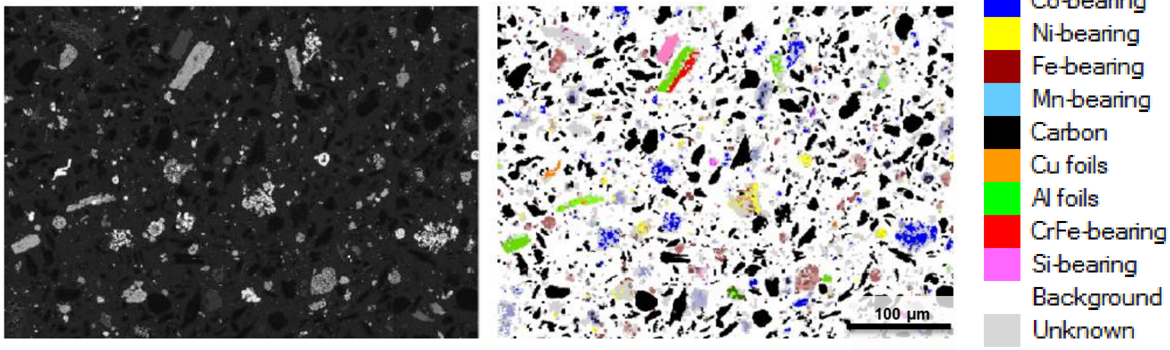
Elemental mapping of a unliberated Al foil particle (Tescan)

HELMHOLTZ INSTITUTE FREIBERG FOR RESOURCE TECHNOLOGY

BOMeRang Black Mass Recycling

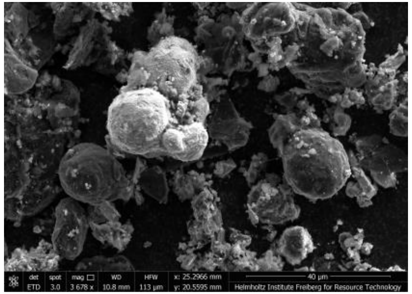
Characterization: *Black mass fine fraction*



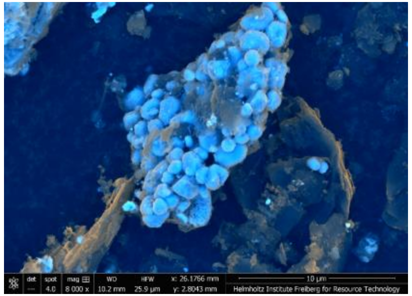


BSE image and processed MLA image of the < 63 µm fraction

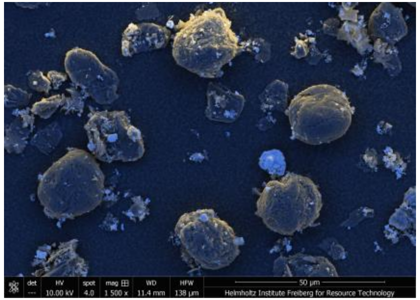
- Graphite liberated: 10-30 µm
- Spheroidized shape is conserved



Fraction below 100 µm



Liberated $LiCoO_2$ particle



Liberated graphite particles

HELMHOLTZ INSTITUTE FREIBERG FOR RESOURCE TECHNOLOGY

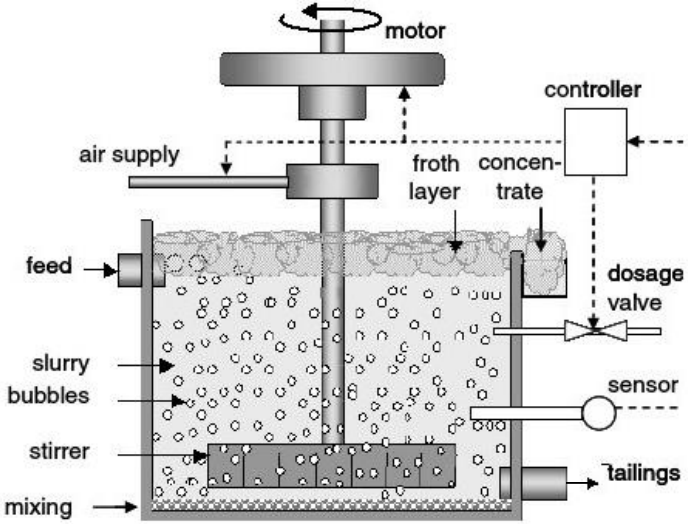
BoMeRang Black Mass Recycling

Flotation theory

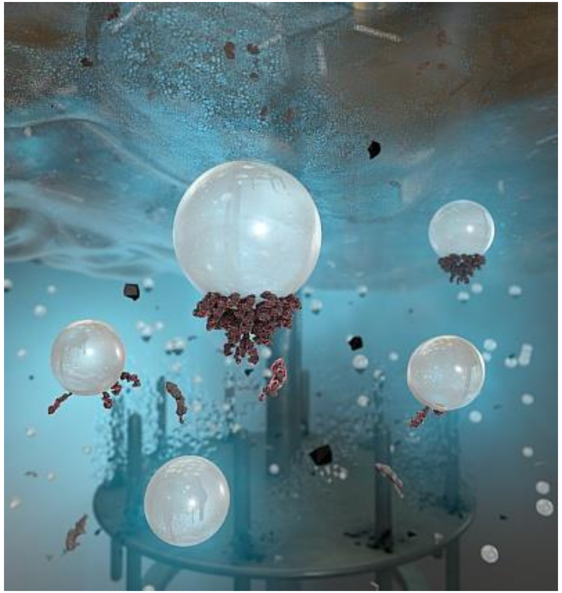
Flotation: separation technique based on physico-chemistry surface properties

→ Liberated particles + surface wettability difference

A 2L Outotec cell (GTK labCell)

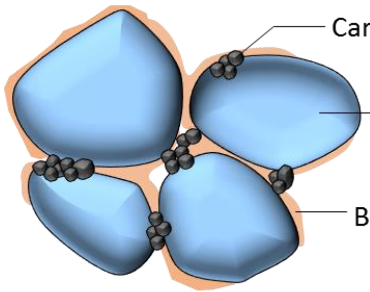


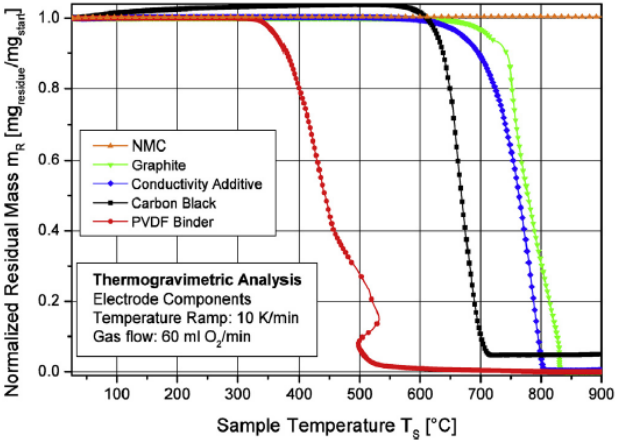
Froth flotation diagram (Kramer et al., 2012)



3D visualization of flotation

Surface properties





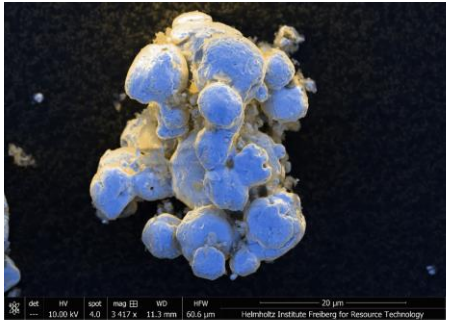
Decomposition of the binder during pyrolysis

→ Binder residuals

Thermogravimetric analysis of single electrode components (Hanisch et al., 2015)

Graphite particles
Hydrophobic

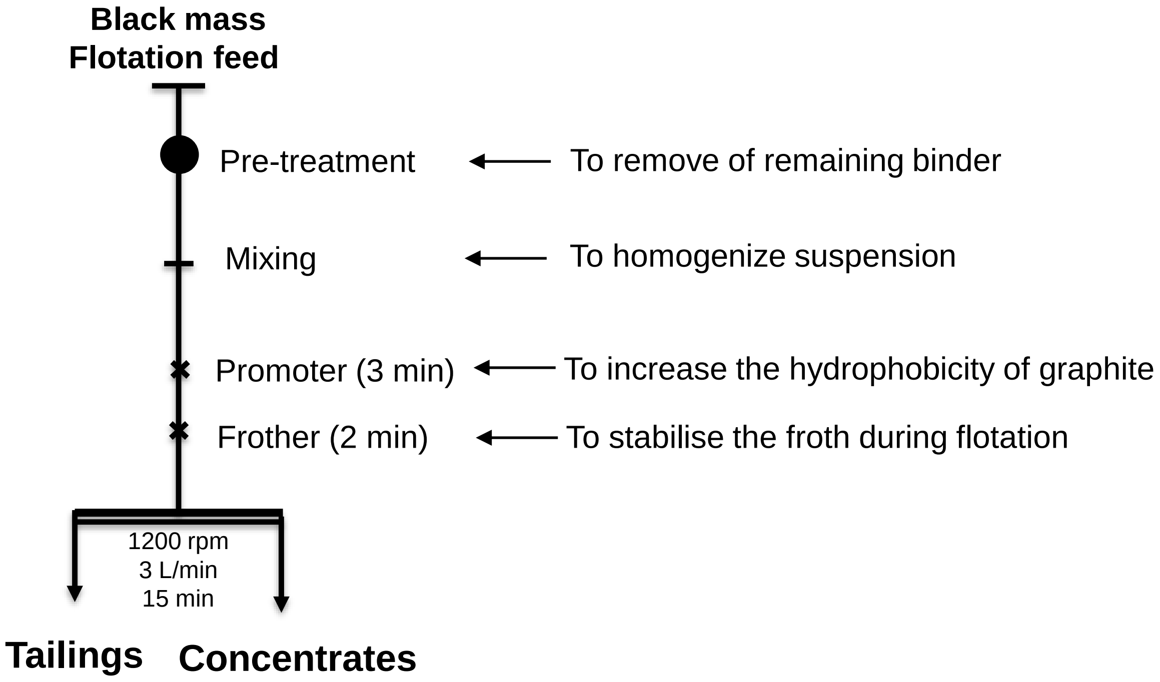
Binder residual
Hydrophobic



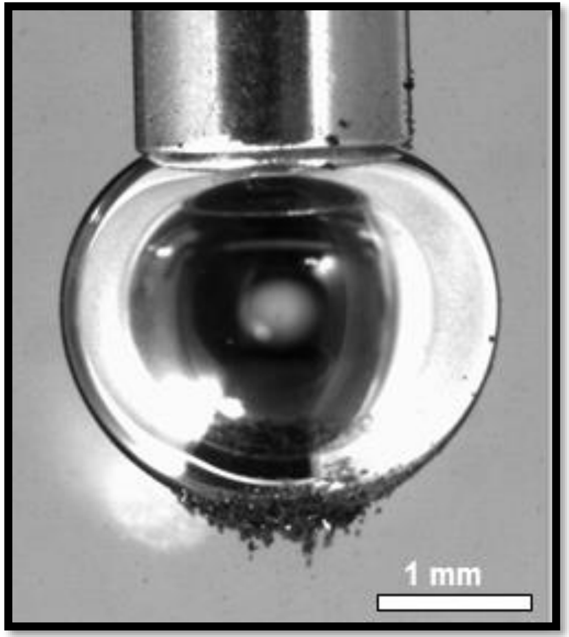
Cathode active particle
Hydrophilic

Difference of wettability → Flotation

Flotation methods

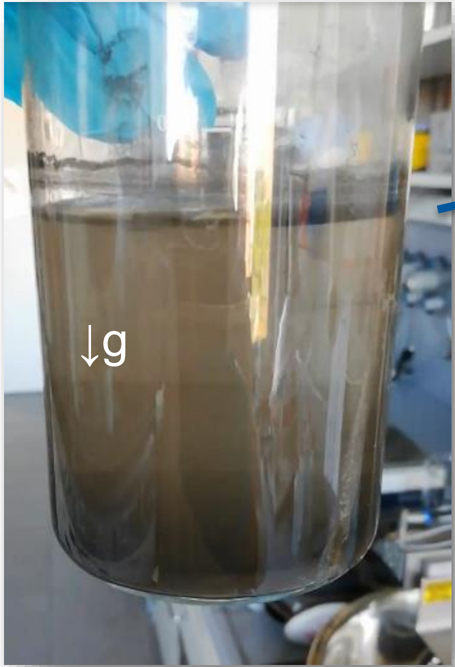


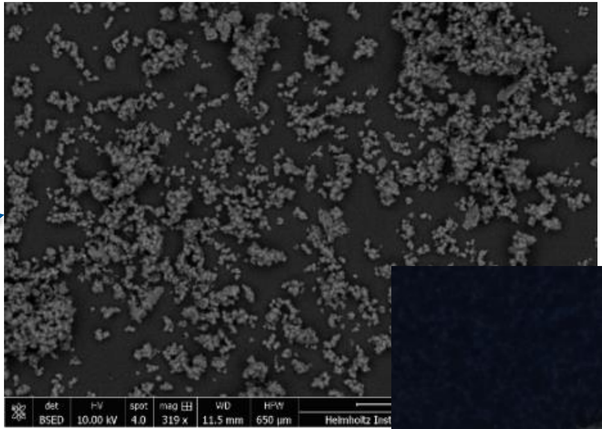
Simplified black mass flotation flowsheet



Black mass in contact with air bubble in water

Flotation: Results and Discussion

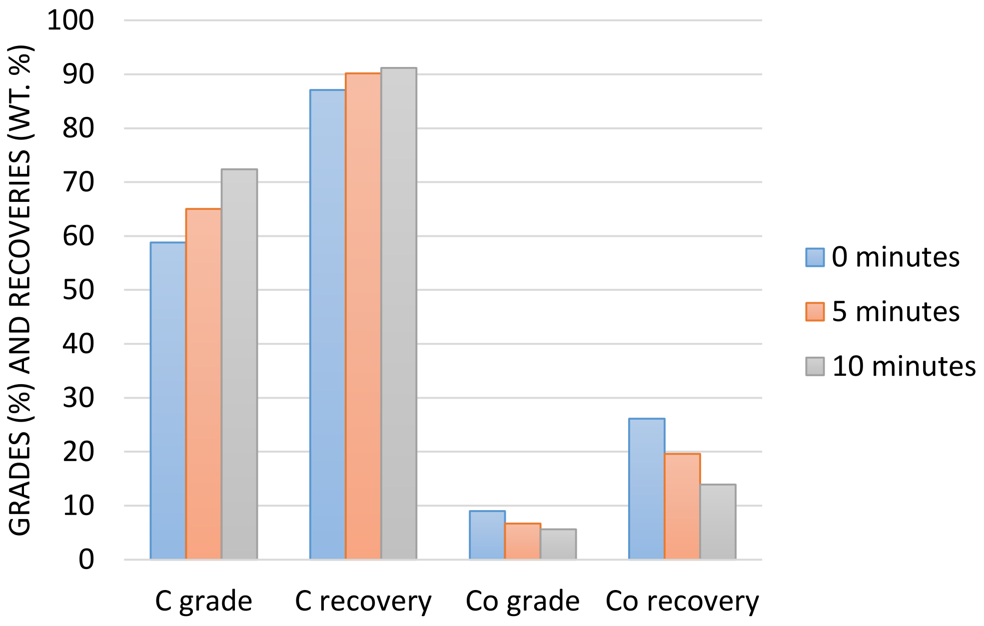




After attritioning, floating deaggregated particles and black mass in sediment

→ Hydrophobic residual binder

Flotation: Results and Discussion



Influence of attritioning on flotation efficiency

Attritioning pre-treatment:

- Remove a part of binder:
  → Should decrease true flotation
- Deaggregate the cathode active particles
- Disperse the fine particles (d_{50} 12 µm)
- Decrease entrainment mechanism

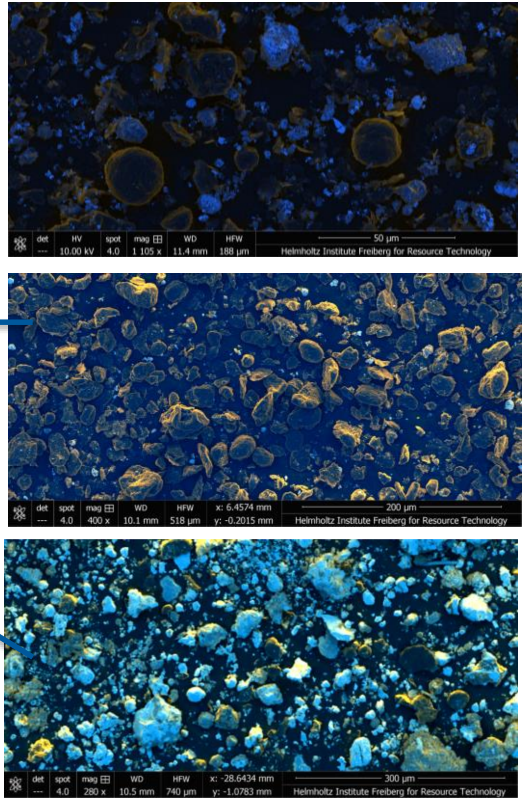
Initial froth forming

20 min attritioning
better drainage
→ Less entrainment

No attritioning

Flotation: Results and Discussion

Rougher flotation



SEM images in false color of flotation products:
Feed (top), concentrate (middle), tailings (bottom)

Flotation feed:
35 wt.% C
17 wt.% Co
10 wt.% Mn
3.1 wt.% Li

Graphite concentrate:
74-79 wt.% C with 94-96% recovery

Metals product:
28 wt.% Co with 80% recovery
11 wt.% Mn with 70% recovery
8 wt.% Ni with 65% recovery
2.4 wt.% Li with 77% recovery

Summary and Outlook

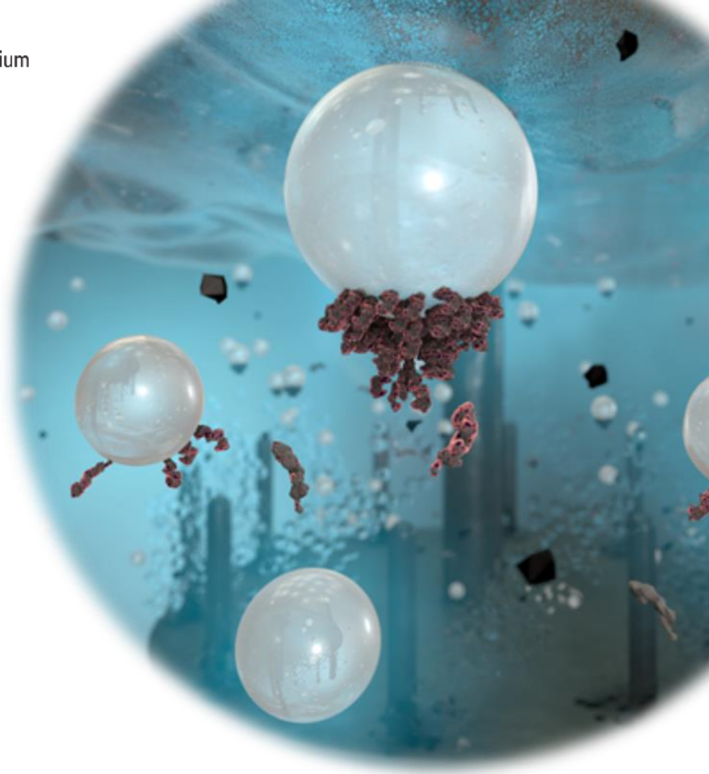
- ✓ It is possible to **recover spheroidized graphite** from Black Mass using flotation after pyrolysis and attritioning (98% Recovery, 79% Grade)
- ✓ With a **leaching post-treatment** it will be possible to obtain anode grade graphite (~96% Recovery, >92% Grade)
- ✓ The flotation "tailings" are **further hydrometallurgically treated** for the resource efficient recovery of **Li**, **Co**, **Ni**, **Mn**…
- ➢ We will focus now on the **battery pre-treatments steps** (mechanical and thermal) and its influence on the **surface properties** of the very fine black mass anode and cathode particles

HELMHOLTZ
RESEARCH FOR GRAND CHALLENGES

BOOMeRang
Black Mass Recycling

Thank you for your attention!

Bundesministerium für Bildung und Forschung



HiF

www.hzdr.de/processing

HELMHOLTZ INSTITUTE FREIBERG FOR **RESOURCE TECHNOLOGY**

HELMHOLTZ
RESEARCH FOR GRAND CHALLENGES

BoMeRang
Black Mass Recycling

Aalto University

Fraunhofer IWKS
Fraunhofer Research Institution for Materials Recycling and Resource Strategies IWKS

TU Bergakademie Freiberg
TECHNISCHE UNIVERSITÄT BERGAKADEMIE FREIBERG
Die Ressourcenuniversität. Seit 1765.

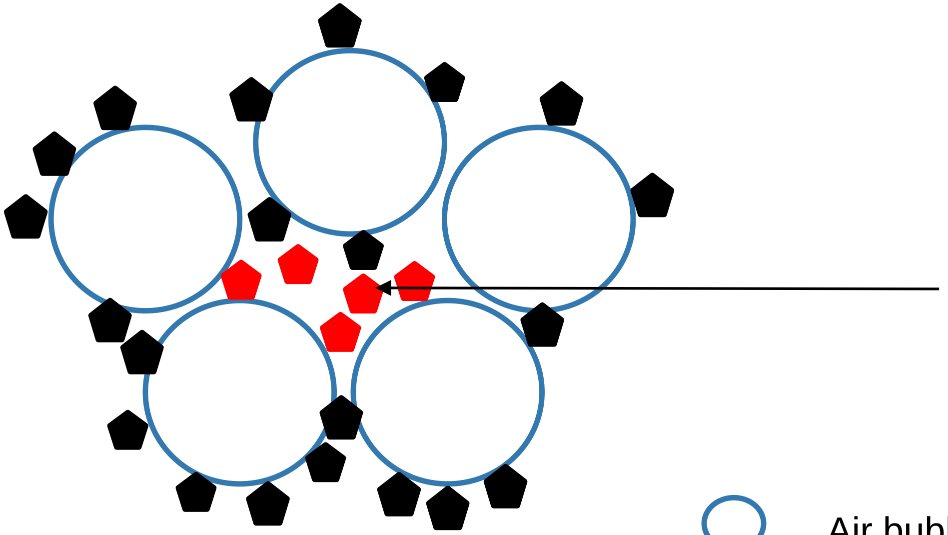
References

- Frey, Christoph. 2018. ‘Processing of Natural Flake Graphite for Lithium-Ion-Batteries’. Proceedings of EMPRC 2018.
- Hanisch, Christian, Thomas Loellhoeffel, Jan Diekmann, Kely Jo Markley, Wolfgang Haselrieder, and Arno Kwade. 2015. ‘Recycling of Lithium-Ion Batteries: A Novel Method to Separate Coating and Foil of Electrodes’. Journal of Cleaner Production 108 (December): 301–11.
- Hatch, Gareth. 2016. ‘Alabama Graphite’s Coated Spherical Purified Graphite For The Lithium-Ion Battery Industry’. Seeking Alpha. 14 June 2016.
- A. Kramer, S. Gaulocher, M. Martins, L.S. Leal Filho. 2012. ‘Surface Tension Measurement for Optimization of Flotation Control’. Journal of Procedia Engineering 46 (2012): 111-118.
- Christophe Pillot from AVICIENNE Energy. ´Lithium ion battery ray material Supply & demand 2016-2025´. Presentation at ICBR September 2019.
- Velázquez-Martínez, O.; Valio, J.; Santasalo-Aarnio, A.; Reuter, M.; Serna-Guerrero, R. A Critical Review of Lithium-Ion Battery Recycling Processes from a Circular Economy Perspective. Batteries 2019, 5, 68.

Critical raw material reports:

- Australia’s Critical Minerals Strategy, Commonwealth of Australia, 2019’ https://www.industry.gov.au/sites/default/files/2019-03/australias-critical-minerals-strategy-2019.pdf
- Critical Minerals and U.S. Public Policy, June 2019. https://www.everycrsreport.com/reports/R45810.html
- Critical Raw Materials - European Commission. January 2018 https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en

Example of entrainment in flotation



Entrapment of hydrophilic particles
→ Particles carried up
into the concentrate

Air bubble

Hydrophobic particle (e.g Graphite)

Hydrophilic particle (e.g Metal)

Anna Vanderbruggen
Helmholtz Institute Freiberg for Resource Technology