Lithium Ion Battery Recycling and Recent IME Activities

B. Friedrich, T. Träger, L. Peters
Recycling driven by the EU & Recycling Motivation

Legal requirement: EU passed the Battery Directive in 2006

- at least 45% batteries must be collected by 2016
- at least 50% of them must be recycled (even 65% of Pb-Batt. and 75% of NiCad.)

Motivations for Recycling:

1. Beneficial production aspects of secondary raw materials vs primary raw materials
   - less energy consumption
   - lower costs
   - less CO\textsubscript{2} emissions
   - mobilisation of valuable (critical) metals, reduced dependence from imports

2. Sustainability, Resources and Environment
   - from battery to battery, Recycling preserves the environment and the earth´s natural resources
Components of Li-Ion Cells

What is included in a typical Li-Ion Battery Scrap fraction?

Casing:

→ Steel, Alumina, Plastics

Electrolyte:

→ non aqueous, organic electrolyte, lithium salt dissolved in an organic aprotic solvent or solvent mixture, typically Li\([PF_6]\)]

Separator:

→ polymeric or ceramic separator

Electrodes:

→ negative alumina electrode (anode) typically coated with carbon or graphite

→ positive copper electrode (cathode) coated with lithium-transition metal oxides (e.g., LiMnO\(_2\), LiNiCoAlO\(_2\), LiNiCoMnO\(_2\), LiFePO\(_4\), LiCoO\(_2\), etc.)
Challenges in Li-Ion Battery Scrap treatment

How can a recycling process for Li-Ion Batteries be evaluated?

1. Quantifying by Indicators, such as:
   - Recovered metal mass → Yield
     \[
     \text{Yield}[\%] = \frac{\text{mass of metal in the target product(s)}}{\text{mass of metal in the input material}} \times 100
     \]
   - Recovered Li mass → Selectivity
     \[
     \text{Selectivity}[\%] = \frac{\text{metal yield in a product}}{\sum \text{all metal yields}} \times 100
     \]

2. Representative sampling

3. Exact chemical determination of input- and output material

4. Considering statistical robustness by the amount of experiments

5. Gross „Recycling Efficiency (RE)“

\[
\text{RE}[\%] = \frac{\sum \text{all element weights from scrap in all products}}{\text{input weight of battery scrap}} \times 100
\]
Flow Chart Part I: Mechanical Treatment and Thermal Conditioning

Li-Ion Battery

Module A
Disassembly to cell pack level

Module B
Autothermal pyrolysis

Module C
Mechanical treatment

to part II: (metallurgical treatment)

Electronic parts, steel components, cables, plastic components

Crack oil (used as oil substitute)

Steel, stainless, Aluminium, Copper

mass flow residue

70 %

~55 %

~ 30 %
Module A: Manual dismantling and disassembly of modules

Dismantling modules of easily removable parts such as power electronics, cable, metal and plastic components

→ Directly marketable fractions with positive revenue

Challenges:
- Cell-module often glued or cast for high cooling contact
- Safety risks
- Manual dismantling is costly
- Low mass throughput
- Difficulty of identifying cell chemistries
Module B: Thermal treatment of cells (VTR)

Vacuum Thermal Recycling (VTR) of battery cells and packs is an autothermal vacuum pyrolysis of electrolytes, plastics and halogens.

**Advantages of the VTR treatment:**
- Single step process and no emissions
- At absence of O₂ and moderate temperatures
  - no loss of valuable components like Al
- Carbon and organics are removed in vacuum atmosphere
- Safe removal of halogens and fluorine
- High energy efficiency

**Challenges:**
- Need for specialized exhaust gas treatment
- Loss of energy by cracking organics and oil
Module C: Mechanical Treatment of Pyrolized Cells

Deactivated cells
- crushing
- grinding
- sifting

Electrode powder
- Metallurgical process
- windsifting
- Magnet separator
- Al-concentrate
- Cu, Al foil scrap
- steel scrap

Mechanical treatment and classification of VTR deactivated cells and packs

→ Directly marketable fractions with positive revenue
Flow Chart Part II: Metallurgical Treatment of Li-Ion Battery Scrap

Module D
Li-phase transformation & recovery

mechan. concentrate from modul C

Li-carbonate

~ 30% residual

Module E
Smelting and reduction

Ni-Co-base metal

~ 22%

Hydrometallurgical treatment

Slag product, offgas

~ 18%

Module F

Metal compounds liquid/solid residue
Module D: Thermal Li-phase transformation & separation from electrode material

Low Temperature Thermal Synthesis (LTTS) of electrode mass powder = thermal synthesis via a phase transformation of lithium metal oxides, which are converted into a water soluble lithium carbonate.

Advantages of the IME LTTS treatment:

- High lithium yield (>80%)
- Ultra-high purity and selectivity of lithium (over 99%)
- Low energy requirement (350°C)
- No chemicals needed
- 2 products, no Co/Ni losses
  - \( \text{Li}_2\text{CO}_3 \)
  - Residue (Mn, Co, Ni etc.) can be used in industrial standard routes
- Easy and safe Process (simple plant construction, low temperature, no critical offgas \( \text{CO}_2 \))
- High energy efficiency
Module E: Smelting and Reduction (Pyrometallurgical Treatment)

Cells/packs from module A
Electrode Powder from module C/D

Slag additives
Furnace (Shaft / EAF)

Alloy (Co, Ni, Mn, Cu)
Slag (Al, Si, Fe, Li)

Offgas / Flue Dust (Co, Ni, Mn, Cu, Al, Si, Fe, Li)
Module F: Hydrometallurgical Treatment

Input material (from module C, D or E)
Cu, Fe, Al, Co, Ni, Mn, (Li) etc.

1. Leaching
   → Solution after C-removal

2. Cu-Cementation
   → Cu-powder

3. Fe-Al precipitation
   → Fe/Al residue

4. Cathode-metal precipitation
   → Solution → Co-, Ni-, Mn-Hydroxide

5. Li-carbonate precipitation
   → Li₂CO₃
## Comparing Hydro- and Pyrometallurgical Process

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Hydromet- Route</th>
<th>Pyromet- Route</th>
</tr>
</thead>
<tbody>
<tr>
<td>• High selectivity, Extraction of base metals is also possible</td>
<td>• Base metals, organics and carbon are used in reduction/ as an energy carrier</td>
<td></td>
</tr>
<tr>
<td>• Carbon remains as raw material</td>
<td>• High productivity</td>
<td></td>
</tr>
<tr>
<td>• Low off-gas</td>
<td>• Direct winning of metals</td>
<td></td>
</tr>
<tr>
<td>• High energy efficiency</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Disadvantages</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>• Using of chemical reagents</td>
<td>• Intensive use of energy</td>
</tr>
<tr>
<td>• High water requirement, Waste water treatment</td>
<td>• Emission control needed</td>
</tr>
<tr>
<td>• Low space-time-yield</td>
<td>• Slag risk</td>
</tr>
<tr>
<td></td>
<td>• Level of funding, high throughput</td>
</tr>
</tbody>
</table>
Battery Recycling at IME

IME – Process Metallurgy and Metal Recycling

→ Continuous research work on battery recycling since the year 2000

• NiCd
• NiMH
• Zinc-carbon
• Alkaline-manganese
• Consumer type Li-Ion Batteries
• Li-Ion Batteries

→ Recycling processes combine Pyro- and Hydrometallurgy

• Pyro: EAF (electric arc furnace), TBRC (top blown rotary converter), VTT (vacuum thermal treatment)
• Hydro: Calcination, leaching, precipitation
Recommended Process Design (Technical View, „EcoBatRec“ concept)

- **Module A** Disassembling of cells
  - Li-Ion Batteries/Packs
  - Electronics, cables, steel-/plastic-casings (product not part of RE- legislation)

- **Module B** Thermal conditioning
  - Condensed/cracked organics (products not counting for RE)

- **Module C** Mechanical treatment
  - Separated and sorted metal fractions of Fe, Cu, Al (all products counting for RE)

- **Module D** Li-phase transformation
  - Separated Li-Carbonate (product counting for RE as compound)

- **Module E** Smelting and Reduction
  - Separated Slag counting for RE as construction material, upon permit
  - Ni-Co-alloy (counting for RE as compound)
Summary

- Safety and resource efficiency aspects demand for a professional dismantling of modules to single cells
- Pyrolysis allows for minimizing of environmental and safety risks by removal of organics early
- Highest impact on RE gained in mechanical pretreatment of cells (careful shredding, sorting, classification)
- Targeting in Lithium a low temperature conversion to easy water soluble Li-compounds avoids a full wet chemical process
- Pyrometallurgical processing of Ni-Co-Mn electrode mass is state of art and allows for further high RE contribution, if C as reductant and slag as product are considered
- Hydrometallurgical processing seems not to be competitive due to high number of process steps, waste water generation, Fe/Al/Mn sludges and chemistry demands
Thank you for your attention!

www.ime-aachen.de
www.researchgate.net/profile/Bernd_Friedrich