Lithium-ion batteries recycling

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SOCIETAL CHALLENGES

- Health and Demography
- Clean Energy
- Food
- Smart and Green Transports
- Climate and Environment
- Raw Materials
- Oil gas metal
CONSUME MORE WITH LESS

Overshot Day (20 August 2015) = when resource use is expected to outstrip the capacity for production—and it’s getting earlier every year

Humanity consumed the whole resource that the earth can produce in only 8 months !!!

1.5 earth to meet our needs !!
In order to face up the world demand, we must extract metals (and more generally raw materials) contained in more and more complex ores from mining and urban mining.
We must develop new processes to recycle spent material in a sake of sustainability and to secure raw material but there are several challenges...

Challenges in Recycle

A good opportunity to diversify the supply of raw materials

Challenges:
- Transform small-scale industry to autonomous and profitable large-scale industry
- Develop efficient and profitable processes
- Improve the recovery of spent materials (WEEE, plastics, batteries, etc.)
Challenges in Recycle

A resource is valuable providing that we know how to transform it!

Present processes have been developed to exploit less complex resources

Next processes should rely on:

- The complementarity of pyro and hydrometallurgy
- A fine knowledge of the resource
- The huge potential of innovation of the European actors
Therefore, recycling appears as a good opportunity to secure raw materials. However, Secondary resources will never replace primary resources!! Each stage of the value chain of the product must be optimized...
Lithium-ion batteries Recycling

1. Why to recycle?
2. How to recycle?
3. Conclusion
1. Why to recycle?

a) Economic reasons

Electric vehicle feet is expected to significantly increase

Lithium batteries production will follow the electric vehicle production

Fig. 3. Fleet size development.

Fig. 6. EV penetration rate estimated using diffusion method [86,92].


Renewable and Sustainable Energy Reviews 21 (2013) 190–203
<table>
<thead>
<tr>
<th>Components</th>
<th>$/EV battery</th>
<th>Cost breakdown</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cell Components</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lithium-ion Battery</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathode</td>
<td>1,663</td>
<td>10%</td>
</tr>
<tr>
<td>Anode</td>
<td>477</td>
<td>3%</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>447</td>
<td>3%</td>
</tr>
<tr>
<td>Copper foil</td>
<td>184</td>
<td>1%</td>
</tr>
<tr>
<td>Separator</td>
<td>608</td>
<td>4%</td>
</tr>
<tr>
<td>Can header and terminals</td>
<td>1,050</td>
<td>6%</td>
</tr>
<tr>
<td>Other materials</td>
<td>375</td>
<td>2%</td>
</tr>
<tr>
<td><strong>Total material</strong></td>
<td>4,803</td>
<td>29%</td>
</tr>
<tr>
<td><strong>Cells</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Labor for cell manufacturing</td>
<td>2,586</td>
<td>16%</td>
</tr>
<tr>
<td><strong>Total cell</strong></td>
<td>7,390</td>
<td>45%</td>
</tr>
<tr>
<td><strong>Electronics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mechanical components</td>
<td>2,053</td>
<td>12%</td>
</tr>
<tr>
<td>Electrical Components</td>
<td>299</td>
<td>2%</td>
</tr>
<tr>
<td>Electronics (battery mgmt. system)</td>
<td>1,381</td>
<td>8%</td>
</tr>
<tr>
<td><strong>Total Electronics</strong></td>
<td>3,733</td>
<td>22%</td>
</tr>
<tr>
<td><strong>Packs</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Labor for pack manufacturing</td>
<td>268</td>
<td>2%</td>
</tr>
<tr>
<td><strong>Total Packs</strong></td>
<td>11,390</td>
<td>69%</td>
</tr>
<tr>
<td><strong>Warranty</strong></td>
<td>228</td>
<td>1%</td>
</tr>
<tr>
<td><strong>Gross Profit</strong></td>
<td>4,979</td>
<td>30%</td>
</tr>
<tr>
<td><strong>Total Cost</strong></td>
<td>16,596</td>
<td>100%</td>
</tr>
</tbody>
</table>

Source: Lithium-ion Batteries for Electric Vehicles: THE U.S. VALUE CHAIN (oct 2010)
Li battery recycling - April, 6th 2016, Gotteborg (Sweden)
b) Geopolitical reasons

Other Materials

Using the same scenario and methods described earlier for lithium, we estimated the potential for lithium to come from the stockpile and recycling, but any new supply will be imported.

Figure 4. Sources of Lithium [11]

Source: commission européenne

Li battery recycling - April, 6th 2016, Gotteborg (Sweden)
c) Regulations


d) Sustainability
CONTENT

1. Why to recycle?
2. How to recycle?
3. Conclusion
2. How to recycle?

We must think about:

- Developing efficient, cheap and sustainable processes to recover valuable materials from spent batteries
- These processes must be able to adapt to the large variety of technologies
- Processes must be developed by thinking about the whole value chain (the process depends on what happens before and after the recycling stage)
2.1. Valuable components to recycle
Large variety of technologies in constant evolution... the process must adapt

Source: Lithium-ion Batteries for Electric Vehicles: THE U.S. VALUE CHAIN (oct 2010)
NEGATIVE ELECTRODE = Graphite today and in the near future (cost=3%)

Prices have more than doubled since 2006

$1,500 per tonne
$700 per tonne

Today, 5% of graphite is used in LiBs
Tomorrow, this percentage will grow: 1.1 million tonnes currently being brought to market will no longer be enough to face electric vehicle market.
NEGATIVE ELECTRODE = Graphite today and in the near future (cost=3%)

China has monopoly

→ Substitute natural graphite by artificial graphite produced from natural carboneous materials
→ Recycling graphite from Lithium-ion batteries

Turbostatic disorder

Soft carbon (can lead to graphite)

small crystallites in almost the same direction
→ low warm → order → graphitization

Hard carbon (cannot form graphite even at T > 2000°C)
NEGATIVE ELECTRODE = Graphite today and in the near future (Cost=3%)

There is only few researches on graphite recycling and industrial processes for LiBs recycling do not recycle graphite

We must develop efficient processes capable to recycle graphite that can be used in other applications or in lithium-ion batteries (quality of graphite?)

We must also develop negative electrodes based on the use of artificial graphite and increase the variety of negative electrode technologies (silicone?)
POSITIVE ELECTRODE (Cost=10%)

![Diagram of the recycling process for lithium batteries](image)

1. Lithium battery
2. Deep discharge
3. Dismantling
   - Electronic, steel shell, plastics
4. Distillation under vacuum
   - Solvent
   - Salt
5. Binder solubilization
   - Cu
   - Al
6. Grinding
7. Leaching
8. Purification/separation
   - (Solvent extraction, precipitation)
   - Salt or Metal (electrowinning)
9. Solvent extraction
10. Ion exchange resin
11. Precipitation

Li battery recycling - April, 6th 2016, Gotteborg (Sweden)
Many flow sheets based on different chemistry are available in the literature

CSIR (Jamshedpur, India) - 02 March 2016
ELECTROLYTE (Cost=3%)

Electrolyte = Lithium salts (high grade)+organic solvents
Recycling

ELECTROLYTE (Cost=3%)

Spent electrolyte

Water

Electrolyte+Water

Na$_3$PO$_4$

Solid Lithium phosphate

Pyridine

Pyridinium,PF$_6^-$ → PF$_6^-$

H$_3$PO$_4$+NaCl

Aqueous phase

I>2 M

Mixture of organic solvents

Phase Separation

Organic phase

Separation by distillation

Solvent 1

Solvent 2

Solvent 3
2.2. Recycling processes

*General Flow sheet in hydro- and pyro-metallurgy*

Lithium-ion battery → Deep discharge → Dismantling → Grinding → Chemical and physical separation → Electronic-steel shell, plastics

- How to decrease the cost?
  - Eco-design
  - New technologies

- How to separate efficiently in an economic and sustainable way?
  - Improving efficiency
  - Reducing effluents
  - Eco-design
Battery assembly process

Source: Gaines, 90th Annual Meeting of the Transportation Research Board (Janv 2011)
Lithium-ion battery

Deep discharge

Dismantling

Grinding

How to decrease the cost?

- Eco-design
- New technologies

Electronic-steel shell, plastics

Chemical and physical separation

How to separate efficiently in an economic and sustainable way?

- Improving efficiency
- Reducing effluents
- Eco-design
2.2.1. Pyrometallurgical processes for LiB recycling

Umicore recycling process

- Plastics, electrolyte solvents, and carbon electrodes are burned in the smelter (carbon = reducing agent and heat fuels the smelter).

- Co and Ni are the main products; Fe can be recovered as well

- Al and Li go to the slag for low-value uses.

- 93% recovery rate for Li-ion batteries (metals 69%, carbon 10%, plastics 15%), but a much smaller percentage actually comes out as usable high-value material.
Detailed in the Umicore recycling process
How to recycle?

2.2.2. Hydrometallurgical processes for LiB recycling

- Lithium battery
  - Deep discharge
  - Dismantling
    - Electronic, steel shell, plastics
  - Distillation under vacuum
    - Solvent
    - Salt
  - Binder solubilization
    - Cu
    - Al
  - Grinding

- Salt or Metal (electrowinning)
Inlet: Mixture of different battery technologies (Zn-MnO2, NiCd, NiMH, NiCo from Li batteries)

Spent portable batteries
ZnMn
Physical Processing
Leaching
Neutralization Purification
Zn Extraction and Recovery
Mn Recovery
Plastic Scrap
Insolubes, Fe pp.
Zn product
Mn product

NiCo
Physical Processing
Leaching
Neutralization Purification
1st Extraction circuit (RE)
2nd Extraction circuit (Cd,Mn)
3rd Extraction circuit (Co)
Plastic and Ferrous Scrap
Insolubes, Fe pp.
Rare-earths product
Cd-Mn for further process.
Cobalt product

Jarosite or goethite

Sieving (polymer/ferrous scrap separated from electrode materials (disaggregated=small))

D2EHPA
pH
Phase volume ratio

D2EHPA
Cyanex 272
pH
Phase volume ratio

Li battery recycling - April, 6th 2016, Gotteborg (Sweden)
- Battery pack is discharged for safety reasons
- Control circuits are removed and tested for possible reuse
- Wires and some other metals are removed for recycling
- Packs are disassembled
- A series of mechanical processes are used to reduce the size of the cell materials
- Products = copper cobalt and lithium carbonate

- Recycling process is mainly mechanical and chemical
  - Minimum emissions and energy consumption (low temperature)
- 60% of the pack materials can be recycled, and a further 10% reused.
**ECOBAT Process**

- Minimal energy use (no high-temperature processing)
- Many of the process details are proprietary, and so cannot be specified here.
- Electrolyte recovery using supercritical CO₂ for salt reuse.
- Separation processes based on surface properties and solubility.
- Over 80% of the material is actually recycled to useful products with potential value of the recovered materials quite high.
- Experimental results are excellent for both cobalt and phosphate cathodes.
- Processing a mixed feed would require additional separation steps to yield high-quality final products.
- Issue: scaling up this process.
Most of the processes are pyrometallurgical processes but there is no doubt that hydrometallurgical processes will be more sustainable and efficient to produce high-grade products.

However, the best compromise is to combine hydro- and pyro-metallurgical processes to achieve the best performances (pyro-pretreatment).
Integrated view of the chain value

*Recycling process must be viewed as a part of the chain value*

Managing spent LiB at the end of life from the user to the mechanic

Eco-design the materials and the batteries

Supporting the development of technologies based on the use of alternative materials instead of Li, Co, Ni and graphite based materials
New processes capable to process various types of streams and capable to anticipation future technologies

Be able to face up the volatility of raw materials price by making innovation for reducing the recycling cost
Decrease recycling price by getting easier the dismantlement

29 robots over 30 meters to disassemble 40 iPhones at the same time within 11 seconds → Capacity=2.4 million iPhones a year
If you are interested by Lithium batteries, lithium batteries recycling and e-wastes recycling...

Published in 2015

Will be published in June 2016
Och tack för er uppmärksamhet!