Li-ion BATTERIES RECYCLING

The batteries end of life ...
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Li-ion batteries recycling: the state of the art

I. Background

The actual best battery performance is given by the lithium ion technology. Since Sony brought the first portable lithium-ion battery in 1992 on the market, the lithium-ion technology had a boom in powering portable devices, like mobile phones and laptops. Today this technology is the preferred one to power electric vehicles. The market shares of Li-ion batteries are constantly rising, while the share of the nickel metal hydride (NiMH) decreases. The lithium-ion technology offers lower weight and volume to power ratios, constant voltage output and long lifetime. But the lithium-ion batteries still are more expensive than other batteries. Traction batteries for powering electric vehicles are batteries with a weight from 20 kg up to 250 kg. For these batteries there are some safety and recycling issues to be resolved. [2, 8, 17, 25, 69]

Progress in material and production process development has lowered the cost and it approaches a justifiable level. [7, 24]

In order to be well prepared for the recovery processes of future end-of-life (hybrid) electric vehicles it is important to develop methods and processes for treating large lithium-ion batteries. With their weight and their sizes and their stored amount of electrical energy the vehicle batteries demand other requirements in the recycling process than the smaller, portable batteries [69].

On European level the Battery directive 2006/66 EG is the legal framework for battery recycling. This directive was taken over into national legislation of the European states. The battery directive defines different battery types and collection schemes and quotas, regulates the market participation, prohibitions of materials in batteries and recycling quotas for different battery types. Lithium-ion batteries from HEV & EV are considered as industrial batteries. Their minimum recycling rate is 50 %. [45, 46] Regarding the recycling efficiency of HEV and EV batteries the calculation method is defined in [47]. By providing this legal framework for battery recycling the product responsibility of battery or car manufacturers is regulated and the disposal of batteries to landfill is counteracted.

In addition to the legal requirements other reasons for recycling are:

• Primary resources are saved by the reuse and / or recycling of battery materials. A shortage of resources is avoided and the price stability for raw materials is increased. [48]

• Recycling contributes to CO2-reduction, saves energy and reduces the amount of hazardous substances that is brought into environment. [49, 50]

• The dependence from countries with lithium reserves could be reduced by recycling. This reduction of dependence could be strategically an advantage for the future.

The recycling of lithium-ion batteries is a complex task. Due to the numerous different materials used in lithium-ion cells and batteries the separation of the material mix is a challenge. Theoretically a lithium-
ion cell could be almost entirely recycled. Recupyl S.A. developed already in 2003 their hydrometallurgical Valibat process with recovery rates high above 90%. At present those high efficient processes are economically not realisable. Today the most common recycling method for used lithium-ion batteries is the pyrometallurgical route. Within this process the battery cells are smelted to an alloy and a slag.

In the past different battery chemistries were used for electric vehicles. Lead-Acid batteries, to Nickel cadmium batteries and nickel-metal hydride batteries were predominant systems. Today there is an increasing use of lithium-ion batteries. [1, 17]

II. Battery materials
The materials contained in a lithium-ion battery can vary somewhat depending on the active cathode material. In the current lithium-ion battery market the small batteries dominate. Normally these use cobalt cathodes but there are also batteries with manganese or iron phosphate chemistry. For electric vehicle batteries the market is less certain but instead of cobalt the batteries will rather use manganese and nickel based cathodes or lithium iron phosphate. [2, 18, 21, 69]

II.1. Material composition of a battery pack
Umicore did a mass balance by identifying all material fractions that were separated in the dismantling process of existing (prototype) batteries and by calculating the average values of the single fractions. Following table 1 summarizes the findings. The relatively low percentage of the cell weight is caused by the reference to existing battery systems (HEV batteries) and prototype batteries. For EV batteries the percentage of cells is expected to be about 60%. [101]

Table 1: materials and components of a type casted battery system [101]

<table>
<thead>
<tr>
<th>Materials / components</th>
<th>Mass [kg]</th>
<th>Relative [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Battery cells</td>
<td>80,0</td>
<td>32,0</td>
</tr>
<tr>
<td>Steel (stainless steel, ...)</td>
<td>75,0</td>
<td>30,0</td>
</tr>
<tr>
<td>Plastics (PP, PA...)</td>
<td>26,0</td>
<td>10,4</td>
</tr>
<tr>
<td>Aluminum</td>
<td>21,0</td>
<td>8,4</td>
</tr>
<tr>
<td>Copper</td>
<td>7,0</td>
<td>2,8</td>
</tr>
<tr>
<td>Electronic components (BMS, fuses, ...)</td>
<td>2,3</td>
<td>0,92</td>
</tr>
<tr>
<td>Elastomers</td>
<td>3,6</td>
<td>1,44</td>
</tr>
<tr>
<td>Composite materials</td>
<td>35,1</td>
<td>14,04</td>
</tr>
<tr>
<td>Summed</td>
<td>250</td>
<td>100</td>
</tr>
</tbody>
</table>

II.2. Detailed material composition of a battery pack
The variety of different sized batteries on the market with different chemistries makes it difficult to calculate relative masses of the included materials. To overcome this problem a battery mass model that includes different cell chemistries has been developed in [101]. The three most common battery chemistries NMC, LCA and LFP have been researched regarding their average weight and material composition. Following table 2 summarizes the findings.
Table 2: mean values for individual cell types [103]

<table>
<thead>
<tr>
<th>Cell type</th>
<th>NMC</th>
<th>NCA</th>
<th>LFP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total mass kg/Battery</td>
<td>141</td>
<td>100</td>
<td>118</td>
</tr>
<tr>
<td>Total mass g/kg</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Energy content kWh/t</td>
<td>86</td>
<td>96</td>
<td>71</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cell materials</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total g/kg</td>
<td>630</td>
<td>598</td>
<td>530</td>
</tr>
<tr>
<td>Cathode g/kg</td>
<td>191</td>
<td>175</td>
<td>173</td>
</tr>
<tr>
<td>-Lithium g/kg</td>
<td>14</td>
<td>13</td>
<td>7.6</td>
</tr>
<tr>
<td>-Cobalt g/kg</td>
<td>39</td>
<td>16</td>
<td>0</td>
</tr>
<tr>
<td>-Nickel g/kg</td>
<td>39</td>
<td>86</td>
<td>0</td>
</tr>
<tr>
<td>-Manganese g/kg</td>
<td>36</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-Aluminum g/kg</td>
<td>0</td>
<td>2.5</td>
<td>0</td>
</tr>
<tr>
<td>-Iron g/kg</td>
<td>0</td>
<td>0</td>
<td>61</td>
</tr>
<tr>
<td>-Phosphorus g/kg</td>
<td>0</td>
<td>0</td>
<td>34</td>
</tr>
<tr>
<td>-Oxygen g/kg</td>
<td>63</td>
<td>58</td>
<td>70</td>
</tr>
<tr>
<td>Electrolyte g/kg</td>
<td>114</td>
<td>101</td>
<td>85</td>
</tr>
<tr>
<td>Separator g/kg</td>
<td>54</td>
<td>50</td>
<td>43</td>
</tr>
<tr>
<td>Anode-Carbon g/kg</td>
<td>140</td>
<td>131</td>
<td>111</td>
</tr>
<tr>
<td>Cathode foil - Al g/kg</td>
<td>39</td>
<td>40</td>
<td>34</td>
</tr>
<tr>
<td>Anode foil - Cu g/kg</td>
<td>66</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>Cell case - Al g/kg</td>
<td>21</td>
<td>20</td>
<td>17</td>
</tr>
<tr>
<td>Others g/kg</td>
<td>6</td>
<td>10</td>
<td>8.5</td>
</tr>
</tbody>
</table>

Battery and module housing

| Total g/kg                 | 370  | 402  | 470  |
| Cables g/kg               | 21   | 50   | 64   |
| -Copper g/kg              | 13   | 30   | 38   |
| -Aluminum g/kg            | 1.4  | 10   | 13   |
| -Stainless steel g/kg     | 7.1  | 10   | 13   |
| Frame g/kg                | 114  | 101  | 128  |
| -Plastics g/kg            | 107  | 81   | 102  |
| -Stainless steel g/kg     | 7.1  | 20   | 26   |
| Casing (stainless steel) g/kg | 199 | 241  | 267  |
| Others g/kg               | 36   | 10   | 11   |
II.3. Safety issues

The high amount of stored energy, toxic components in the battery and a potential risk of fire when the batteries are mistreated or damaged are reasons why lithium-ion batteries pose several safety issues. In a first step it was therefore necessary to think about the channels and the conditions under which a battery arrives at recycling.

Applicable legislation regarding the storage, transportation and handling of LIB has been found to be extensive. Basically the safety requirements for the transportation of LIB are described in the UN Model Regulations (UN Recommendations on the Transport of Dangerous Goods) and in the international Dangerous Goods Regulations.

Nevertheless, the compilation and analysis of current regulations has shown that regarding the treatment of LIB in a damaged and potentially instable status stays quite vague. Only the “Multilateral Agreement M228 (RECHARGE "Packaging requirements for damaged & defective lithium batteries")31/10/2012) proposes some orientation. When damaged, LIB in particular present greater demands on the safety of the collection system.

Therefore, the whole take back process has been analyzed by an FMEA (Failure Mode and Effects Analysis) taking into consideration both basic LIB conditions “damaged” versus “intact”. Assuming a 12 staged take back process, the majority of safety risks and the most severe occur during the first steps of “removing”, “diagnosis” and “packaging” as these steps also build the basis for all following treatment and recycling steps.

Especially damaged LIBs may carry the safety and environmental risk like thermal runaway, electrical shock and the emission of hazardous substances. In charged state Lithium-ion batteries for vehicles contain a large amount of electric energy. Voltages of 400V and currents of several hundred amperes are common. For the workers who handle charged batteries this is a severe safety risk. For the work on high voltage systems a special qualification and education of the workers is necessary. [58]

Regarding the actual recycling process, dismantling on cell level further specific safety aspects need to be considered. Batteries that carry charge contain lithium intercalated in the anode graphite and used batteries will have some lithium in the anode even if they are discharged. The intercalated lithium reacts with water to produce lithium hydroxide (LiOH) and hydrogen gas (H2) but the reaction is not as violent as with lithium metal. Batteries subjected to overcharge will obtain lithium plating on the anode surface. It is not unlikely that used batteries are disposed as a result of malfunction. Therefore, the presence of lithium metal cannot be discarded in recycling processes. Besides the hazard of lithium metal other risks are somewhat dependent of the battery design.

The electrolytes are usually considered to comprise the main toxicity. Especially the conduct salt LiPF6 forms in contact with water or moist air hydrofluoric acid (HF). [8, 26]

III. General recycling procedures and pre-processing

The aim of recycling processes summarized in figure 1 is to separate the constituents into different fractions where they can be reintroduced into production. The separation can be made on several levels but generally are purer and better defined fractions more valuable than mixed and impure ones. Breaking every chemical bond and separating all elements into different fractions could be seen as an ideal recovery process but the energy requirements for such recycling makes it far from ideal. The real effort is to produce useable products, minimise waste, reform hazardous substances and to do this in an environmental energy efficient and economical way. [16, 23, 26, 69]
In order to meet with the demands stated above the waste materials need to be separated into different fractions. Recovery of metals (such as Ni, Co, Copper ...) is one of the primary incentives with battery recycling. Energy intensive raw production and high market values put the metal components in focus for recovery. [16, 23, 28, 69]

A possibility to treat large lithium-ion batteries is a cryogenic approach. To reduce risks the lithium is passivized before the crushing process starts. The battery therefore is cooled down to -195 °C in a bath of liquid nitrogen. The reactivity of lithium is reduced to 1/250,000 which enables a riskless crushing of the battery.

In order to minimize risks most recycling processes involve a pre-processing step to establish a safe working environment. A discharge of the batteries before the recycling process reduces the risks for the workers. Often the batteries are dismantled to module or cell level and then totally discharged to ensure a safe processing. There are approaches for the complete discharging of modules or batteries in a bath of a conductive liquid solution (e.g. sodium chloride, calcium carbonate, acid sulphur, hydrochloric acid or nitric acid) or with the help of external resistances.

![Battery Pack Diagram](image)

**Figure 1: battery pack pre-processing and general recycling procedures**

**III.1. Cell disruption**

Crushing, shredding, shearing and other mechanical manipulations can break material into smaller pieces and expose the interior. This is frequently used as the first operation in industrial waste treatment. In battery recycling mechanical opening of the cells is important unless they are smelted. Shredding and crushing activities are sometimes performed in inert or cryogenic atmospheres as to prevent violent reactions of lithium and to minimize risks from the presence of organic solvents. [5, 23, 28, 41, 69] A contact between metallic lithium with water or moisture results in intense exothermic reactions. Hydrogen and oxygen are formed which leads to a high risk danger of explosion. [69]
Vehicle batteries are large devices that are making cell disruption more hazardous and complicated. The crushing step usually is done in an inert water free atmosphere of carbon dioxide, nitrogen, argon or helium because of the reaction of lithium and because of the presence of solvents. The lithium components can as well be passivized in a base as alkyl carbonate, alkyl ether or an acid. [79, 80, 81, 82, 83, 84, 85, 86]

### III.2. Physical separation

Following mechanical treatments, breaking apart plastic and cells, some physical separations by means of gravity and magnetism can be performed directly.

From crushed batteries the plastics from shells can be separated by flotation. Steel parts originating from containers can be separated using magnetism. For larger batteries with many cells manual dismantling can be a more convenient and profitable way to remove plastics and electronics. [5, 23, 28, 41, 69]

Besides the manual dismantling of the battery system and the modules, physical separation processes are performed on cell level after crushing. The yield is to separate cell casings, aluminium, copper and plastics from the electrode powder. Especially for hydrometallurgical processes a separation of the electrode materials is necessary. [41, 92, 93]

Physical separation processes are efficient and affordable in relation to other processes. Some of the most common separation technics in recycling processes are mentioned below in figure 2. [41, 92, 93]

---

<table>
<thead>
<tr>
<th>TECHNOLOGY</th>
<th>MATERIALS TARGETED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screening</td>
<td>Large: film plastics, large paper, cardboard, misc.</td>
</tr>
<tr>
<td></td>
<td>Mid-sized: recyclables, organics, misc.</td>
</tr>
<tr>
<td></td>
<td>Fines: organics, metal fragments, misc.</td>
</tr>
<tr>
<td>Hand Picking</td>
<td>Recyclables, inert and chemical contaminants</td>
</tr>
<tr>
<td>Magnetic Separation</td>
<td>Ferrous plus contaminants associated with ferrous met.</td>
</tr>
<tr>
<td>Eddy Current Separation</td>
<td>Non-ferrous metals</td>
</tr>
<tr>
<td>Air Classification</td>
<td>Lights: paper, plastic</td>
</tr>
<tr>
<td></td>
<td>Heavies: metals, glass, organics</td>
</tr>
<tr>
<td>Wet Separation</td>
<td>Floats: organics, misc.</td>
</tr>
<tr>
<td></td>
<td>Sinks: metals, glass, gravel, misc.</td>
</tr>
<tr>
<td>Ballistic Separation</td>
<td>Light: plastic, undecomposed paper</td>
</tr>
<tr>
<td></td>
<td>Medium: compost</td>
</tr>
<tr>
<td></td>
<td>Heavy: metals, glass, gravel, misc.</td>
</tr>
</tbody>
</table>

*Figure 2: materials targeted [87]*

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**III.2.1 Sieve classification**
Sieve processes (figure 3) are separating the material based on material particles size. It divides the volume stream quantitatively and prepares it for further processes. Sieves and vibrating tables are separating the rough and fine fractions. [41, 92, 93]

![Figure 3: sieve classification](image)

### III.2.2. Airstream classification
The airstream sorting separates with its simulated airstream light materials from heavy ones (figure 4). [41, 92, 93]

![Figure 4: airstream sorting](image)

### III.2.3. Magnetic separation
Strong electromagnets separate magnetic materials from the material stream. [41, 92, 93]

### III.2.4. Electrostatic processes and separation by frictional charge
With the usage of frictional charging effects materials as PVC and PET can be separated according to electrostatically charge (figure 5). [41, 92, 93]
III.2.5. Eddy current process
In this process (figure 6) a rotating bullet magnet induced electric streams in the remained non-ferrous metal as aluminium. As a result these parts are revolted. [41, 92, 93]

III.2.6. Flotation process
With the help of a liquid, fractions could be separated according to their density and weight. Besides the different density the different wettability of materials could be used to separate material fractions (figure 7). [41, 92, 93]
III.3. Dissolution
The active cathode and anode material is bond onto the collector foils with binder. In production of the electrodes the active material is mixed with solubilised PVDF and then painted onto the collector foils, as the solvent evaporates the layer is fixed [69].

The reverse procedure is possible and by submerging the electrodes in Nmethylpyrrolidone (NMP) the active material can be separated from the collector plates. This is a very convenient way of parting the collector foils (Cu and Al) and the active material. If the coils are removed from the container without crushing the long foils (for cylindrical cells) can be taken out of the solution and further treatment be performed on the solution now free from aluminium and copper. [23, 41, 69]. Disadvantages of this method are the high solvent costs, the time needed for dissolution and the toxicity of NMP. [41]

III.4. Thermal treatment
It can serve several purposes depending on temperature. At low temperatures (<380°C), decomposition of the binder material PVDF [118] and oxidation of carbon can be achieved. Decomposition of harmful solvents could also be the target for temperatures lower than 350°C. Higher temperatures allow the incineration of plastics and solvents or pyrolysis if the atmosphere is controlled. [5, 24, 26, 69]

The thermal treatment is carried out for safety reasons because the electrolyte is extracted and possibly existing metallic lithium is transferred to more stable and safer compounds. Furthermore the treatment enables a good separability of the active materials from the electrode foils by the decomposition of the binder.

IV. Extractive metallurgy
To separate metal from other materials is relatively easy but to separate metals from other metals can prove challenging. Separation and refinery of individual metal elements involve the processes of extractive metallurgy [69].
Extractive metallurgy can be divided into wet processing and dry processing. Wet processing involves aqueous solutions and the boiling point of water (even if pressurised) limits the methods to rather low temperatures. Dry processes concern solid material reactions, which include the high temperatures of melting the metals or treatments with ionic liquids. [16, 69]

Table 3: wet and dry processes for extraction of metals. [16]

<table>
<thead>
<tr>
<th>Wet processes</th>
<th>Dry processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrometallurgy</td>
<td>Pyrometallurgy</td>
</tr>
<tr>
<td>• Leaching</td>
<td>• Calcination</td>
</tr>
<tr>
<td>• Precipitation</td>
<td>• Roasting</td>
</tr>
<tr>
<td>• Ion exchange</td>
<td>• Reduction</td>
</tr>
<tr>
<td>• Solvent extraction</td>
<td>• Chlorine metallurgy</td>
</tr>
<tr>
<td>• Electrolysis of aqueous solutions</td>
<td></td>
</tr>
</tbody>
</table>

In table 3 and figure 8 a general division of wet processes and dry processes is made. Processes not relevant to the treatment of battery waste have been omitted.

Figure 8: classification of the recycling processes

IV.1 Hydrometallurgy

Hydrometallurgy concerns treatments on aqueous solution and includes bringing material into solution and operations to separate different components. Containing metal materials and metals are handled, cleaned or intermediates are manufactured. At the hydrometallurgy is a process under lower temperature where contained metals are transferred into water soluble metal salt through acid, bases or salts. With the process of electrolysis, cementation, pressure precipitation or crystallisation metal is gained from the liquid solution. The advantage of this process is its selectivity. A directed separation and retrieval of several materials which a high efficiency is reached. The usage of energy is at a low level according to the low temperature necessary. The level of emission is slight so that nearly no air pollution effects the environment. On the other hand chemical reactions are time-consuming and less productive as the
pyrometallurgical processes. The process as well depends on different chemicals that are needed in high volumes. [80, 94, 95, 96]

**IV.1.1. Leaching**

Leaching is a common technique of recycling. Extracting a soluble element (often metal) from a solid with a solvent is denoted leaching. The process can serve several purposes depending on the situation [69].

Leaching can be used to get metals into solution for further refinery but the leaching itself can also be selective towards specific elements [69].

The leaching selectivity of a specific material, of course, depends on the composition of the leaching medium. Acid leaching is standard procedure in many recovery processes where multiple metals are present. Leaching with bases can also be performed but is not as common. Except for the choice of acidic or basic leaching media there are also other configurations that can change the selectivity or leaching efficiency. Reductive leaching can improve the efficiency by changing the oxidation state of the metals, for instance is Co2+ much more water soluble than Co3+. [7, 22, 28, 69]

Another way to improve leaching efficiency is by complexometric leaching. The method includes an extractant that is allowed to form complexes with the leached species. The complex formation removes solvated metal from the leach liquor, keeping its metal concentration low. Lower metal concentration increases the leach efficiency by altering the phase equilibrium.

Leaching can be performed on the electrode material directly after crushing or after other separation. It is also possible to leach the remaining slag after pyrometallurgical treatment but slag can be hard to leach effectively. [16, 23, 29]

The separated electrode powder is mixed with solutions to solubilise all metals of the powder. Usually aqueous solutions of muriatic acid (HCl), nitric acid (HNO3) and sulphuric acid (H2SO4) are used. With a filtration the solid residuum of graphite and PVDF is separated from the solution. The disadvantage of this process is the slow dialysis and the usage of aggressive acids. [41]

The goal of the biological leaching is to solubilise the metal in the electrode powder. Therefore sulphur bacteria (acidithiobacillus ferrooxidans) are using sulphur, sulphide and 2-valuable ferric Ionics as energy source and are producing the metabolic products sulphuric acid (H2SO4) and 3-valuable ferric Ionics. The leaching of the metal consequently is indirect with the produced sulphuric acid. [41]

**IV.1.1 Precipitation**

Precipitation is the process of getting elements out of solution by producing insoluble compounds. This process takes place after the leaching to remove metals from the solution as hardly soluble compounds. Common procedure is adding other chemicals that react with solvated species forming insoluble salts that precipitate. Altering pH or temperature may also give precipitation by changing the solubility. [16, 41, 69]

The precipitate can be recovered by centrifugation or filtration. The advantage of the precipitation reaction is the re-use of the material if a suitable solidifying agent was used. A disadvantage is a possible rest solubility of the connection and the soiling of the metal connections which makes an additional cleaning step necessary. [41]

Most of time precipitate requires a washing step to remove impurities which are drifted during the precipitate formation. Hydroxide or metal salt forms can be produced by precipitation.

**IV.1.2. Ion exchange**
In ion exchange a solution with metal (or other ionic compound) in solution is passed through a bed of resin with high affinity for certain ions. Usually the affinity is limited to either anions or cations. [16, 41, 69]

Weak acid resins (cation exchange resins) have a high affinity for the hydrogen ion and are therefore easily regenerated with strong acids. The acid-regenerated resin exhibits a high capacity for the alkaline earth metals associated with alkalinity and a more limited capacity for the alkali metals with alkalinity. No significant salt splitting occurs with neutral salts. However, when the resin is not protonated (e.g., if it has been neutralized with sodium hydroxide), softening can be performed, even in the presence of a high salt background. Strong acid resins are sulfonated copolymers of styrene and DVB. These materials are characterized by their ability to exchange cations or split neutral salts and are useful across the entire pH range.

Weak base resins (anion exchange resins) do not contain exchangeable ionic sites and function as acid adsorbers. These resins are capable of sorbing strong acids with a high capacity and are readily regenerated with caustic. They are therefore particularly effective when used in combination with a strong base anion by providing an overall high operating capacity and regeneration efficiency.

After absorption the resin phase is washed with another fluid to extract the absorbed metals. Depending on the affinity properties of the resin material selective absorption of a certain metal may be achieved. The process can also be used for concentrating metal solution by passing large volumes of low concentrated metal through the ion exchanger and then wash with a small volume of suitable eluent. [16, 41, 69]

Ion exchange regeneration technology has developed over the years from the early co-flow regenerated systems to counter-flow block systems and through to packed bed technology process. Counter-current regeneration systems [119] have reduced chemical costs, improved water quality and less waste volumes compared to traditional co-flow regenerated systems. They are also more productive, utilizing smaller vessels, faster regenerations and fewer mechanical failures.

IV.1.3. Solvent extraction

Solvent extraction makes use of a two phase system normally consisting of an organic phase and an aqueous phase which are immiscible. Separation of substances can be achieved because of uneven distribution of a substance between the two phases. As metals in aqueous solution are present as charged species they are generally not soluble in organic non-polar solvents. [16, 41, 69]

Adding complexing agents to the solution makes possible the formation of uncharged (and other) species. Hydrophobic complexes will easier transfer to the organic phase giving an uneven distribution of the metals allowing them to be separated. A complexing agent with higher selectivity towards forming complexes with a specific metal improves selectivity. Even if the selectivity is only slightly higher for one metal very good separation can be achieved by using multiple stages.

Elements belonging to the same group of the periodic table are often close in chemical properties are harder to separate. [16, 69]

Extractants as di-(2-ethylhexyl) phosphoric acid (D2EHPA), bis-(2,4,4-tri-methyl-pentyl) phosphinic acid (Cyanex 272), trioctylamine (TOA), diethylhexyl phosphoric acid (DEHPA) or 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) are usually used to separate the metals in some hydrometallurgical process. [120-123]
A possible method is the selective linkage of specific metal ions through a water-insoluble organic dissolver. The rest of the metal ions remain in the liquid solution. Both solutions can be separated through its difference of density. To recover the in the solution bounded metals, a vaporization or an electrolysis is possible.

Another technique is to separate both solutions with metal ions as a result of their density difference. Then the precipitation of the metals is possible at clearly defined pH-values. [41]

The advantage of solvent extraction is the selectivity. It is possible to extract single metals ions, e.g. lithium ions, from a solution. The regained complexes often have a higher quality than precipitated complexes. It big disadvantage is the high price and the toxicity of the solvents (benzene, toluene, kerosene,...) [69].

For instance this technique is used by Rhodia, leader in the separation of rare earths. The plant located in La Rochelle (France) has more than 1500 steps of separation in order to separate and purify rare earths [124]. Rare earths are produced in salt form. For the separation step, several solvents are used such as di(2-ethylhexyl) phosphoric acid, tri(n-butyl) phosphate, ammonium salt, carboxylic acids.

### IV.1.4. Electrochemical separation

To extract metal components out of solution electro-winning can be used to achieve the necessary reduction. In electro-winning two electrodes are used to supply energy to the solution and yields oxidation and reduction of ions in the solution. The method requires differing reductive and oxidative potentials for the metals present in the solution. Solvent extraction can be used to separate metals into different solutions thereby allowing for electrochemical deposition to produce very high purity metals. [16, 41, 69]

Another method is an electrolysis cell in which the electrodes are separated through a membrane. This membrane is just porous for metal ions. On the cathode side the metal ions are concentrated until the solubility product is exceeded and solid metal hydroxides are precipitating. In another technique gaseous carbon dioxide is brought into the electrolysis cell that initiates the precipitation of lithium carbonate at the cathode side. Electrochemical processes are slow and their productivity is low. [41]

### IV.2. Pyrometallurgy

Any pyrometallurgical process involves heating and the addition of thermal energy causes reactions that transform the material. At lower temperatures the reactions involve phase transitions and structural changes while at higher temperatures chemical reactions are involved to a greater extent. Using high temperatures batteries can be smelted. This gives a metallic fraction, slag and gases. The gaseous phase contains volatile decomposition products of the organic materials; it also contains any volatile metal (such as Hg and Zn if present). [16, 29, 41, 69]

The pyrometallurgical technique is usually used in industrial furnaces where metalliferous materials and metals are produced or cleaned. The processes are handled with oxidation or reduced process steps. The metallurgical process is a technique of smelting with reducing agent to gain metal. Refinement is the direct removal of contaminant of the metals. A further method is the liqation where the melted mass is decomposed during their coagulation. A process of distillation is also possible. [97]

Pyrometallurgical processes are fast and easy to handle. After smelting the batteries or cells a metal alloy and a slag are produced. There is no safety risk through the electrolyte. Furthermore a reduction of the fuel consumption by burning plastics, electrolyte and carbonate is reached. On the other hand the formation of the metal alloy makes it nearly impossible to gain specific metals. Organic components of the battery are burned and not recyclable. Aluminium or lithium is found in the slag. The recovery from the
slag could be realized by condensation or hydrometallurgical processes. Through its high temperature pyrometallurgical processes have a high energy consumption. Furthermore complex and costly flue gas cleaning is necessary. [80, 94, 95, 96]

**IV.2.1. Calcination / Pyrolysis**

Calcination is the process of mild heating in order to thermally decompose material for instance to change the structure of a crystalline phase. It can also be utilised in order to evaporate volatile components from the other material. The reactions that occur during calcination are internal reactions that only involve the material itself. [16, 26, 69]

At temperatures up to 700°C the organic components of the cells are decomposing. When the atmosphere is controlled carbon stay as rest of the organics. The metallic components are stable in the metallic or oxidized form.

**IV.2.2. Reduction / Smelting**

Heating the material extensively produces a smelt. Since metals are oxidised (donate electrons) when forming chemical bonds the reverse reaction must supply electrons. Adding reducing agents (e.g. coke) allows for the (bound) metals to be reduced to metallic phase. The metallic smelt contains the ferrous metals while those with low affinity to oxygen ends up in a slag. Depending on the addition of slag formers and other chemical agents the slag inertness and its contents can be altered. [16, 23, 29, 69]

**V. Recycling processes**

There are several existing processes for the recycling of lithium-ion batteries. Most of them are focused on recycling of the small portable batteries that dominate today and the primary objective is cobalt recovery. [8, 24, 41, 69]

For the recycling of tractions batteries several processes has been adapted and developed. Following figure 9 gives a brief overview on alternative routes in recycling processes.
Figure 9: overview over recycling processes

Toxco and Sony were the first processes for recycling lithium-ion batteries. Both facilities are still in operation but in recent years several others have started. [5, 8, 23, 69]

Umicore has an industrial operation in Hoboken, Belgium with an industrial capacity of 7,000 tonnes of batteries per year which is equivalent to some 150,000 (H)EV batteries or 250 million mobile phones batteries.

Table 4: Overview on existing, industrial battery recycling processes [98]

<table>
<thead>
<tr>
<th>Process name</th>
<th>Enterprise</th>
<th>Process</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>Fernwärme Wien</td>
<td>No data</td>
<td>A</td>
</tr>
</tbody>
</table>

Recycelt materials
No longer in use metals
<table>
<thead>
<tr>
<th>Process Type</th>
<th>Company/Institution</th>
<th>Technology</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>Umicore process</td>
<td>Umicore Recycling Solutions</td>
<td>Pyrometallurgy</td>
<td>B</td>
</tr>
<tr>
<td>Batrec-Sumitomo process</td>
<td>Batrec Industrie AG</td>
<td>Pyrometallurgy</td>
<td>CH</td>
</tr>
<tr>
<td>Vacuum distillation</td>
<td>Accurec Recycling GmbH</td>
<td>Pyrometallurgy</td>
<td>D</td>
</tr>
<tr>
<td>Valibat process</td>
<td>Recupyl</td>
<td>Hydrometallurgy</td>
<td>F</td>
</tr>
<tr>
<td>Sony-Sumitomo process</td>
<td>Sony Corp. &amp; Sumitomo Metals and Mining Co.</td>
<td>Pyrometallurgy</td>
<td>J</td>
</tr>
<tr>
<td>AEA process</td>
<td>AEA Technology Batteries</td>
<td>Pyrometallurgy</td>
<td>UK</td>
</tr>
<tr>
<td>Toxco process</td>
<td>Toxco Incorporation</td>
<td>Hydrometallurgy</td>
<td>USA</td>
</tr>
<tr>
<td>Salesco Systems</td>
<td></td>
<td>Pyrometallurgy</td>
<td>USA</td>
</tr>
<tr>
<td>AERC</td>
<td></td>
<td>Pyrometallurgy</td>
<td>USA</td>
</tr>
<tr>
<td>OnTo Technology</td>
<td></td>
<td>Solvent extraction</td>
<td>USA</td>
</tr>
<tr>
<td>INMETCO</td>
<td></td>
<td>Pyrometallurgy</td>
<td>USA</td>
</tr>
</tbody>
</table>

Li-ion batteries recycling: ELIBAMA Breakthrough

To overcome the technical or environmental issues shown through the state of the art which limit the recovery efficiency, several investigations have been done during the ELIBAMA project on:

- Electrolyte recovery,
- Dry sorting techniques,
- Hydrometallurgical treatment for metal extraction and new active materials recycling,

Electrolyte recovery
In order to recover the electrolyte solution composed of a Li salt (LiPF6, LiTFSI,...) and fused carbonates (propylene, ethylene, dimethyl, ethyl-methyl carbonate,...), used batteries must not be exposed to pyrolysis treatment. The recovery process developed is based on a liquid phase extraction and consists in a liquid extraction of electrolyte solution by a second solution. Then, carbonates and Li salt are separated in different fractions for their selective recovery as it is shown in the figure 10.

![FTIR analysis of solutions used and obtained in the electrolyte extraction](image)

**Figure 10: FTIR analysis of solutions used and obtained in the electrolyte extraction**

The study led in ELIBAMA mostly by CEA and SOLVAY was focused on:

- The selection of the second solution which extracts electrolyte solution. In this frame, various organic solvents were evaluated. For this evaluation, several criteria were defined such as cost, HSE risk, electrolyte species solubility and evaporation temperature.
- The management of HF formation from LiPF6 in contact to water or moisture which is considered as a key point. Here, several HF capture components were considered and their efficiency to prevent the HF formation were studied. A reduction of HF formation about 70% was measured with less than 120 ppm in solutions.
- The separation of recovered carbonates was also investigated to produce relatively pure carbonates.
- The regeneration of extracting solution was also considered in the project and shown a promising results.

**Dry sorting methods**

**Electrostatic technique**

An electrostatic separator is based on the principle of corona discharge, where two plates are placed close together and high voltage is applied (figure 11). Electrostatic techniques is used to separate crushed particles of materials mixture. Electrostatic separating is most often used in the process of sorting large amounts of mineral ore at industrial scale. But other materials sorting can also use the same principle such as metals separation or polymers separation.
By ELIBAMA project, Fraunhofer IPA has investigated the electrostatic technique (figure 12) in order to separate materials contained in samples produced by SNAM after pyrolysis and crushing. The samples were composed of Al, Cu, carbon and Li mixed oxides particles.

According to experimental conditions such as plates distance, plates inclination, applied voltage and rotor velocity, some concentration effects were measured on materials fraction produced. Indeed, it was shown that the separation between Al and Cu, between metals and none metallic materials, between carbon and Li oxide materials are possible. For instance, a sample containing 78% of carbon was produced with a single run on the device.

**Dry sorting by crushing and screening**

The separation technique of materials by screening is very used because cost efficient and easy to carry out and in many applications such as in building materials sorting.
By a very different mechanical behavior of metal sheets (current collectors) and active electrode which are composed of powders (carbon and oxide), the crushing operation leads to the formation of large population of particles depending on the mechanical materials properties. As metals present a very ductile behavior, the size reduction during the crushing step is lower than the electrode materials.

The work done here was focused on the determination of most suitable screen mesh to separate materials after crushing to produce different materials fractions concentrated in a targeted material.

According to the mesh size used in the screening step, a relative separation is observed as it is indicated by the figure 12.

![Figure 12: Materials distribution versus particles size](image)

As it is shown, metals are rather concentrated in the coarsest size fraction whereas in oxide and carbon particles are rather concentrated the finest particles fraction.

**Hydrometallurgical treatment**

Regarding the hydrometallurgical process to extract and/or purify metal elements from a mixture, several studies were conducted by CEA with the objective to operate as possible in closed loop:

- NCA based batteries in order to recover separately Co and Ni
- NMC based batteries in order to separate Ni, Co and Mn,
- LFP and LTO based batteries which represent an economical issue due to the low value of elements (Fe, li and P).

Hydrometallurgical processes investigated here are based on a dissolution or leaching step thanks to strong acids (sulfuric, chlorhydric or nitric) and a chemical separation to extract relatively pure species from others.
For instance, the table 4 gives a chemical analysis of recovered hydroxides from NCA used battery showing the ability to recover elements with low impurities. Moreover, some residual impurities (Na, Li) can be removed easily by extensive washing.

Table 4: Composition of recovered metal elements from used NCA battery

<table>
<thead>
<tr>
<th>Precipitate</th>
<th>Purity</th>
<th>Li</th>
<th>Ni</th>
<th>Co</th>
<th>Al</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_2$O$_3$, 3H$_2$O</td>
<td>90.25 ± 0.45</td>
<td>0.49 ± 0.04</td>
<td>5.78 ± 0.23</td>
<td>–</td>
<td>3.31 ± 0.17</td>
<td>0.18 ± 0.17</td>
</tr>
<tr>
<td>Ni(OH)$_2$</td>
<td>96.36 ± 0.04</td>
<td>0.18 ± 0.01</td>
<td>–</td>
<td>2.26 ± 0.03</td>
<td>1.06 ± 0.02</td>
<td>0.13 ± 0.02</td>
</tr>
</tbody>
</table>

The leaching of active materials is very depending on the battery chemistry (i.e. Li mixed oxide composition). The NMC chemistry shows a specific behavior with the presence of Mn$^{4+}$. Indeed, during leaching a passivation layer very rich in Mn is observed and stop the dissolution reaction. The figure 13 shows an EDX cartography of a Li mixed oxide particle after leaching.

Figure 13: EDX cartography of a Li mixed oxide particle after leaching in sulfuric acid

For LFP and LTO based materials, the approach was to study the release of elements versus the pH of leaching solution. Indeed, as it is shown in the figure 14, Li, Fe and Ti have a specific range of pH where they are soluble selectively. By such approach, it is possible to extract selectively elements and reduce the chemical reactants consumption in comparison with a typical complete materials dissolution approach. Moreover, the purity of recovered elements is higher as well.
Li-ion batteries recycling: Perspectives for the future

Considering the current processes of recyclers today, several ways of improvement can be formulated:

- Regarding the handling of damaged batteries more specific regulations should be developed to give better orientation and a more specific action guideline.
- The Li-ion batteries chemistry is a key point to design the relevant process. Indeed, according to the global composition (packaging, modules and cells scale) and the batteries design, the efficiency of a recycling process can change significantly. A normalization aiming at indicating the batteries specific chemistry could improve the recycling efficiency and operating cost.
- To perform the recycling process has to be flexible enough to accept most of chemistry with a high efficiency.
- Electrolyte recovery is also to consider in order to increase the global materials recovery rate. This component represent about 12 to 20%wt of the cell weight. To date no industrial scale process is able to do this operation. In addition, electrolyte recovery means the ban of pyrolysis which is sometimes used to secure the batteries.

One of key points for the recycling process will be to reduce the cost and recover the maximum of materials.
The battery design must allow an easy access to modules and cells, the standardization of connectors will help also in the standardization process.

Regarding the thermal process, some investigations are needed in order to optimize the energy consumptions. The recovery of energy spent during the process must be investigated. Base on the first trails, the off gas treatment is different according to batteries technologies. Recovery of some elements (Li, Zn) can be done in the bag house filter.

The target will be to work with a continuous process with a low temperature in the beginning, and then an increase with energy contained in the battery.

In parallel of materials recovery, the second life of the battery must be developed. Many points need to be solved. Standardization of the packaging and the electrical wire connection. Access to the BMS. Easy replacement of bad parts, cells modules...

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Contacts

CEA: Richard LAUCOURNET
richard.laucournet@cea.fr

SNAM: Gilles GARIN
gilles.garin@snam.com

EDI VEOLIA: Elise SENECHAL
esenechal@sarpindustries.fr

UMICORE: Begum YAÇICI&_OGLU
begum.yazicioglu@umicore.com

The ELIBAMA project is granted by the European Commission under the “Nanosciences, nanotechnologies, materials & new production technologies” (NMP) Theme of the 7th Framework Programme for Research and Technological Development.