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CRITICAL REVIEW ON LITHIUM ION BATTERY RECYCLING TECHNOLOGIES

Master´s Programme in Chemical, Biochemical and Materials Engineering
Major in Functional Materials

Master’s thesis for the degree of Master of Science in Technology
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Abstract

The purpose of this thesis is to offer a critical review of existing and emerging recycling technologies for lithium ion batteries (LiBs), based on a literature research. Additionally LiBs as sources of secondary raw materials are described, and the current status and possibilities of mechanical processing methods in LiBs recycling is studied. Five industrial and four emerging technologies are analysed in detail based mainly on information provided by scientific articles and patents.

LiBs are used increasingly for providing energy to portable applications and electric mobility. The operation principle of LiB is based on the layered active electrode materials that enable Li-ion insertion and transfer between the electrodes during discharge and charge. The performance and properties of LiB are especially dependent on the active cathode material. In present commercial LiB cells it consists of one of the five different compound types containing Co, Ni, Mn and Fe in different proportions, in addition to Li. Other materials in LiBs are graphite, Al and Cu foils, polymeric separator, electrolyte consisting of Li salt and organic materials, and the cell casing of stainless steel, Al or polymer. End-of-life batteries can have charge left, they can produce flammable and toxic gases, and they can contain flammable elemental Li – facts that have to be considered in recycling process.

In the studied technologies, mechanical, pyrometallurgical and hydrometallurgical techniques are utilized in different combinations for the recovery of LiB materials. Usually pyrometallurgical or mechanical treatment starts the process, followed by hydrometallurgical recovery of the cathode materials. Pyrometallurgical treatment loses Al and Li in slag but has the capability of treating mixed feed. In mechanical treatment, more materials can be saved but extra attention is needed for safe handling of the batteries: the batteries are discharged prior to crushing, and/or comminution is carried out in protective medium. The crushed materials are separated with magnetic (Fe, SS) and density based materials (Al, Cu, polymers), and differing particle size of particular materials. Combination of several crushing and separation steps or thermal treatment can be used for improved detachment of active cathode material from the foil which is crucial for the success of the recovery of cathode materials in the following hydrometallurgical treatment.

Only part of the once high-cost primary materials of the cell can be feasibly recycled to be used again. Co has been the driving force for recycling LiBs. Li is usually recovered in the end as a carbonate. For graphite and electrolyte recovery there exists methods, but the economic feasibility is questionable. Different organic materials have in general lost their value in the end-of-life of the cell. In some emerging technologies the goal is to produce cathode precursor material directly as an outcome of the mechanical and hydrometallurgical steps. This potentially saves more of the original cathode compound value, but requires also stricter processing conditions and control of the feed. Novel technologies consider the recovery other cathode compound materials than just Co, but are not able to treat the mixed cathode materials at the same time. Especially $LiFePO_4$ is challenging material, because it has a low recycling value, and constitutes an impurity in the leaching process.

Keywords Lithium ion battery, recycling, recovery, mechanical processing, circular economy

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Tiivistelmä

Työssä analysoidaan teollisia ja orastavia litiumioniakkujen kierrätysteknologioita sekä mekaanisten prosessointimenetelmien asemaa ja mahdollisuuksia niiden osana. Analysoitavana on viisi teollista ja neljä orastavaa teknologiaa, ja tietolähteinä ovat pääasiassa tieteelliset artikkelit ja patentit.

Litiumioniakkuja käytetään energialähteenä kannettavissa sovelluksissa ja sähkökäyttöisissä liikennevälineissä. Kennon toiminta perustuu elektrodimateriaaleihin, joiden kerroksittainen rakenne mahdollistaa litiumionien liikkumisen elektrodilta toiselle akkua purettaessa ja ladattaessa. Tämänhetkisissä kaupallisissa litiumioniakuissa aktiivinen katodimateriaali on yleensä jokin viidestä vaihtoehtoisesta siirtymämetalliyhdisteestä, jotka sisältävät litiumin lisäksi kobolttia, nikkeliä, mangaania tai rautaa eri yhdistelminä. Kenno sisältää myös grafiittia, kuparia ja alumiinia, litiumsuolasta ja orgaanisista yhdisteistä koostuvan elektrolyytin sekä polymeerierottimen elektrodien välissä. Kennokotelon materiaalina voi olla alumiini, ruostumaton teräs tai polymeeri. Kierrätysprosessissa on huomioitava, että kennoissa on useimmiten latausta jäljellä, ja anodille on käytön aikana voinut pelkistyä herkästi syttyvää alkuainelitiumia. Lisäksi kennoissa voi käsittelyn aikana muodostua herkästi syttyviä ja myrkyllisiä kaasuja.

Tutkituissa kierrätysprosesseissa käytetään mekaanisten, pyrometallurgisten ja hydrometallurgisten tekniikoiden erilaisia yhdistelmiä. Katodimateriaalien talteenotto toteutetaan lähes aina hydrometallurgisella menetelmällä. Pyrometallurgian epäkohtana on, että alumiini ja litium menetetään kuonaan. Toisaalta pyrometallurgisen prosessin syötteenä voi olla laajempi materiaalien kirjo. Mekaanisessa prosessoinnissa suurempi osa materiaaleista voidaan ottaa talteen, mutta toisaalta akkujen turvallinen käsittely vaatii erityistä huomiota. Akut on purettava ennen murskausta, joka on lisäksi suoritettava suojakaasussa tai -liuoksessa. Murske voidaan jaotella eri materiaaleihin (rautapohjaiset materiaalit, alumiini, kupari, polymeerit) seulonnan sekä magneettisuuteen ja tiheyteen perustuvien menetelmien avulla. Useammilla murskaus- ja luokittelukerroilla tai lämpökäsittelyllä voidaan parantaa katodijauheen erottamista alumiinista ja kuparista, mikä on tärkeää hydrometallurgisen liuotusprosessin onnistumiseksi.

Vain osa alun perin arvokkaista kennon materiaaleista voidaan kannattavasti ottaa talteen. Erityisesti koboltti on ollut kannustin litiumioniakkujen kierrätykselle. Litium otetaan yleensä talteen karbonaattina. Grafiitin ja elektrolyytin talteenotolle on olemassa menetelmiä, mutta se ei ole taloudellisesti kannattavaa. Suurin osa orgaanisista materiaaleista on menettänyt arvonsa käytetyssä kennossa. Osassa nousevia teknologioita pyritään tuottamaan suoraan mekaanisen ja hydrometallurgisen käsittelyn tuloksena katodiyhdisteen esiastetta, kuten siirtymämetallioksidia. Näin menetellen säilytetään mahdollisesti enemmän alkuperäisen katodiyhdisteen arvosta, mutta haittapuolena on, että prosessointiolosuhteita ja syötteen koostumusta on vastaavasti kontrolloitava tarkemmin. Nousevat teknologiat pyrkivät pääsääntöisesti ottamaan talteen myös muita katodiyhdistemateriaaleja kuin koboltin, mutta ne eivät pysty käsittelemään erilaisia katodiyhdisteitä samalla kertaa. Haastavin katodimateriaali on litiumrautafosfaatti, jonka kierrätysarvo on alhainen ja jonka sisältämä rauta on epäpuhtaus koboltin, nikkelin ja mangaanin liuotusprosessissa.

Avainsanat Litiumioniakku, kierrätys, talteenotto, mekaaninen prosessointi, kiertotalous

Foreword

This thesis was performed with the support of the Academy of Finland as part of the "CloseLoop for high-added value materials (CloseLoop)" project.

I wish to thank my supervisor Professor Rodrigo Serna for the interesting thesis subject and the inspiring conversations we had. Equally, I want to thank my advisor Annukka Santasalo-Aarnio for the enthusiasm, the knowledge and the support she provided, and for leading me to this subject in the first place.

Many people have believed in me during this journey and I am most thankful for that. However, my studies would not have been possible without my ever understanding and supporting husband, Ari. Thank you so much!

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Abbreviations

DMC	Dimethyl carbonate
EBRA	European Battery Recycling Association
EC	Ethylene carbonate
EMC	Ethyl methyl carbonate
EV	Electric vehicle
GNI	Gross national income
HEV	Hybrid electric vehicle
LiB	Lithium ion battery
LCO	Lithium cobalt oxide, $LiCoO_2$
LFP	Lithium iron phosphate, $LiFePO_4$
LMO	Lithium manganese oxide, $LiMn_2O_4$
LNO	Lithium nickel oxide, $LiNiO_2$
MeO	Metal oxide
NCA	Lithium nickel cobalt aluminum oxide, $LiNiCoAlO_2$
NiMH	Nickel metal hydride (battery)
NMC	Lithium nickel manganese cobalt oxide, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
PC	Propylene carbonate
PHEV	Plug-in hybrid vehicle
PP	Polypropylene
PVDF	Polyvinylidene fluoride
SEI	Solid-electrolyte interphase
SLI	Start, light and ignition
SS	Stainless steel

1 Introduction

Since the launching of LiBs in the beginning of 1990's, the world has developed remarkably both from a technological and economical perspective (HDR 2015). Unfortunately, this has also resulted in an accelerated exploitation of natural resources. For example, the Earth Overshoot Day – the day when the Earth's yearly "production" of resources has been used – has consistently moved earlier and, in year 2016, it was already on the 8th of August (Earth Overshoot Day n.d.). It is hence obvious that the Earth cannot bear the linear economy of expendable goods, but circulating goods and materials in use for longer periods of times and several rounds should be favoured, hence move to circular economy.

A major part in the implementation of the targets of a circular economy model is recycling. As a general definition, recycling refers to the processing of constituent materials of an end-of-life product and incorporating them back to the material value chain. However, it is important to understand, that recycling does not come without consequences, environmental and economical. Recycling has to be a feasible and safe business that has customers for the recycled end products. Additionally, recycled components and materials should not have environmental effects exceeding those of the primary materials. Recycling complex, variable and constantly developing objects is bound to increase the costs of recycling (van Beukering et al. 2014, p. 480), and the uncertainty related to this issue affects the development and boom of new technologies. Uncertainties could be to some point alleviated with supporting operations and cooperation between different actors in the life cycle of products.

Recycling is also a question of balancing targets and costs in an uncertain context: what end products to pursue, what investments to make for the future, etc. Optimizing the recovery of specific components or material might lead to loss of some other materials. Moreover, the closer the recycled material is to the pristine material or a recycled/reusable product to the new product, the more obligations by the performance and safety requirements of the new products are associated. In summary, several possibly contradictory objectives have to be taken into consideration when designing economically and environmentally sustainable recycling process and trying to close the loop for resource circulation.

Lithium ion batteries (LiBs) for example, contain valuable metals such as Co, Ni, Cu and Al and their manufacturing has required substantial amount of energy especially considering the active materials that require high purity levels. LiBs have become an increasingly important product as they are used to power a wide range of devices, including mobile phones, tablets, electric cars and other consumer electronics. In the year 2015 alone, an estimated 5.6 billion LiB cells were sold worldwide (Pillot 2016). One would think that this kind of precious waste is widely and efficiently recycled. However, at the moment only 5% of LiBs are officially recycled to some extent, while the majority ends up to landfills or is just hoarded by the users. This situation can be attributed to several factors, ranging from incomplete legislation, shortage of efficient collection systems, up to the lack of feasible recycling technologies for the rapidly evolving, mixed LiBs waste. Whatever the causes, the current situation represents a severe waste of natural resources and needs to be improved. The purpose of this thesis is to offer a critical review of existing and emerging recycling technologies for LiBs. Another important task is to describe LiBs as sources of secondary raw materials, hence identifying incentives and challenges of recycling them and providing background for different levels of recycling. A particular aim of this thesis is to study the current status and possibilities of mechanical processing methods in LiBs recycling. This review work is part of the Academy of Finland "Closing the Loop for High-Added-Value Materials (CloseLoop)" project.

The present thesis is organized as follows. Chapter 1 provides definitions for some of the main concepts related to batteries used later in this thesis. The second part of Chapter 1 elucidates the methodological principles used in the composition of this thesis. Chapters 2 and 3 give background to the analysis of recycling processes: in Chapter 2 the constructions and chemistries of Li ion batteries are described and Chapter 3 is focused on describing recycling as a concept and LiBs as recyclates. The recycling processes are described in Chapter 4 and further analysed in Chapter 5 before final conclusions are provided in Chapter 6.

1.1 Definitions of main concepts

In order to have a clear understanding of the topic being discussed in the present thesis, it is necessary to clearly establish the definition of some main concepts related to battery technologies. In this context, **"cell"** is a basic electrochemical unit that is operational and consists of electrodes, separator, electrolyte, container and terminals. A "**battery"** can contain one or multiple cells and electrical connections to transfer the electrical power contained in such cells (Linden and Reddy 2011; p. 1.3). One cell is typically enough to provide sufficient energy for small scale applications, but batteries used for mobility or storage consist of more complicated assemblies (Daniel 2008). For example, to provide a conventional operation voltage of 100-500 V for an electric vehicle (EV), a combination of tens or hundreds of cells (á 3-4 V) is required (Corrigan and Masias 2011, p. 29.10).

Another distinction worth mentioning is the classification of batteries based on its reusability. A **"primary battery"** can supply the energy it contains only once until reaching its end-of-life, whereas a "**secondary battery"** can be recharged several times during its life cycle (Linden and Reddy 2011, p. 1.4-1.5; Reddy 2011, p. 15.8). Usually, a secondary battery is considered serviceable as long as it can provide a charging depth of 80% compared to its original capacity (Reddy 2011, p. 15.8). When the battery is being used (i.e. when an external load is connected to it), the electrons flow from the negative to the positive electrode through the external circuit until it is eventually discharged, as depicted in the Figure 1. At the same time, positive ions (i.e., cations) move from the negative to the positive electrode through the electrolyte to balance the charge. At the positive electrode, a reduction reaction takes place while the negative electrode undergoes an oxidation reaction.

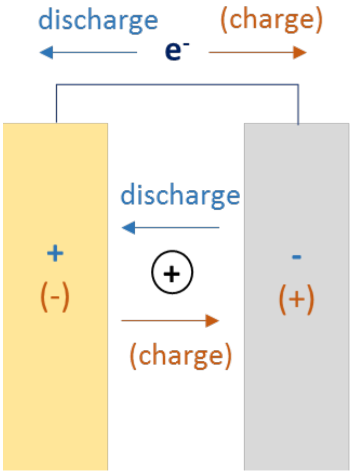

Figure 1 Schematic representation of a cell during the discharge and charge. During discharge, electrons flow in the outer circuit from the negative to the positive electrode, and the charges are balanced by the positive ion flow to the same direction, but through the electrolyte. During charge the flow of electrons and positive ions is the opposite.

When a secondary battery is re-charged, the electrons are forced to flow from the positive electrode to the negative electrode through an external circuit and the flow of cations through electrolyte is from positive electrode to negative, hence also the redox reactions take place at opposite electrodes.

In the explanation above it is necessary to understand that in primary battery, the electrodes considered as **anode** (**negative electrode)** and **cathode** (**positive electrode)** will remain so until the end of their life. However, in secondary batteries, whether an electrode is considered as anode or cathode depends on whether the battery is charged or discharged. It is a convention to refer to an electrode as anode or cathode based on its operation during discharge in secondary batteries, thus in Figure 1 the right-hand-side electrode is anode and the left-hand-side electrode cathode. This convention is used also in this thesis complying with the trend in the LiBs recycling literature.

While the present work will focus on secondary Li-ion batteries, it is worth noting that **primary Li batteries** have been used since 1970's. They consist of elemental Li anode and varying cathode materials such as SO_2, $SOCl_2$, MnO_2, FeS and CF depending on the manufacturer. Various combinations of electrolyte solvents and Li salts are used. Despite their good electrochemical performance, they have remained unpopular compared to some other primary batteries mainly due to high cost and safety issues raised by the reactiveness of elemental Li. (Reddy 2011, p. 14.1-14.2). Their relevance considering this thesis lies in the fact that they usually end up to the same recycling processes as LiBs.

Regarding the operation of secondary batteries, a **charge cycle** refers to one complete charge and discharge event in a battery. **Cycle life** on the other hand, gives information of the longevity of the cell: how many charge cycles it is expected to provide. The **average voltage** of a battery refers to the averaged potential available in practice for electric current production when the battery is used (Linden 2011, p. 3.2).

The **specific capacity** (mAh/g) describes how much electricity is involved in the electrochemical reaction of the cell (Linden and Reddy 2011, p. 1.9). **Theoretical** specific capacity refers to the amount of electricity the cell could produce in total with the active materials it contains and the **practical** specific capacity to the electricity produced in practice i.e. the electricity left for use after energy losses. The greater the capacity the more energy the cell stores and provides. **Specific energy** (Wh/kg) on the other hand, expresses the available energy – duration of operation – per mass, while **power density** (W/kg) is the rate of electricity utilization per mass.

Rechargeable batteries are essential considering electric mobility devices, namely electric vehicles (**EV**), plug-in hybrid electric vehicles (**PHEV**) and hybrid electric vehicles (**HEV**). Additionally, large scale stationary energy storage applications constitute another important sector of utilization of secondary batteries (Linden and Reddy 2011; p. 1.4-1.5). Especially in the context of storing energy, the term **"accumulator"** is used instead of secondary battery (Linden and Reddy 2011 p. 1.5). In the European Union Council Directive 2006/66/EC (commonly referred to as the "**Battery Directive"**), the concepts battery and accumulator are used interchangeably. When in turn the applications are considered, the EU Battery Directive gives the following classification and definitions for batteries:

- **Portable** battery: “*sealed, can be handheld and is neither an industrial nor automotive battery*”
- **Industrial** battery: “*Designed exclusively for industrial or professional uses or is used in any type of electric vehicle*”
- **Automotive** battery: “*Used for automotive starter, lighting or ignition (SLI) power*”

Even though in the Battery Directive the traction batteries (i.e., the batteries that power the different types of electric vehicles) are classified as industrial batteries and the term automotive battery stands only for SLI, in the literature these terms are sometimes used in an interchangeable manner and the term automotive battery might either encompass or signify specifically traction batteries. It is important to bear this in mind when comparing different statistic related to batteries, for example. In the Battery Directive, the industrial battery stands also for the larger scale energy storage batteries that are not portable. The focus of this thesis is on the portable and traction batteries.

1.2 Methodology

This thesis presents a review on Li-ion battery recycling technologies based on a deep literature research used both for constructing background (Chapters 2 and 3) and providing data for the analysis (Chapters 4 and 5). Chapters 2 and 3 provide relevant information about construction, component materials and future perspectives of LiBs and introduce the concepts and principles of mechanical processing for recycling. This background sets up a basis for Chapters 4 and 5 that introduce and discuss the LiB recycling processes, respectively.

This research used existing reviews about the battery recycling technologies in general as a starting point, although such reviews were not specifically focused on LiBs. The purpose was to get acquainted with the history and current state of battery recycling practices (e.g. Espinosa et al. 2004; Ferella et al. 2008; Bernardes et al. 2004; Sayilgan et al. 2009) and the typical mechanical processing technologies currently used (Ruffino et al. 2011). Next, the attention was directed more specifically to LiBs through a compilation of published literature dealing with recycling technologies at industrial and laboratory scale (Xu et al. 2008; Vezzini 2014; Ordoñez et al. 2016; Zeng et al. 2014). Some articles were found including discussions on the state-of-the-art of battery recycling and new suggestions to existing problems related to mechanical processing during recycling (Al-Thyabat et al. 2013; Wang et al. 2016; da Costa 2015; Zhang et al. 2013; Zhang et al. 2014; Li et al. 2016; Meshram et al. 2014; Marinos and Mishra 2016; He et al. 2015; Granata et al. 2012).

As the focus was transferred to industrial LiB recycling processes, queries in scientific publications databases (Scopus and Google Scholar) were conducted using the search terms “Lithium ion battery recycling” or “LiB recycling” with and without additional key words such as “mechanical processing”, “separation” etc. For the analysis presented in Chapter 4, the focus was narrowed to the processes where LiBs specifically were the recycling target, alone or mixed with other type of batteries. Thus, processes that accept LiBs but do not specifically address recovering their materials were not included in the detailed analysis. As a result of this phase, the processes from Umicore VAL’EASTM, Retriev Technologies, Recupyl Valibat, AkkuSer and Sumitomo-Sony were identified as the relevant objects of analysis.

Although critical reviews of the existing industrial LiB recycling processes are available, the present study aimed at analysing emerging technologies too. An important incentive for this decision was the apparent mismatch between the existing industrial technologies and the several commercial cathode types. The newer technologies included to this thesis are not merely lab-scale prototypes, but also include technologies at a pilot plant scale (LithoRec), under permitting procedure (Accurec), under commercialization (Gratz), or having several patents already published (Steven Sloop: Onto Technology). In addition to having “commercial potential”, the selected references had to depict the complete recycling process with some precision, thus not concentrating only on one component (e.g., cathode material recovery). As this thesis if part of the wider CloseLoop project, any process claiming to be “closed-loop” was of special interest. Finally, even though lab-scale processes were not themselves objects of analysis, findings of several laboratory-scale studies or other early stage research were analysed. The idea of sustaining the different levels of the recycled product discussed especially in Chapter 5.1 in the context of cathode material recovery, was adopted from the work accomplished by Argonne National Laboratory (e.g. Dunn et al. 2012a).

Scientific articles, patents (granted or applications) and edited books in the field of LiBs were used as sources for details of the processes whenever they were available. Supplementary information was in some occasions obtained from company homepages and other internet based sources (e.g. presentations, battery recycling organization pages) in order to obtain as up-to-date information as possible. In such cases, process/company names and patent owners/assignees were used as search terms. The possibility of missing any relevant technology was tried to diminish by reading about the suspected non-LiB-oriented recycling processes from several sources and by trying to find as recent sources as possible. Research in the

"ResearchGate" web-based portal was occasionally carried out to corroborate that all the studies relating to certain recycling process had been identified. When seeking an article in the database, the automatically generated article suggestions were considered if they matched the central keywords. Literature research was done until no relevant new articles were identified using the search terms or in the references.

When the most relevant recycling processes were identified, it was attempted to extract the following information:

- What are the main products of the process and of what grade/quality are they?
- What phases does the process contain and what is the extent of it?
- What are the mechanical processing techniques used in the process?
- What are the phases following mechanical pre-processing: pyrometallurgical/hydrometallurgical/both/something else?
- What external inputs other than batteries do the processes require?
- What materials are separated throughout the process and with which methods?
- Where/how are the separated materials used?
- What kind of limitations or trade-offs are identified in the process?
- How flexible is the process considering the changing chemistries of the LiBs?
- Is the process limited to certain application types of batteries, e.g. traction batteries or consumer electronic batteries?

Answers to preceding questions were obtained with an acceptable degree of success. Regarding information from patent sources, challenges were found due to the vague details sometimes presented in order to maximize the patent coverage: in some cases, several optional technical solutions for certain process step might have been expressed without underlining the preferred one. In these cases, all claimed options were included in the process description. Another identified uncertainty is related to the ability to obtain proprietary information about the state-of-the-art especially regarding the earliest processes: improvements have most probably been carried out, even though details are not published. If new information had been obtained for recent reviews it was used also in this thesis to provide as up-to-date picture of the process as possible.

2 Lithium ion batteries (LiB)

A LiB is a secondary battery where both positive and negative electrodes are composed of a special Li-ion insertion material – structure that was developed as a concept already in the 1970’s (Tarascon and Armand 2001). When the battery is cycled, light Li-ions exchange between the positive and negative electrode (Dahn and Ehrlich 2011, p. 26.1) enabled by the active electrode material structure suitable for Li ion movements (Dahn and Ehrlich 2011, p. 26.6) as shown in Figure 2.

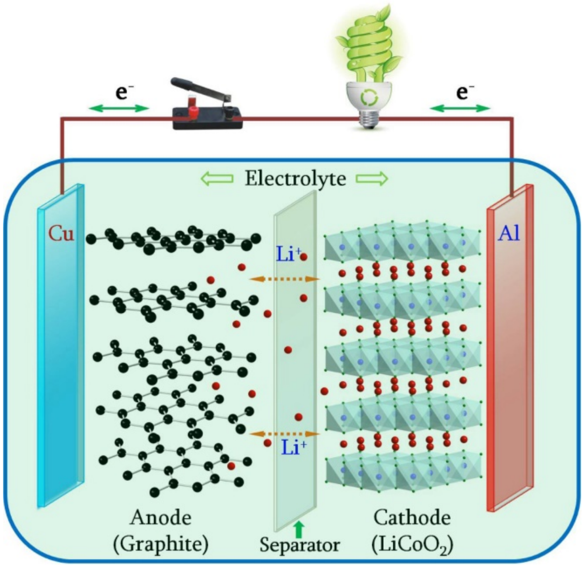

Figure 2 Operation principle and insertion materials of lithium ion battery. Figure from Liu et al. 2016.

LiBs were developed during the 1980’s and placed on the market at the beginning of the 1990’s (Nishi 2001). They soon became the chosen battery type in portable consumer electronics because of their light weight, high specific energy, high efficiency and long life time (Scrosati and Garche 2010; Gratz et al. 2014). Presently, LiBs are also the most appealing option for EVs and PHEVs as their energy density enables an extensive driving range without increasing the vehicle weight excessively. For the HEV-type electric car, the battery has more of a supporting role to a traditional combustion engine and thus a nickel metal hydride battery (NiMH) is a more used battery type in this case. (Xu et al. 2008; Corrigan and Masias 2011, p. 29.28, 29.45). In fact, among the secondary batteries, LiB represents the fastest growing battery type in the market, even though this group is still clearly dominated by Pb-acid batteries with a 90% market share (Pillot 2016), due to the extensive use of Pb-acid batteries in SLI and industrial applications (Salkind and Zguris 2011, p. 16.6-16.7). Compared to Pb-acid batteries, LiBs represent a more complex side of the rechargeable batteries: present commercial LiBs show a wide variation in composition materials especially considering the cathode materials. To clarify the complexity, the main components and variations of LiBs are introduced next, followed by a discussion about the future perspectives of LiBs.

2.1 LiB construction and components

As was already mentioned in section 1.1 the main electrochemical unit in batteries is a cell. Considering LiBs the four main cell construction types are cylindrical, prismatic, button and pouch cell, as presented schematically in Figure 3.

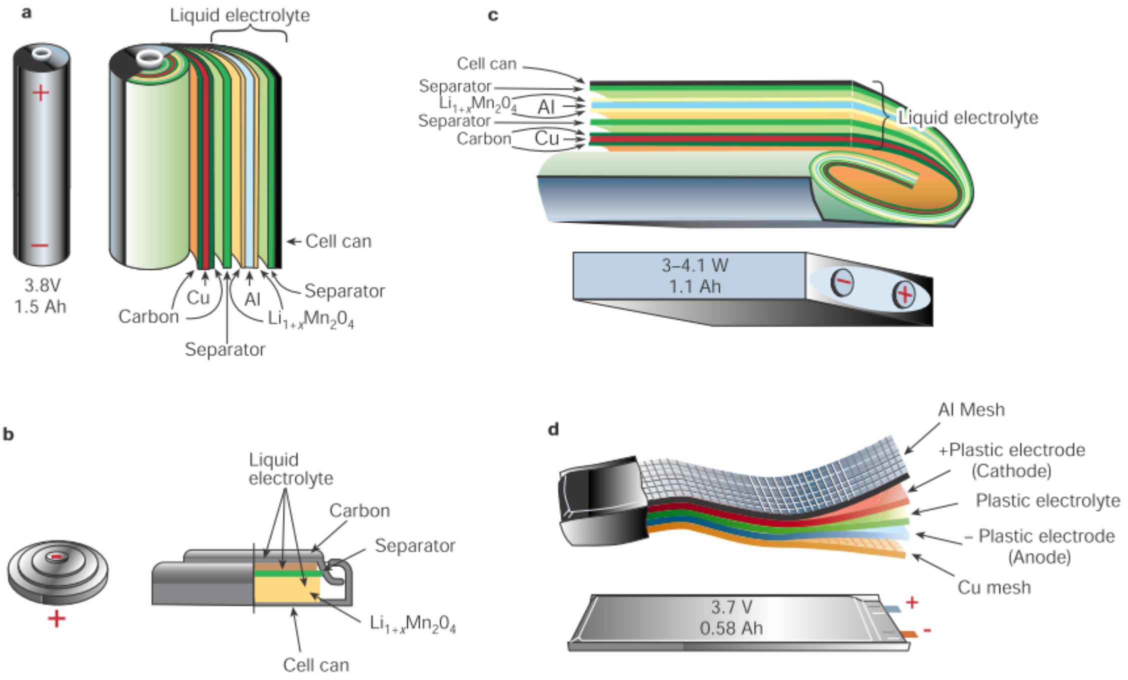

Figure 3 Main construction types of LiBs: a) wound cylindrical, b) button cell, c) wound prismatic and d) a pouch cell, also called a "polymer" Li ion cell. Figure from Tarascon and Armand 2001

Despite the differences in size and form, the cell types shown in Figure 3 also resemble each other regarding their component materials. All cells contain a cathode made of transition metal compound, an anode, two current collectors, an electrolyte, a separator and a cell casing (Dahn and Ehrlich 2011, pp. 26.41-44; Tarascon and Armand 2001). The cathode compound is the source of intercalating Li-ions and mainly defines the obtainable cell voltage. Usually it is a lithiated transition metal oxide or transition metal phosphate. (Dahn and Ehrlich 2011, p. 26.3). Since the cathode material is the component that varies the most in commercial batteries, thus affecting the recycling process, currently used cathode compounds are discussed separately in section 2.2.

The anode material should enable the efficient flow of Li-ions without excessive structural and volume changes (Scrosati and Garche 2010) and be able to conduct electrons. Compared to cathodes, the materials used in LiB anodes present a smaller variation. The most common anode active material is graphite since its layered structure provides a good basis for Li-ion intercalation. LTO ($Li_4Ti_5O_{12}$) is another commercial option used mainly in stationary applications due to its claimed combination of long cycle life, stability and inferior energy density (Dahn and Ehrlich 2011, p. 26.25-26.26). Nowadays, it is also common to use Si as additive to graphite for an improved specific capacity (Blomgren 2017).

To enable the conduction of electric current from the cell, the anode and cathode are connected to Cu and Al foil, respectively (Daniel 2008; Heelan et al. 2016). Al is a suitable material due to its light weight and good electrical conductivity. Furthermore, it offers corrosion protection for the surface by forming a passivation layer. However, Al cannot be used on the anode side because it would form an alloy with Li at low potentials, thus heavier and more expensive Cu is used instead. (Heelan et al. 2016). Between the electrodes there is also a separator preventing the electrodes from contacting each other and causing a short-circuit. Separator is a film like polymer made, for example, of microporous polyolefin. (Dahn and Ehrlich 2011, p. 26.39). Simultaneously, the separator has to provide a conduction path for the Li ions (Heelan et al. 2016) to enable cell operation. In the more recent cells, an additional ceramic coating can be used on one or both sides of the separator for more efficient prevention of conductive particle penetration (Blomgren 2017).

The main requirement for the electrolyte is to conduct Li-ions efficiently while preventing electron conduction. The electrolyte in LiBs consists of several components: a Li salt, most often $LiPF_6$, dissolved in a solvent that is usually a mixture of linear and/or cyclic carbonates such as ethlyne carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and an organic binder, usually polyvinylidene fluoride (PVDF). To enhance the cell performance or safety, different additives such as carbonates or phosphonates can also be added. (Heelan et al. 2016; Sloop 2010; Grützke et al. 2015). Finally, all the cell parts are enclosed with a casing that is most often steel or Al (Dahn and Ehrlich 2011, p. 26.42), of which the latter is favoured due to its lighter weight (Scrosati and Garche 2010). Also polymer casings are used, especially in the so-called “pouch-type” cells.

When selecting cell materials, compromises between several performance and safety-related requirements have to be made: e.g. energy and power capacity, cell voltage, cycle-life, thermal stability and temperature range of operation (Scrosati and Garche 2010; Christmann et al. 2015, p. 9). These properties are especially dependent on the selection of the cathode material. Moreover, it is essential that the chosen materials are compatible with each other and enable a safe use of the battery. Finally, both the materials and the manufacturing process must be technically and economically feasible. Depending on the specific intended application and its special needs, these criteria may have different order of importance, partly explaining the use of several cathode chemistries, as will be discussed later.

The exact manufacturing process of a cell depends on the each manufacturer's technology, but in order to further elucidate the construction and complexity of the cells, general steps are briefly described here. Both of the electrodes are in fact composite-like structures: in their manufacturing process, the current collector foil is coated with a paste consisting of active material powder (anode or cathode material), binder, solvent and a carbon-based additive to enhance conductivity. After spreading the paste on the foil, this construction is calendared and the dimensions of the structure are adjusted. Electrodes and separators are stacked in an inert atmosphere and fit into a casing filled with electrolyte. When the electrolyte has wetted the separator and the electrodes, the outer parts of the cells, such as seals and safety devices, are connected. (Daniel 2008). An essential part of the manufacturing process is to conduct the first charge and discharge cycles under controlled procedures. During this preparation cycle, typically referred to as the "formation phase", the capacity and voltage of the cell are controlled and the quality is confirmed. (Dahn and Ehrlich 2011, p. 26.41, 26.37; Daniel 2008). One important function of the formation phase is the controlled evolution of the solid-electrolyte interphase (SEI), which is discussed in more detail in the section 3.4.2 Degradation mechanisms.

In the battery packs for high energy-demanding applications consist of several cells, and external controlling systems e.g., for overcharging and temperature are required. The most complex non-stationary LiBs are the vehicle battery systems, one of which is depicted in the Figure 4.

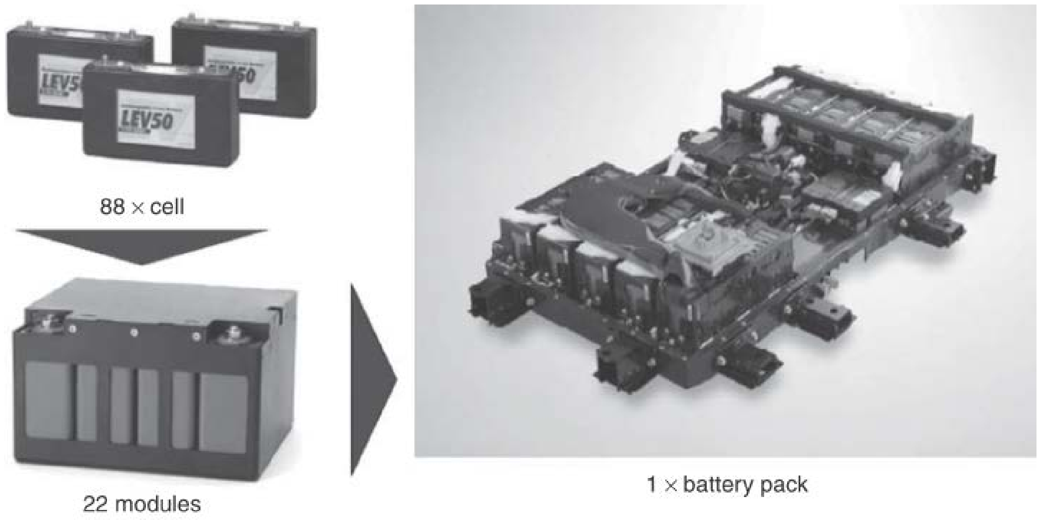

Figure 4 Example of an EV battery pack: Mitsubishi iMiEV battery consisting of 88 prismatic cells. Corrigan and Masias 2014, p. 29.19; original figure "Courtesy of Mitsubishi"

As shown in Figure 4, the battery packs used in electric vehicles consist of several parts: cells are first combined electrically and mechanically to modules that constitute a battery pack system. In addition, thermal management, cell voltage monitoring and control electronics have to be included for full and safe functioning of the system. (Corrigan and Masias 2014, p. 29.10). Unlike in the Figure 4, the EV battery packs often contain light pouch cells instead of cylindrical or prismatic construction (Sonoc et al. 2015). In an EV battery pack system, approximately 55% of the weight of the system results from the cells (Diekmann et al. 2017) and thus, almost half of the weight consists of the aforementioned control systems.

2.2 Cathode compounds

Li ion batteries are usually classified according to their cathodic active compound. Currently, five commercial types of cathode materials are dominant. Due to their particular strengths and weaknesses, each cathode type has suitable application areas that are shortly described in this section. A first point of comparison can be performance, as presented in Table 1, where the specific practical capacities and average voltages obtainable with different cathode materials are gathered.

Table 1 Specific practical capacities and average voltage provided by the main commercial cathode chemistries. The value ranges constructed based on Dahn and Ehrlich 2011, p. 26.8, Julien et al. 2014 and Nitta et al. 2015

CATHODE MATERIAL	SPECIFIC PRACTICAL CAPACITY, mAh/g	AVERAGE VOLTAGE, V
$LiCoO_2$	140-155	3.8-4.2
$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$	140-180	4.1
$LiMn_2O_4$	100-120	3.7
$LiNiCoAlO_2$ / $LiNiO_2$	140-200	3.7-4
$LiFePO_4$	160	3.4-3.5

In the first LiBs produced commercially, the cathode material was $LiCoO_2$ (LCO) (Nishi 2001), a layered oxide structure (rock salt) that enables an efficient Li insertion in between the layers (Dahn and Ehrlich 2011, p. 26.6). LCO provides a good specific capacity and a high voltage but at the expense of cost (Dahn and Ehrlich 2011, p. 26.8) and safety concerns caused by overheating (Christmann et al. 2015, p. 9). The main option for replacing the expensive Co, either partially or completely, is with Mn. Some of the advantages of Mn are its lower-cost and toxicity, its higher stability and tolerance to overcharging (Scrosati and Garche 2010; Nishi 2001). What makes $LiMn_2O_4$ (spinel) cathode a less appealing option is an irreversible loss of capacity during use induced by disproportionation reaction of Mn-ions which causes Mn^{2+} ions to dissolve to electrolyte (Nishi 2001) and pollute the protective SEI layer (Broussely et al. 2005). As can be seen in Table 1, the specific capacity of the LMO is the lowest among the commercially available cathode components, and consequently, larger amounts of cathode material would be needed to obtain the same total capacity (Dunn et al. 2015a).

Replacing Co with Ni in lithium nickel oxide $LiNiO_2$ (LNO) provided comparable capacity and lower cost compared to $LiCoO_2$, but the problem was the tendency of Ni^{2+} ions substituting Li^+ ions leading to a disordered and unstable structure with a conductivity loss (Nitta et al. 2015; Vetter et al. 2005). Hence, this cathode material was not considered a good commercial cathode (Julien et al. 2014) but based on it, the commercial $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) was invented, in which small amounts of Ni were replaced with Co and Al (Nitta et al. 2015). NCA has better electrochemical performance and thermal stability compared to LNO, but there is a risk of capacity fade at elevated temperatures (Nitta et al. 2015). NCA is also considered a premium cell material and has thus high cost (Blomgren 2017). Another transition metal mixture, Ni, Co and Mn (NMC) in an oxide has proven to provide similar or higher specific capacity compared to LCO, along with stability and lower cost (Nitta et al. 2015) making it a popular cathode material (Blomgren 2017). The most common ratio of Ni, Co and Mn is 1:1:1, thus the compound is $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. The main problem of this cathode material is similar to LNO: Ni^{2+} and Li^+-

cation mixing in the crystal structure, resulting in a decrease of electrochemical performance (Julien et al. 2014), although the effect is milder due to existence of the third type of transition metal ion.

The presently prevailing commercial phosphate structure is the lithium iron phosphate, $LiFePO_4$ (LFP). Some of its advantages include good thermal stability and high power capability. On the other hand, some of its downsides are a quite low discharge voltage and low electrical and ionic conductivities (Nitta et al. 2015; Nishi 2001). It is used, e.g., in power tools and energy storage applications due to its good power capability (Blomgren 2017) and is also considered a promising candidate for future large-scale batteries in EVs and HEVs as it is considered as a safer option (Julien et al. 2014).

Cathode compounds are in general manufactured from two precursors: Li metal oxide/phosphate and Li carbonate/hydroxide with solid state or hydrothermal synthesis (Dunn et al. 2015a). Traditionally, cathode precursors, cathode compounds and cells are produced by different parties, but it has been estimated that there is now a tendency of integration and cooperation between these parties (Bernhart 2014, p. 562-563). At the moment, over 90% of the LiBs are manufactured in Japan, South Korea and China (Georgi-Maschler et al. 2012) and the production of cathode precursor materials is dominated by Japanese and Chinese companies (Watabe and Mori 2011).

2.3 Future perspectives

Present and estimated future shares of the commercial LiBs per cathode material are relevant to the recycling processes, and therefore are now shortly discussed. The different cathode chemistry shares of the sold cells in 2008 and 2014 are presented in the Table 2.

Table 2 Different cathode type shares of the sold LiB cells. Reproduced and rounded from Heelan et al. 2016.

CATHODE MATERIAL	MARKET SHARE OF COMMERCIAL LI ION BATTERY CATHODES (%)	
	2008	**2014**
LCO	61	40
NMC	19	31
LMO	11	16
NCA/LNO	7	5
LFP	4	9

Figures in Table 2 indicate that the shares of the different cathode chemistries in the sold cells have changed remarkably in six years. The share of LCO has decreased, as this particular cathode material has been replaced by NMC, LMO and LFP. One reason for this is undoubtedly that the areas where LiBs find applications have grown and diversified, affecting the demand for the different cathode materials. Indeed, since the beginning of the 1990's, the fields of LiB applications has grown from computers and mobile phones to a plethora of consumer electronics, toys, power tools, etc. (Blomgren 2017), while the demand is expected to increase further due to the increasing need of traction power for moving. Also, the increasing purchasing power in developing countries is expected to influence the demand for portable batteries. Furthermore, the demand for industrial-scale, energy storage batteries is increasing due to the generalization of renewable energy production (Freedonia 2015). One indication of the rapid expansion of LiBs is the comparison of production rate growth. In 2011, nearly 4 500 million cells were produced, an estimated increase of 43% compared to 2008 (Bernhart 2014, p. 555). In 2015, at least 5 600 million LiB cells were sold as part of the major applications (Pillot 2016).

The rapid growth of LiB demand and production raises the question on the future distribution of cathode material shares. Pillot (2016) estimates that by 2025, NMC will have the largest market share based on tons produced with an estimated 48%, while both LFP and LCO are estimated to have 16% share, LMO 11% and NCA 9%. In the estimates by Roland Berger for the year 2020 (Roland Berger 2012; Bernhart 2014) based on produced energy (in Wh) NMC, LMO and LFP will be the chosen chemistries for traction batteries, constituting approximately 90% of the market. NMC is expected to be the major chemistry for tablet and notebooks also (60%), followed by LCO (25%) and NCA (15%). Only in mobile phone battery cells, LCO is the dominating cathode compound (83%) leaving NMC the remaining 17% share. When discussing estimates based on different variables, it should be acknowledged that the specific capacities of the cathode materials affect the amount needed for a certain level of performance. For example LFP is clearly a lower cost option compared to NMC or LCO when on the per mass basis but due to its lower specific capacity the amount of active material needed per Wh is within the similar range with the Co containing chemistries. (Bernhart 2014; Watabe and Mori 2011). Hence caution is advised in the interpretation of the just presented estimates.

Even though the actualization of the production and demand of different chemistries in the future remains to be seen, it is obvious that a mixture of different chemistries in LiB waste is inevitable. Moreover, existing commercial cathode materials may be mixed to composites in order to provide adequate cells in terms of performance and safety, especially for EVs (Weng et al. 2013). Additionally, new elements and element combinations, coatings, additives and structures may be explored for the electrodes and electrolytes in order to develop more efficient and safe batteries (recent reviews provided e.g. by Blomgren et al. 2017 and Nitta et al. 2015). Therefore, it is realistic to predict an ever more complex LiB waste mixture in future.

3 Recycling

The purpose of this chapter is to explain different aspects of recycling and to define basic terms of the field relevant to this thesis. Recycling is introduced here as part of the waste management hierarchy and in the context of circular economy. Different levels of recycling are also discussed along with the position of recycling in the waste management chain. Mechanical processing techniques are an important part of minerals refining but they are utilized also for instance in the treatment processes for the waste electrical and electronic equipment, hence they are presented shortly. Finally, LiBs as objects of recycling, recyclates, are analysed in order to describe the LiB waste stream and the present status of recycling.

3.1 Recycling as a concept

The Battery directive defines recycling as: "…*the reprocessing in a production process of waste materials for their original purpose or for other purposes, but excluding energy recovery*" (Council Directive 2006/66/EC). Hence it is stated that the act of recycling batteries can consist of reusing battery materials in new batteries or in some other products, but utilizing materials to produce energy is not regarded as recycling. Therefore the recycling efficiency target assigned for the LiBs in the directive: "*recycling of 50 % by average weight of other waste batteries and accumulators."* (Council Directive 2006/66/EC) is also tied to this definition implying that at minimum 50% of the LiB material contents should be used again

The definitions given in the Battery directive stem from the waste management hierarchy that is assimilated to the European waste management policy. This hierarchy is a general recommendation of the procedures for managing end-of-life products originally arisen from the problems related to landfilling in Europe. (Van Ewijk et al. 2014; Dijkgraaf et al. 2004). In the hierarchy, the waste management options are presented from top to bottom in an order of decreasing advisability (Figure 5), where recycling as one of them.

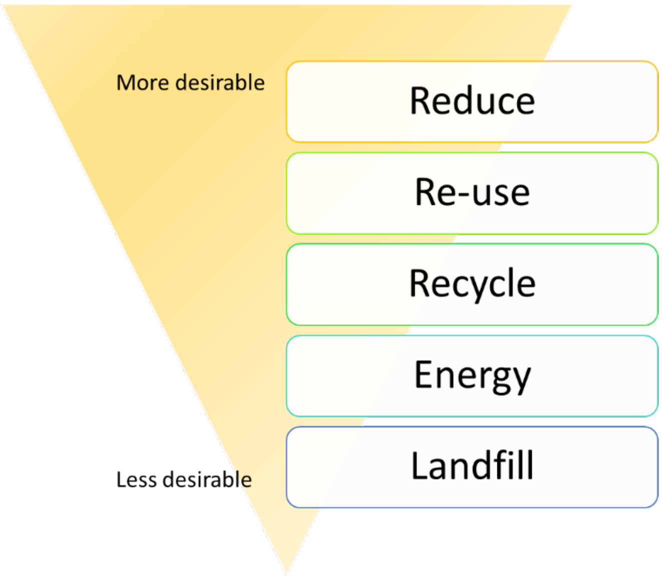

Figure 5 Waste management hierarchy is one presentation and recommendation of waste treatment options, the most recommendable option on top.

According to the waste hierarchy, the primary target in waste or product management should be **reducing** product and material use and waste production in the first place, e.g., by increasing product life time and facilitating repair and maintenance (Allwood 2014, p. 461). The next favourable option is to **reuse** a product which has lost its function or purpose to its current user. Reusing signifies utilizing the product in its original or in some other purpose without modifying, i.e., without investing energy to it (Allwood 2014, p. 460-461), thus preserving the component parts of the object (Clark et al. 2016). Following the hierarchy, only after these two options **recycling** comes advisable: investing energy for processing the component materials to be used again. The least recommended options according to waste hierarchy are using material as **energy or landfilling** it.

In a closer examination, the level of recycling can be specified. When the recycled material can substitute a large share of virgin material in a new product and has properties close to the original quality, the level of recycling is considered high. Using the material in a commodity that has clearly lower quality or functionality than the original one is in turn referred to as "downcycling". (Worrell 2014a, p. 499). It is hence thought that more of the original material value and the energy investments made for it are restored by higher level of recycling.

Clark et al., (2016) classify the level of recycling by the retained composition of the product. In their terminology, **reusing** maintains the component parts intact whereas **recycling** destroys the form and the function of the product, but preserves the material or molecular composition.

Moreover, **renewing** loses also the molecular composition and the material is preserved only at elemental level. Thus, in their theory, the level of recycling is defined in relation to the complexity of the starting material and how that is modified during the process. From the economic and market driven perspective, the order of preference for the aforementioned recycling levels is mainly based on the material value: its form and available functions. (Clark et al. 2016). To give an example: battery materials have elemental value determined by the metal/scrap price in the market. On the other hand, they have also compound value consisting of the elements and the processing to high purity and refined structure, or material form value as in Al foil that has been worked to specific shape.

Recycling is also an important part of the "circular economy". The general idea of circular economy is opposing the linear system where materials and resources are used just once and then discarded. In circular economy, the target is to keep materials and resources in circulation for as long as possible, thus mimicking the natural ecosystems (Worrell 2014a, p. 498), as presented schematically in Figure 6.

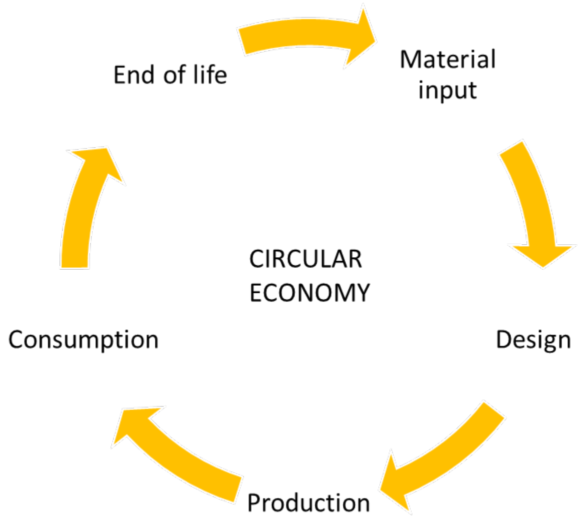

Figure 6 Schematic presentation of the circular economy. Reproduced and modified from Elia et al. 2017.

Circular economy consists of several interlinked processes such as design, production and consumption. Recycling is part of the end-of-life phase and it is linked to the material input phase closing thus the loop for resource use. (Jawahir et al. 2016; Elia et al. 2017). Circular economy can be seen as one strategy among many others for supporting a sustainable system (Geissdoerfer et al. 2016) and has been classified into a group of business models based on the idea of "creating value from waste" (Bocken et al. 2014). Conventionally, circular economy has had a strong economic point of view but it has been recently supplemented also with environmental and social aspects (Geissdoerfer et al. 2016).

One thing circular economy has been criticized for, is simplifying the possibility to match the quality criteria for the materials needed in today’s applications and the properties the recycled materials can offer (Allwood 2014, p. 445-446). Pursuing a high level of recycling, one might indeed encounter some challenges, for instance, in convincing the potential customers of the material quality. Hence it could happen that, as the targeted level of the recycled product/material rises, along with it increases the uncertainty concerning the market. Often it is a necessity to mix some amount of virgin material with recycled one to achieve some specified level of quality in material (Allwood 2014, p. 474). There are also limits after which the costs and the environmental impacts of reprocessing material surpass those of virgin material (Allwood 2014, p. 446), hence the sustainability of recycling processes should be critically evaluated (Van Ewijk et al. 2014). On the other hand, considering only the highest level of recycling in the context of circular economy is quite a strict interpretation. A better approach is to aim at optimizing the complete technical system utilizing appropriately and flexibly different levels of product and material circulation (Ellen MacArthur Foundation 2015). One possible representation of these levels is the one seen in Figure 7.

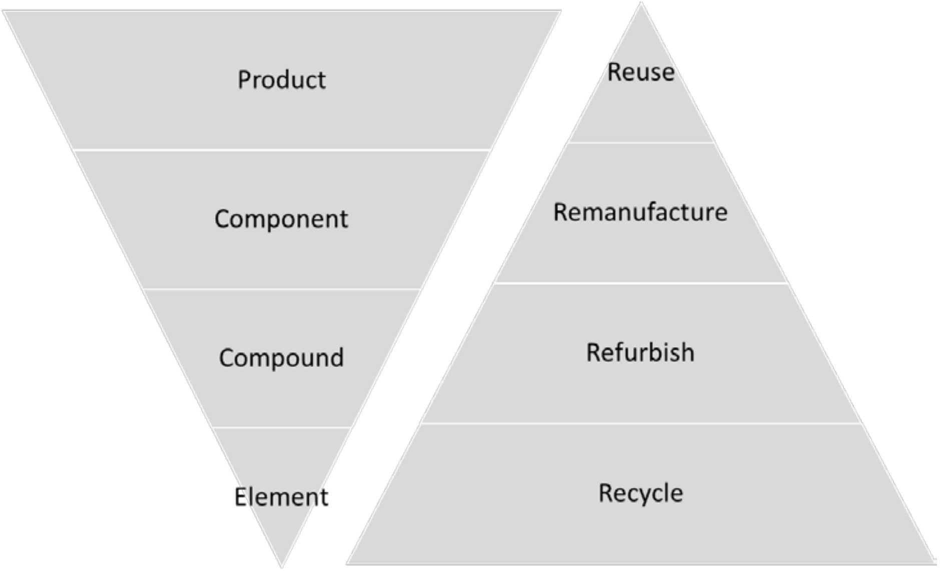

Figure 7 The product value levels and different stages of resource circulation.

In Figure 7 the inverse pyramid on the left-hand-side represents different value levels of a product. In addition to the finished product itself its components can have reuse value. Also, the compounds that the material consists of can have special value, in addition to the constituent elemental value. The inverted pyramid shape reflects the accumulative energy that is invested to the product through the manufacturing steps, however, it does not intend to acclaim anything about the proportionality of these energy investments. The right-hand-side pyramid, in turn, depicts different levels of resource circulation. Here the form indicates the increasing amount of processing needed when proceeding from the "reusing product as such" downwards up till recycling. Also in this case proportionality is not suggested with the figure. The key to economically and environmentally feasible circulation of resources is finding the optimal level: what state of the product value once existed can be recovered and with what costs.

The main driving forces for recycling and reusing include concerns about the health and environmental impacts of waste, material scarcity and disposal costs (van Beukering et al. 2014, p. 479), often promoted with legislation that provides an important incentive to recycling, when adequately implemented. A relevant case for this thesis that is worth mentioning is Pb, which in many countries is classified as hazardous waste. Thus, it is obligatory to recycle lead acid batteries (van Schaik 2014, p. 327). Recycling can be further encouraged by economic incentives. For example, in many states in US, a part of the lead acid battery price consists of a deposit that is compensated to the customer when the battery is returned for recycling (Gaines 2014). As recycling is also driven by economic motives (van Beukering et al. 2014, p. 479), also the business side of recycling has to be considered: the technical solutions implemented for sustainability must have solid business models in order to survive (Heelan et al. 2016). Also, geopolitical issues have in recent years led to considering recycling as means to alleviate the uncertainty associated to the various resources classified as critical (Worrell 2014b, p. 494).

In addition to the potential value of the recovered materials, the feasibility of recycling process must take into consideration aspects like collection and recycling costs (Wang et al. 2014a). Consequently, to close the material cycle in batteries or any other product, several participants are needed. The user of the battery has to bring the battery to a collection site that is part of the wider collection system. Within the collection system, the battery has to be delivered to the recycling processing plant, but there can also be subsequent recycling plants performing different tasks along the value recovery chain. Last but not least, there has to be a recipient and a market for the recycled materials and products, where they will be remanufactured into products that will start a new life cycle for the material.

3.2 Status of LiBs recycling

Considering specifically the recycling of LiBs, a present global problem is that approximately 95% of LiBs are not recycled, being mostly landfilled or not even collected (Heelan et al. 2016). However, the situation has a strong variation throughout the various geographical areas around the world, hence some examples of the LiB recycling status are provided next.

In Europe, the European Battery Recycling Association (EBRA) represents the majority of the European battery recycling companies. EBRA gathers statistics about the recycled battery volume by its members. The amount of recycled Li ion batteries – portable, industrial and automotive - almost doubled in three years: from nearly 1 900 tons in 2009, to approximately 3 500 tons in 2012. In comparison, the European LiB market 2013-2014 was more than 65 500 tons, thus over 18-fold. (EBRA n.d.). In EU, the target for collection rate for all kinds of batteries is at the moment 45% and the target for recycling efficiency has been 50% of average weight for LiBs since September 2011 (Council Directive 2006/66/EC).

In U.S. (as in Canada), a collection program called “Call2Recycle” coordinates the voluntary waste battery collection system. According to its home webpage this is the largest battery recycling program in North America, channelling the Li ion batteries to two companies in Canada and in South-Korea. Handling the end-of-life LiBs is legislated at state -level and recycling them is obligatory only in three states: California, Minnesota and New York. (Call2Recycle n.d.). Additionally, it has been stated that enforcement of these laws is not strict (Heelan et al. 2016). In China there are nearly no recycling plants at all to handle the spent LiBs that are therefore mostly disposed to landfill (Zeng et al. 2015) and there is no specific legislation considering LiBs (Zeng et al. 2014). In Australia on the other hand, the lack of processing facilities for LiBs is solved by transporting LiBs to other continents for processing (Boyden et al. 2016) with the associated economic and environmental impacts.

3.3 Mechanical processing in recycling

The purpose of mechanical processing when recycling solid state waste is not in general different from the purpose in minerals processing: the target is to liberate and separate materials to a point where subsequent refining and/or processing steps are economically and technologically feasible. Another objective can be the removal of hazardous components or contaminants (Schubert and Thomas 2007; Wills and Finch 2016a; p. 4-5). These objectives are usually achieved with a combination of processing stages including comminution, classification and separation, each of which can be carried out with a variety of unit operations.

With comminution, several objectives can be achieved: decreasing particle size, increasing active surface area, liberating materials and modifying particle shape (Schubert and Thomas 2007, p. 991). The principal idea of comminution is to expose the particles through the application of a stress that is distributed in the material according to its mechanical properties and the possible flaws in its matrix. At some point the applied stress leads to the fracture and eventual break of the material. The main force types used to cause stress in comminution are crushing, impact and attrition – leading to compressive, tensile or shear fracture. (Wills and Finch 2016b, p. 110).

An essential part of mechanical processing is the separation of materials, in other words, the separation of components into fractions by exploiting differences in their physical properties in order to concentrate the materials of interest. Screening can be used for material separation based on particle size and shape (Kaya et al. 2016). Separation can also be based on differences in visual appearance, relative density, surface properties, magnetic susceptibility or electrical conductivity (Wills and Finch 2016a, p. 7; Kaya et al. 2016). Relative density of the materials can be used for separation both in wet or dry conditions, although separating processes are inevitably associated to particle size as well. Shaking tables, air jigs and dense medium separators represent different types of techniques based on density. (Wills and Finch 2016a, Kaya et al. 2016). Surface properties – in the context of mechanical separation referring mainly to differences in hydrophobicity of the materials – are the underlying principles in froth flotation. In magnetic separation, the response of materials to an external magnetic field is utilized and in electrostatic separation conductivity/resistivity differences act. (Wills and Finch 2016a; Kaya et al. 2016).

3.4 LiBs as recyclates

3.4.1 Characteristics

LiBs for consumer electronics reach the end–of-life approximately after 3-4 years of use (Li et al. 2016). For the EV and HPEV batteries the target of service time is 10 years (Corrigan and Masias 2011 p. 29.13). Thus the content of the LiB waste lags behind the market composition by 3-4 year for consumer batteries (Heelan et al. 2016) and even longer time for EV and HPEV batteries. Nevertheless, changes in the battery materials and construction design will appear in the recyclable waste sooner or later. Compared to Pb-acid battery, for example, in the case of LiBs the recycling process has to be prepared to deal with a more fluctuating waste stream.

Together with the wide variety of composition in LiBs, the low collection rates generate challenges for a recycler as mentioned earlier. The contribution of certain types of chemistry to the overall composition of the total recycling stream might establish limitations to feasible processes (Wang et al. 2014a). Additionally, cells, batteries and battery packs present different types of construction that require different demands of manual treatment before any possible automated recycling process. In EV and PHEV batteries, cells form only the part of the battery back system that still has to be handled completely in the recycling process, thus manual work is required for the disassembly. Batteries for the consumer electronics on the other hand are often buried inside the apparatus and hence, also here some manual work is likely needed until the battery or cell is exposed and ready to be recycled.

There are factors both hindering and helping the recognition of different chemistry types of LiBs in the waste stream. It is known that there is no relation between shape and size of the battery and its composition (Espinosa et al. 2004). Moreover, one shape can have several sizes. Even though more detailed letter codes notifying, e.g., the cathode chemistry have been developed as standards (Wicelinski 2011, p. 4.7), in the battery label it presently suffices to simply state main battery type, i.e., "Li-ion". Hence information on the cathode material is not stated on the cover of the battery – changing this would help sorting and recycling tremendously (CEC 2015, p. 62). Additionally, the development of new type of LiBs is abundant, thus the contents of the waste stream are also constantly changing. A further complication can be that the wrong kind of batteries or incorrectly labelled ones enter in the recycling stream (CEC 2015, p. 62). On the other hand, there are some probabilities of the chosen LiB cathode chemistry for the main application groups. For the traction batteries part of electronic vehicles, the end-of-life of the battery can be expected to be quite well in control considering that car recycling processes are well established. At the moment, it is also helpful that a traction battery pack contains only one type of chemistry.

The structure and materials of the battery cells present composite-like constructions: they consist of different material types (metals, non-metals) and haven been constructed from different material forms (powders, foils etc.) that are interconnected to each other (Xu et al. 2008). In this sense, they resemble printed circuit boards (PCBs) and their challenges in recycling (Kaya et al. 2016): e.g., in comminution there is not a single specific size range where liberation of all valuable components is accomplished, but rather different components are liberated at different size fractions (Ghosh et al. 2015). The cell components may also behave differently under mechanical treatment, which might bring additional challenges. Also it is typical for the LiB cell construction that the most valuable materials are present deepest in the structure.

Moreover, due to the reactive materials used in the cells, certain chemical and electric hazards are related to them and must be taken into consideration in the recycling process (Diekmann et al. 2016).

Compared to natural ores, batteries form quite different kind of feed to comminution equipment. According to Schubert and Bernotat (2004) the behaviour of non-brittle materials (e.g., steel or non-ferrous wrought alloys) upon crushing/grinding is much less understood compared to brittle materials (e.g. many ores). This is relevant considering that batteries contain a combination of brittle and non-brittle materials. In tests conducted by Ruffino et al., (2011) several battery types were processed using a Hazemag impact mill, a type of mill that is typically used for brittle materials (Schubert and Thomas 2007, p. 1003). In such study, it was noticed that at least part of the batteries crumpled up instead of breaking. Cutting systems thus seem more suitable for battery comminution since an excessive compacting of the material can be avoided (Cabral et al. 2010). Indeed, Shubert and Bernotat (2004) claim that for non-brittle materials shearing, cutting, bending and tearing stresses are the suitable types for particle size decrease. Furthermore, they state that for successful liberation of materials only tearing stress is advisable. Tearing stress consists of bending and torsion combined with tensile stress and can be produced with a swing-hammer shredder, for example (Schubert and Bernotat 2004). In a study conducted by Zhang et al. (2012) the effects of different stress types on mobile phone LiBs in wet crushing conditions were compared. The result was that bending, shearing and impact seemed the most effective forms of stress to comminute LiBs (Zhang et al. 2012), thus indicating similar stress behaviour to PCBs.

3.4.2 Degradation mechanisms

In this section, the degradation and aging mechanisms of LiBs are depicted to elucidate the possible conditions of the cell parts and materials at their end-of-life. It is relevant to know the potential stage of these components if materials are recovered to be used in new batteries or if cell components can be re-used. The discussion is limited to the phenomena inherent in the cells and caused by normal life cycle of the battery, thus e.g., external mechanical stress directed suddenly to the battery and causing failure is excluded. The research on this topic is ongoing and on many subjects, there is still no consensus.

The aging and failure of LiBs can be caused by several reasons often interconnected and dependent on the cell materials, impurities and design. Aging can be related to both storing and cycling, and these two degradation types are considered additive to each other. During the storage, the inherent thermodynamical instability of the components causes side reactions leading to degradation, whereas in cycling more rapid phenomena such as volume changes or concentration gradients can cause adverse effects. The critical spot regarding the anode is the interface it has with the electrolyte. In the case of the cathode, there is not a single primary cause of failure but a variety of degradation mechanisms that are often characteristic to individual battery chemistries. (Vetter et al. 2005; Barré et al. 2013).

When the battery is charged for the first time, a passivating SEI layer is formed on the surface of the anode due to the reaction of Li-ions and liquid electrolyte (Peled 1979). A schematic representation of this layer in the electrode and electrolyte interphase is presented in Figure 8.

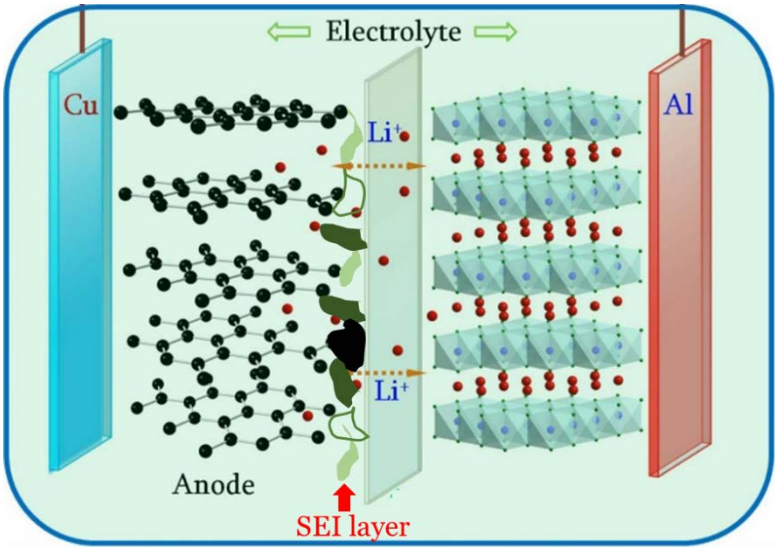

Figure 8 Schematic depiction of the inhomogenous and multi-species SEI layer on the graphitic anode (Verma et al. 2010). Figure modified from Liu et al. 2016.

The exact composition of the SEI layer is a debated subject, but it is generally accepted that the composition depends at least on the anode and electrolyte composition, the anode pre-treatment and the cycling conditions (Verma et al. 2010). This protective layer prohibits electron transport but allows Li ion penetration. Hence, although some of the cell capacity is lost within the SEI formation, the layer is still essential protecting the anode from corrosion and the highly-reactive electrolyte from further reduction. (Broussely et al. 2005; Vetter et al. 2005). Nevertheless, this layer is also the source of the main degradation mechanisms on the anode side. Being brittle by nature, the layer can be cracked due to stress caused during the normal cycling of the battery, consequently exposing lithiated graphite to corrosion (Vetter et al. 2005). As a consequence of high temperature or prolonged high state of charge, SEI layer can also continue to grow, leading hence to an increased consumption of Li ions which together with the thickening layer decrease achievable capacity and power (Vetter et al. 2005). Additionally, the continuous chemical reaction reduces the electrolyte thus changing its composition (Diekmann et al. 2017) – also the composition of SEI layer changes during aging (Winkler et al. 2016).

The routine charging and discharging of the battery during its life cycle degrades both anode and cathode, e.g., due to volumetric changes and other phenomena inside the cell. On the electrode composite structure, the contacts of different constituents – active material, binder, conductive carbon – can deteriorate due to mechanical changes in structure (Vetter et al. 2005). Therefore, as the ionic conduction pathway deteriorates, the cell impedance increases decreasing the cell power performance (Abraham et al. 2005, p. 2). In the active electrode material, disordering of the crystal structure and dissolution and migration of the species can lead to active material loss. Because on the cathode side no protective layer against the electrolyte is produced, there can be some reactivity between these two components possibly leading to an increase in resistance. A typical phenomenon for LMO cathode is that $Mn2^+$ ions generated by disproportionate reactions dissolve to the electrolyte and are transported and incorporated to the SEI layer. (Vetter et al. 2005; Broussely et al. 2005). Overcharging the battery can also lead to CO_2 gas formation on the cathode side that consequently degrades. A high charging rate on the other hand can lead to Li plating on the anode which produces a risk due to the reactivity of the elemental Li. (Palacín et al. 2016). Altogether, being a complex system, several changes might occur in the cell simultaneously effecting the life time of the system.

When batteries are discarded, they are in different stages of degradation which has consequences for the suitable reuse/recycle options. Because several mechanisms and their combinations can lead to capacity and/or power fade and impedance rise, it is challenging or even impossible to detect the underlying degradation mechanisms (Berecibar et al. 2016). Therefore, even though the general state of health of the battery could be detected in the end-of-life, the exact state of the different cell materials might remain uncovered. This indisputably generates some uncertainty considering the available life-time and safety of the recycled cell materials and components.

4 Recycling processes for LiBs

In the following section, some processes that aim to recycle LiB are introduced. Both existing industrial scale processes and emerging processes in pilot plant phase or under commercialization are discussed, whereas processes recycling LiBs as a secondary feed are briefly introduced. The often used classification to hydrometallurgical and pyrometallurgical processes (Bernardes et al. 2004) or additionally to physical/mechanical processes (e.g. Al-Thyabat et al. 2013; Sayilgan et al. 2009; Xu et al. 2008) has been omitted. This is considered a valid choice because it is more important for this thesis to gain an understanding of relations, requirements and possible trade-offs of all techniques available. It would thus be more relevant for this work to compare the techniques based on the extent in which the materials can be recycled. Furthermore, in this way the challenge of implicitly comparing processes that deal only with a specific stage of the recycling process is avoided. In fact, there are multiple lab-scale suggestions for recovering certain, usually the most valuable materials of the LiBs but these proposals are often not examined in the context of complete, feasible battery recycling process (Krüger et al. 2014; Wang et al. 2014b). This is understandable since processes dealing specifically with LiBs are only just emerging, compared to Pb-acid or NiCd batteries that are more mature inventions. Nonetheless, since battery recycling processes are considered relevant objects of this study, only processes having at minimum a complete cell as their starting material are included in the following review.

4.1 Industrial processes

4.1.1 Umicore VAL'EAS^{TM}

Due to the fact that the Umicore VAL'EAS^{TM} process focuses on recovering the currently most valuable metals found in batteries (i.e., Co and Ni), both LiBs and NiMHs are processed together. Starting with pyrometallurgical treatment in a single shaft furnace enables omitting the discharging phase. It also renders crushing the batteries and separating Al and Fe unnecessary, because they are usually considered impurities in the subsequent leaching phase and are slagged during the smelting process. (Georgi-Maschler et al. 2012; Cheret and Santén 2007). Even though the Umicore process is often described as a pyrometallurgical method for LiBs recycling, in fact a combination of pyrometallurgical and hydrometallurgical steps are needed to recover the final products. A schematic representation of this process can be seen in Figure 9.

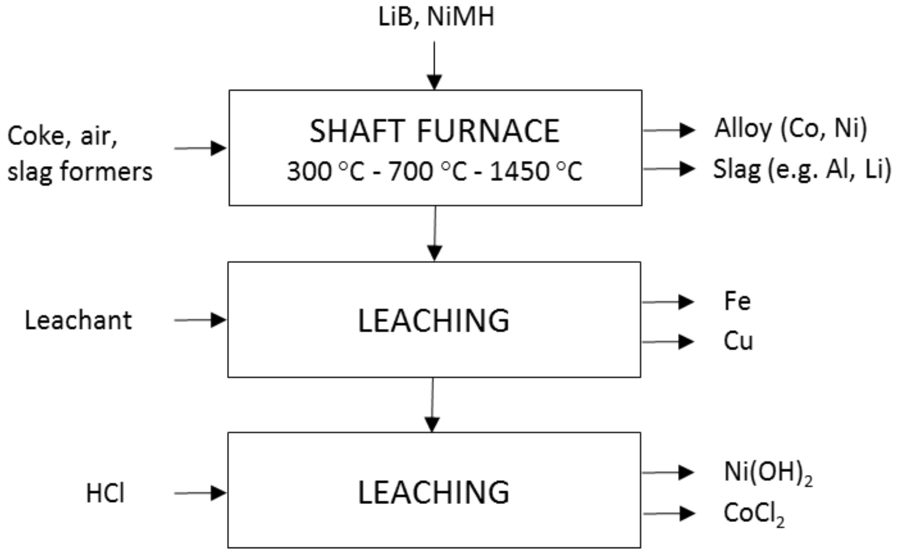

Figure 9 A schematic representation of the Umicore VAL'EAS^{TM} process for recycling LiBs and NiMHs. Additional inputs to the process are marked with arrows on the left side and outputs – recovered or removed items - on the right side. Modified from Vezzini 2014, p. 548 and Gaines and Dunn 2014, p. 497.

The previously dismantled batteries are fed into the furnace along with coke, slag formers and potentially with silicon oxide and limestone (Vezzini 2014, p. 546) and air is delivered to the furnace from the bottom (Cheret and Santén 2007). During the subsequent heat treatment steps three functions are fulfilled: as the feed is slowly heated, the electrolyte is evaporated at near 300 °C; plastics are pyrolized at 700 °C and finally the rest of the feed is smelted and reduced at 1200-1450 °C (Vezzini 2014, p. 546). Part of the organic materials contained in the batteries is used as reducing agent in the process (Georgi-Maschler 2012). The two outputs from the furnace are an alloy and a slag – the alloy contains Cu, Co, Ni, Li and part of the Fe and the slag consists of Al, Si, Ca, Fe, Mn, Li and REEs (Vezzini 2014, p. 546; CEC 2015, p. 45).

An important part of the technology is cleaning or utilizing the gases produced in the plastics pyrolysis phase in a safe and controlled manner. Hot gases are recycled and provide the heat needed in the first evaporation phase. Waste gases for their part are heated with a plasma torch to prevent their condensation and Na, Ca or ZnO is added for capturing halogens and other volatile compounds. If there are alkaline batteries in the feed mixture, the ZnO contained in them could also be used for this purpose. (Vezzini 2014, p. 546; Gaines and Dunn 2014, p. 496). In the final phase, the gases are quickly cooled in the post-combustion chamber by injecting water vapour: with this rapid process, the formation of dioxins and furans is avoided, because organic compounds cannot recombine with halogens. A filtering stage finalizes the cleaning process. (Vezzini 2014, p. 546; Cheret and Santén 2007).

To recover the valuable metals Co, Ni and Cu, the alloy is further processed with hydrometallurgical techniques, as shown in the Figure 8. First Cu and Fe are removed from the solution in subsequent leaching steps, although the exact composition of the leachant is not public knowledge. In the solvent extraction phase, HCl is added to the solution and $Ni(OH)_2$ and $CoCl_2$ are obtained. The latter compound is used by another company in LCO cathode production (Gaines and Dunn 2014, p. 496-497; CEC 2015, p. 55-56).

The slag is at the moment used as an additive in construction materials and thus its contents are downcycled, although hydrometallurgical methods could also be used for recovering Li (Gaines and Dunn 2014, p. 496). While Li is presently not recovered, Umicore has expressed an interest for that if the price of Li were to increase (CEC 2015 p. 45; Cheret and Santén 2007). If Li becomes of interest, additional processing steps will be required in the Umicore process.

4.1.2 Retriev Technologies (Toxco)

Originally a process called “Toxco”, this was developed for recovering Li from industrial scale primary Li batteries safely and efficiently (McLaughlin and Adams 1999), but today the same technology is applied also for recycling LiBs (CEC 2015, p. 39). The process is presently owned by Retriev Technologies in U.S. and it combines mechanical and hydrometallurgical methods (Gaines and Dunn 2014, p. 498). The target of the mechanical processes is to obtain uniformly sized particles that are active and easy to handle in the hydrometallurgical treatment (McLaughlin and Adams 1999). A schematic description of the Retriev process is represented in Figure 10.

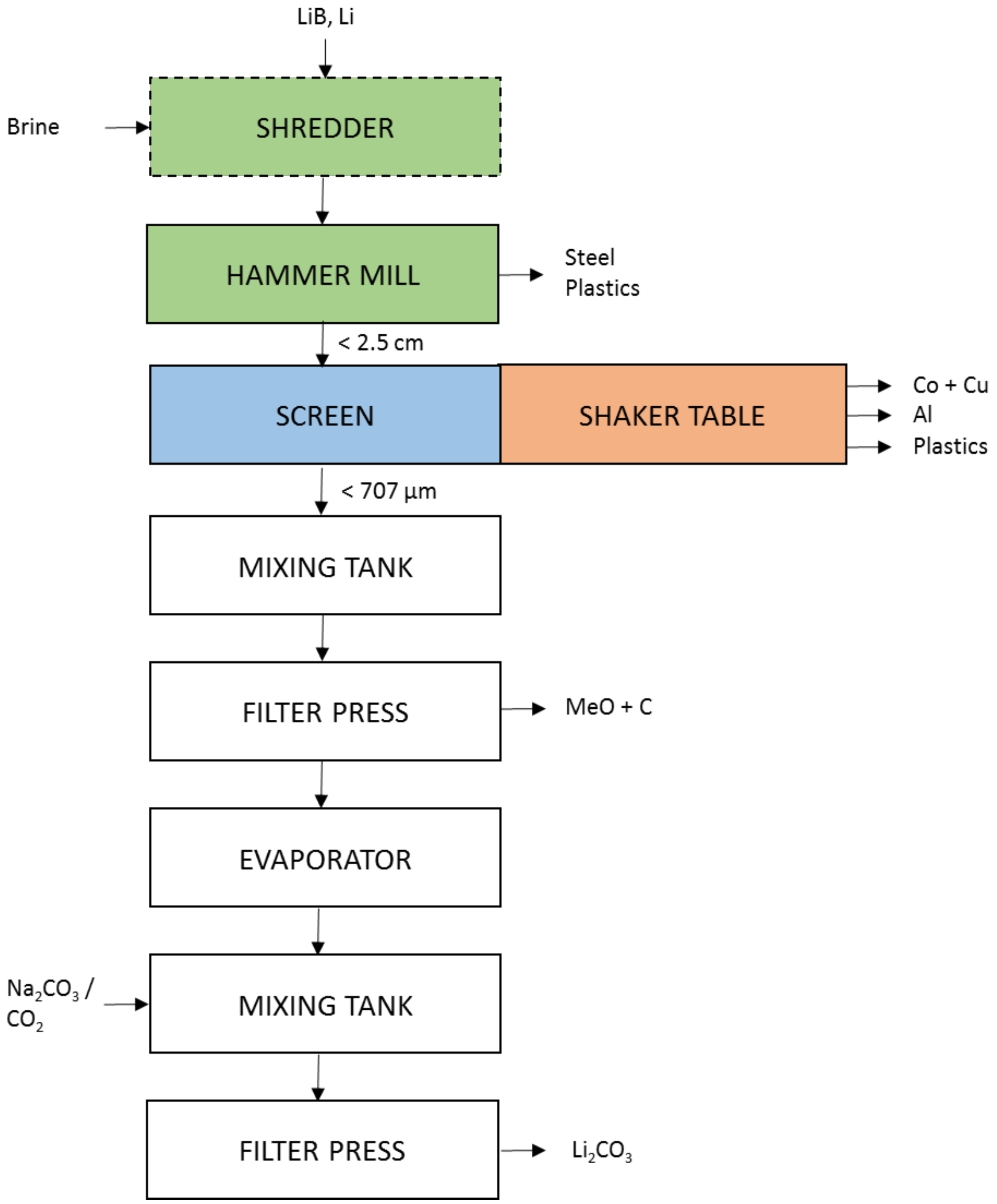

Figure 10 Schematic representation of the Retriev Technologies process. Additional inputs to the process are marked with arrows on the left side and outputs – recovered or removed items – on the right side. Physical processing steps are indicated with colours: comminution with green, screening with blue and density based separation with orange. Particle size range resulting from comminution or screening step is marked below the said step. Modified from Vezzini 2014, p. 548 and Gaines and Dunn 2014, p. 497.

As indicated in Figure 10, comminution is performed with a shredder and/or hammer mill, most often in a brine solution with the aim to deactivate the cells and prevent fires caused by reactive elemental Li oxidation. Small batteries and cells are fed to the process as such, but larger battery packs are disassembled manually in advance. (McLaughlin and Adams 1999; Vezzini 2014, p. 545). The crushing conditions of the Retriev process have changed since the technology was launched. In the beginning liquid N_2 was used as a protective environment, i.e. cryogenic crushing (McLaughlin and Adams 1999; Retriev Technologies n.d.; Vezzini 2014, p. 545), but at the moment cryogenic crushing is utilized only in the presence of high amount of elemental Li (Gaines and Dunn 2014, p. 498), thus larger share of primary Li batteries.

The resultant slurry of the comminution phase still contains all the battery materials from the feed. From this mixture, the fraction consisting of steel and plastics from the battery casings is subsequently separated with a method that is not public knowledge. If this fraction contains sufficient amounts of steel, it can be further processed to recover it. The remaining slurry is screened and from the overflow Cu and Co –mixture, Al and the remaining plastics are recovered using a shaker table (orange box in Figure 10). The metal fractions are utilized for instance in the steel making process. (Vezzini 2014, p. 545; CEC 2015, p. 39; Smith and Swoffer 2014; Gaines and Dunn 2014, p. 499). The undersized metal-rich part of the slurry is filter-pressed to produce a cake consisting of mixed metal oxides (indicated in Figure 10 with “MeO”) and C. From the remaining Li-containing slurry, Li_2CO_3 is produced either by reaction with Na_2CO_3 (Gaines and Dunn 2014, p. 499) or with CO_2 (McLaughlin and Adams 1999). Both the filter cakes, the one containing metal oxides and the other, composed of Li_2CO_3 are used in metals manufacturing industry (Gaines and Dunn 2014, p. 499; CEC 2015, p. 40).

Likely due to the decreasing share of primary Li batteries in the waste stream compared to LiBs, the crushing conditions of the Toxco process have changed, as smaller amounts of primary Li in the scrap reduce the risk of fire. Since the recovered main products (MeO+C filter cake and Li_2CO_3) are utilized in subsequent metallurgical processes, maximum purity of separated products or abundance of separation steps are not needed. On the other hand, these materials are downcycled: they are not re-used in similar components or applications they originated from. Most likely the target to recover Li_2CO_3 is originally based on the Li amounts present in primary Li battery anodes. Since the share of LiBs in the feed has increased, it raises a question how feasible Li_2CO_3 production from the mixed feed is.

Retriev Technologies has also been granted a patent for the innovation of recovering and regenerating cathode material for LiBs. Especially large prismatic cells of automotive and energy storage applications have inspired this process. (Smith and Swoffer, 2014). The company has announced that it will work on commercializing the technology in the upcoming years (Retriev Technologies 2013), but until today there is no indication of the fulfilment of this goal (Retriev Technologies n.d.). This new process is depicted in Figure 11.

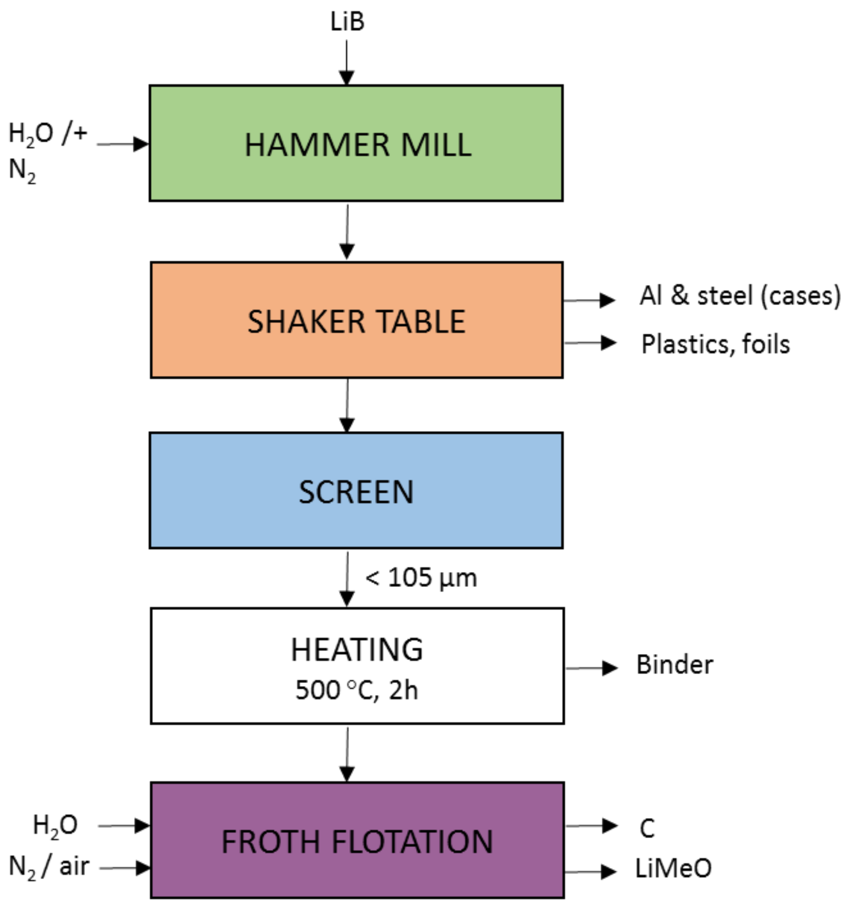

Figure 11 Schematic representation of the Toxco's patented recycling process proposal planned for producing Li metal oxides suitable for cathode material synthesis. Process inputs are marked with arrows on the left side and outputs – recovered or removed items – on the right side. Physical processing steps are indicated with colours: comminution with green, screening with blue, density based separation with orange and flotation with purple. Particle size range resulting from comminution or screening step is marked below the said step. Also known process times and temperatures are expressed within the particular phase.

The patented regeneration process starts with particle size reduction of batteries with a crusher, shredder or hammer mill under water spray and/or N_2. In the subsequent separation steps the slurry is fractioned: with a shaker table Al and steel are separated from the other coarse particles and the fine mixture of carbon and cathode particles is further screened with 140 mesh (105 µm). Part of the water is then removed from the fine underflow that is heated at 500 °C under limited amount of O_2. During a 2 hour-long thermal treatment, the binder is evaporated and the surface of the carbon is modified. Controlling the process temperature and keeping it at 500 °C is important, as it enables efficient oxidation of the binder but not yet igniting the carbon of the anode. Heating is essential, because the binder would interfere with the separation of carbon in the following froth flotation step, which would lead to an impure cathode material. The purpose of the froth flotation phase – final step in Figure 11 – is to separate carbon from the metal containing fines. The binder-free material is mixed with distilled water and placed in a stirred floatation vessel under bubbling N_2 or air. After mixing for 30 min, the actual frothing starts and results in carbon particle flotation to the froth phase. The sunk cathode particles can be recovered and used for regenerating a cathode material. (Smith and Swoffer 2014).

As can be seen above, the separation techniques used in the latter process whose target is to recycle the active cathode materials back to the battery manufacturing process, differ slightly from the methods used in original Retriev process. In the new, proposed process, the materials of main interest are ground to a smaller particle size (i.e., under 105 µm vis-à-vis 707 µm) probably to more successfully separate materials from the active electrode materials using froth flotation. It also appears that the comminution environment is adjusted according to the absence of primary Li batteries. For the recovery of valuable materials, froth flotation is used alongside with screening to provide pure active powder precursor. It is mentioned that removing the binder is essential for successful carbon separation in the flotation phase, but other works (e.g. Dunn et al. 2012a; Sloop 2016a) suggest that the used binder also deteriorates the performance of the re-manufactured cathode material and should therefore be eliminated. What comes to wet crushing, Zhang et al., (2013) have suggested based on their experiments, that compared to dry crushing, the detachment of electrode powder from the foil in wet crushing conditions is less successful – implying that there is also more binder present in the particles. In this case, however, the binder is removed from the material after the wet crushing phase by heating and the possible adverse effects of wet crushing are thus prevented.

Considering the targeted use of materials in new cathode material production, the utilization of froth flotation might generate problems. It has been stated that water (e.g., used during crushing) contaminates the battery component materials (Sloop 2010). Hence, it would be expected that also water used in froth flotation in the newly proposed Retriev process would have adverse effects on the reutilization of the cathode material. However, the more detailed discussion of the impact of water to cathode materials is missing in this context and would require further studies.

4.1.3 Recupyl Valibat

The Recupyl process was developed to recycle both LiBs and primary Li batteries. Additionally, it attempted to address the challenges in the state-of-the art industrial, Toxco and Sumitomo-Sony processes. These issues include handling of gas emissions in the pyrometallurgical methods and the safety issues triggered by the H_2 emissions from wet crushing. The purpose was to enable maximum recovery of the materials with a low-temperature method (Tedjar and Foudraz

2010). At the moment, plants using the Recupyl process are in operation in Singapore, France and UK (Vadenbo 2009, p. 31). The process flowsheet is represented schematically in Figure 12.

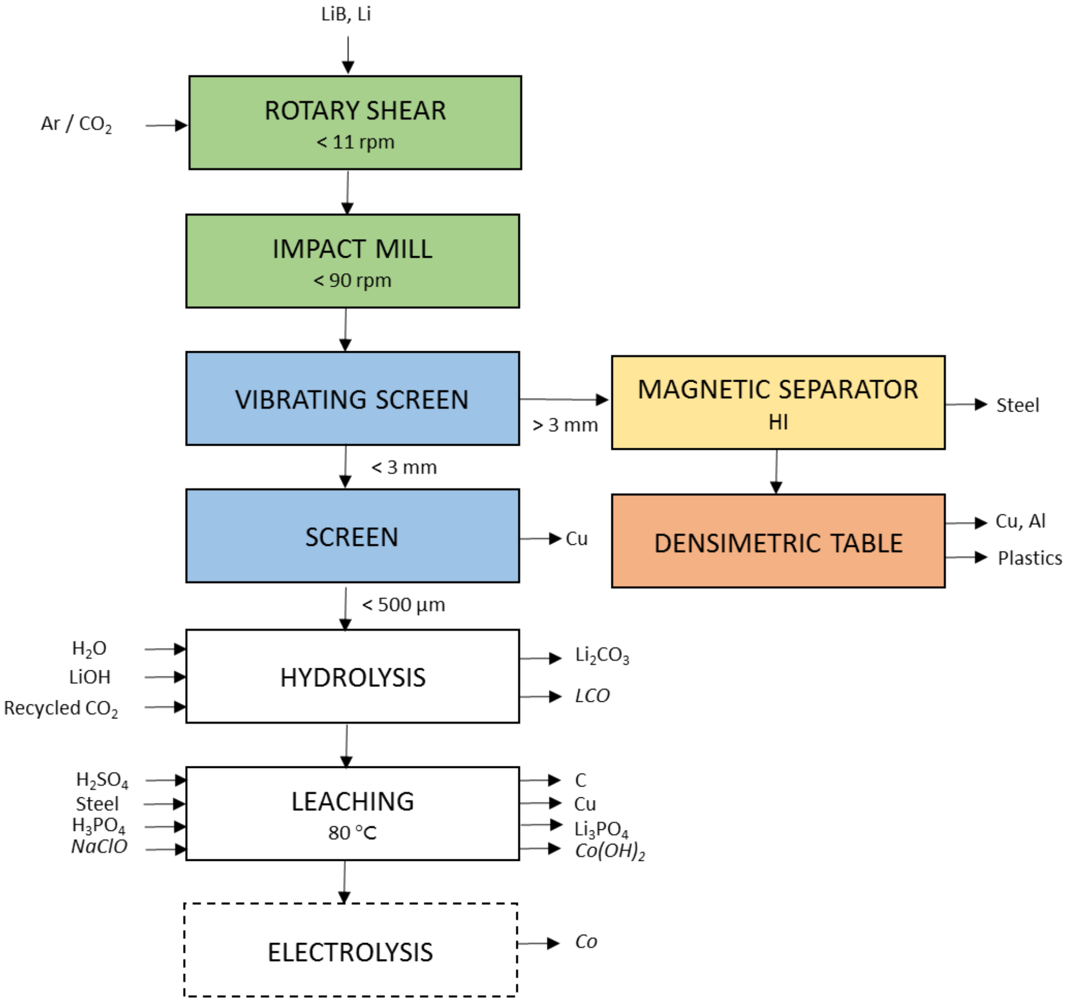

Figure 12 A schematic representation of the Recupyl Valibat process. Process inputs are marked with arrows on the left side and outputs – recovered or removed items – on the right side. Physical processing steps are indicated with colours: comminution with green, screening with blue, magnetic separation with yellow and density based separation with orange. Particle size range resulting from comminution or screening step is marked below the said step. Recovery of LCO, $Co(OH)_2$ and Co are presented in literature as optional products and the final electrolysis phase is implemented only if recovering elemental Co is pursued, thus the phase is represented in the process sheet with dashed line. Modified from Meshram et al. 2014 and Vezzini 2014, p. 549.

To ensure the safe handling of potentially undischarged batteries, crushing is performed in an inert atmosphere consisting of Ar, CO_2 or a mixture of them. An additional benefit of using CO_2 is that it reacts with metallic Li that can be present on the anode producing Li_2CO_3 and therefore passivating the surface. Comminution is performed in a low speed rotary shearing that is meant to free the internal stresses of the batteries thus supporting safe handling of them. In a second comminution step, the batteries are grinded with an impact mill at under 90 rpm. The targeted cut-off particle size is 3 mm, which is achieved using a vibrating screen. The oversized portion is treated with a high induction magnetic separator for removing Fe-based material from the feed. The rest of the coarse fraction is further processed with a densimetric table to produce streams of high density non-magnetic and non-ferrous metals, and a low density mixture of paper and plastic. (Tedjar and Foudraz 2010). To improve the subsequent leaching process, Cu is further removed from the metal oxide and C rich undersized fraction: after screening with 500 µm mesh the Cu content is diminished to under 0.3% (Tedjar and Foudraz 2010; Vezzini 2014, p. 548).

The fine fraction is suspended in water and the mixture is heavily stirred. By adding LiOH, the solution is alkalized to over pH 12. The hydrolysis reaction results in the formation of H_2, but the potentially hazardous effects of this are diminished by controlling the amount of feed that is processed and by creating a turbulence above the leaching bath. As a result of the hydrolysis reaction, Li salts are dissolved to water while other components remain insoluble: hence, by filtering the mixture a solution of Li salts and a suspension of metal oxides and carbon are produced. If it is of interest to recover Li as carbonate, this can be accomplished at this stage. CO_2 gas generated during the milling phase, is introduced to the Li-salt solution and the pH is decreased to 9, resulting in precipitation of Li_2CO_3. It is also possible to retrieve Co as LCO in this phase by solid/liquid separation. (Tedjar and Foudraz 2010).

The treating method of the remaining solution depends on the proportion of primary Li batteries and LiBs and the resultant share of Mn and Co. However, here only the process developed specifically for LiBs is discussed. The remaining LiB scrap is leached in H_2SO_4 at 80 °C. Carbon is filtered off from the solution and Cu, herein considered the most harmful impurity, is cemented with steel (i.e., reduced to elemental form). If Li was not recovered at the end of the previous hydrolysis phase, that can be accomplished at this point. Accordingly, H_3PO_4 is added to the solution and pH is adjusted resulting in Li_3PO_4 precipitation. Also, for Co recovery there are still two alternative options to the aforementioned solid/liquid separation. Co can be precipitated as $Co(OH)_2$ with NaClO or it can be recovered in a discrete electrolysis phase as elemental Co – depicted with dashed lines in Figure 12. (Tedjar and Foudraz 2010). Thus for Co recovery, there are three different procedures, which are presented as optional or concurrent in the patent description (Tedjar and Foudraz 2010.) and thus it is not known if one option is in practice favoured on top of the other.

According to the creators of this technology, the presented methods enable also the recovery of the constituent ions of $LiFePO_4$ cathode (Tedjar and Foudraz 2010) but it is not known if this is implemented in practice (Vadenbo 2009, p. 33). It is additionally possible to precipitate PF_6 –

originating from the electrolyte salt $LiPF_6$ – with ammonium salt in the hydrolysis phase. A requisite for this practice is the presence of LiCl due to its stabilizing effect on the electrolyte salt. (Tedjar and Foudraz 2010). Apparently, primary Li battery cells constitute the source for Cl, otherwise it must be introduced to the solution separately. As with $LiFePO_4$ treatment, the industrial execution of PF_6 recovery is not confirmed (Vadenbo 2009, p. 33), neither is the purity or intended use of the product discussed.

4.1.4 AkkuSer

AkkuSer has developed a low temperature, dry technology for crushing and separating battery component materials that are further processed either with pyrometallurgical or hydrometallurgical methods (Pudas et al. 2015; Vezzini 2014, p. 543). The company accepts all kinds of batteries but pre-sorts them by type (e.g. LiBs, NiMHs, etc.) in order to treat each of them with an optimal procedure (Pudas et al. 2015). In the following section, only the process encompassing LiBs recycling is covered, as depicted in Figure 13.

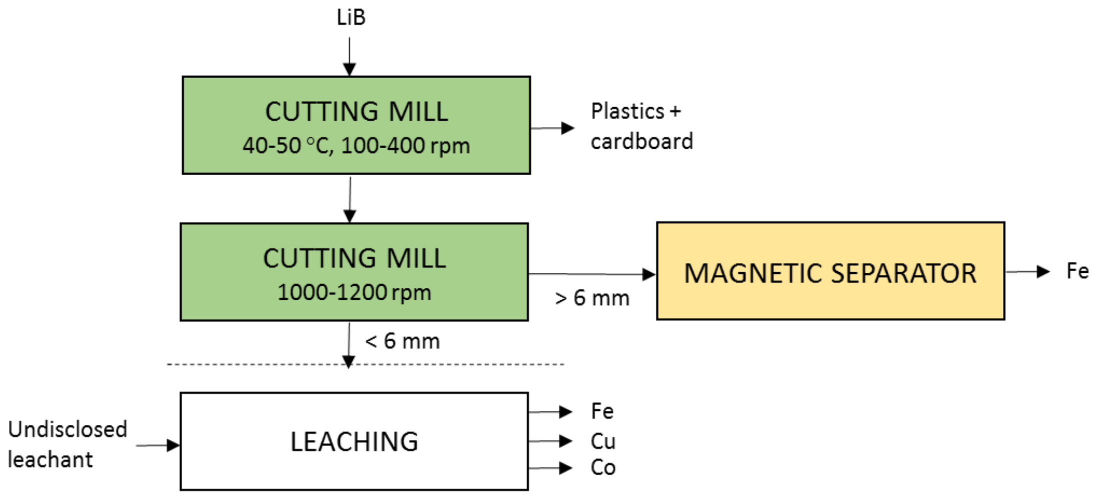

Figure 13 Schematic depiction of the AkkuSer process for recycling LiBs. Process inputs are marked with arrows on the left side and outputs – recovered or removed items – on the right side. Physical processing steps are indicated with colours: comminution with green and magnetic separation with yellow. Particle size range resulting from comminution step is marked below the said step. Known process parameters such as temperature or milling speed are expressed within the particular phase. The dashed line above the last step, leaching, denotes the end of the Akkuser process and the beginning of hydrometallurgical phase.

In the AkkuSer process, batteries are comminuted in two consequent steps that have distinct process parameters. First, the batteries are treated with a cutting mill at 40-50 °C and 100-400 rpm speed down to pieces of 1.25-2.5 cm long. Apparently, no protective atmosphere is used in the chamber during milling, but the low process temperature serves as means to minimize the risk of fire. Due to H_2 and O_2 release upon crushing, the chamber is equipped with a cyclonic air remover. The exhaust gases are withdrawn and filtered twice – from the first filter, light plastics and cardboard can be separated. As plastics can have metals attached, they are later directed for Ni recovery in the NiMH recycling process and for Co recovery. The exhaust gases are filtered again and once becoming particulate-free, are released to the atmosphere. (Pudas et al. 2015)

To produce a metal-rich fraction suitable for further refining, the process continues with another comminution stage. An air-tight tube that leads the feed to the second crusher enables also cooling. This time, crushing takes place at room temperature with high cutting speed (ca. 1000-1200 rpm) to produce particles of <6 mm. To prevent the release of fine dust to the atmosphere, also here a cyclonic air remover is used. Finally, the ferrous fraction is removed with a magnetic separator and transferred e.g. to a smelting process. The remaining Co and Cu rich powder is ready to be refined with pyrometallurgical or hydrometallurgical techniques. (Pudas et al. 2015). As indicated in Figure 13 with a dashed line, the AkkuSer process ends at this point.

In practice, the AkkuSer plant operating in Finland delivers the Co-containing black powder to a hydrometallurgical refiner specialized in Co products manufacturing (Pudas 2010); one product group being cathode material precursors (Pudas 2009). According to the knowledge gained by Ekberg and Petranikova (2015) based on personal communication with Pudas, the process steps used in refining are leaching, Fe precipitation, solvent extraction of Cu and solvent extraction of Co, but the steps are of course dependent on what the desired product is. Ni-containing waste in turn is processed in a smelter and Ni production plant to produce metallic Ni (Pudas 2010). The fate of Al in the AkkuSer process is not discussed in the sources available, apart from noting in the introduction of a patent that Al is one of the materials of interest (Pudas et al. 2015).Considering also the subsequent hydrometallurgical treatment, it is probable that majority of Al has to be recovered in advance and the final impurities precipitated before the actual precipitation process of Co. This issue is discussed in more detail in the context of Gratz and LithoRec processes.

The composition of the final powder of the Akkuser process apart from Cu and Co is not known. However, based on the flowsheet of the process and on the fact that some battery raw materials, such as active electrode materials are also readily ground to powder (Zhang et al. 2014), it is most likely that graphite is mainly present in the final fine powder fraction. Additionally, it is probable as was already mentioned, that some Al originating from the cathode foil is also present in the fine powder due to its similar crushing properties with Cu as demonstrated by Zhang et al., (2014) with a process combining shear crushing and impact crushing.

AkkuSer has stated that their process provides recycling/reuse efficiency of over 90% (Pudas 2009). It has also been estimated that the technology consumes energy at only 0.3 kWh/kg (CEC 2015, p. 58). However, it should be remembered that even if these claims were valid, the technology used by AkkuSer does not offer a complete recycling process of Li-ion batteries. As depicted in Figure 13, for the final recovery of the materials, hydrometallurgical techniques are additionally needed, consequently increasing energy demand and affecting the final recycling efficiency.

4.1.5 Sumitomo-Sony

The information available on the Sumitomo-Sony process for recycling LiBs is scarce. Nevertheless, it is known that the technology was developed in cooperation between Sony Electronics who produces and employs batteries, and Sumitomo Metal Mining Company a metal refinery (Cardarelli and Dube 2007). The leading target of this process is to recover CoO of high enough grade to be used in the manufacturing of new LiBs (Cardarelli and Dube, 2007). In the first phase, the electrolyte and organic materials are removed from the batteries with calcination. This is followed by a further pyrometallurgical treatment, leading to recovery of a Co, Ni and Fe-containing alloy but also to the loss of Li to the slag. Co is recovered from the alloy by a hydrometallurgical process and Cu and steel are separated mechanically as by-products. (Cardarelli and Dube 2007; Al-Thyabat et al. 2013)

4.1.6 Other industrial recycling processes accepting LiBs

In this section, some additional industrial processes recycling LiBs among other battery types or as secondary material are discussed shortly. The common denominator of the processes presented here is that they were not invented to recycle LiBs (or primary Li batteries) specifically, nor do they treat them individually.

Batrec started battery recycling in the end of the 1980's with mixed household batteries due to their mercury content (Batrec n.d.), thus the technology is primarily developed for Zn and Hg recovery from alkaline and Zn-C batteries (Sayilgan et al. 2009). The technology was evolved and modified from the Japanese Sumitomo process (Bernardes et al. 2004). To address reactivity issues, LiBs are stored and shredded under protective CO_2 atmosphere and then neutralized by moist air (Zenger et al. 2010). Crushed, neutralized battery scrap can be further treated with different methods (CEC 2015, p. 57; Georgi-Maschler et al. 2012). Details of the subsequent steps in recycling LiBs are not available (Zenger et al. 2010; Vadenbo 2009, p. 25).

Two other processes, namely *Inmetco* and *Glencore plc. (former Xstrata)* recycle LiBs among other materials. *Inmetco* technology was primarily developed for processing electric arc furnace dusts. The batteries and other scrap are fed to a rotary hearth furnace with reducing pellets and further refined in an electric arc furnace. Only Co, Ni and Fe are recovered in the form of an alloy. Other metals are slagged and organic materials burned. (Espinosa 2004; Georgi-Maschler et al. 2012). *Glencore plc.* targets the recovery of Co, Ni and Cu utilizing pyrometallurgical and hydrometallurgical methods. Other component materials of LiBs either service the process as a source of energy or reducing agents, or are slagged. (Georgi-Maschler et al. 2012; Rombach and Friedrich 2014). In neither of these processes the special issues of the LiBs recycling are addressed, but one should keep in mind that batteries are considered only as secondary feed to a process dedicated to another cause.

4.2 New processes under commercialization

4.2.1 Accurec

Accurec GmbH vacuum thermal recycling (VTR) process dedicated to recycling portable LiBs is currently under permitting procedure in Germany (Accurec n.d.). A high recovery rate of Co alloy and Li_2CO_3 is pursued by a combination of physical separation, hydrometallurgical and pyrometallurgical methods (Vezzini 2014, p. 542), although it is also mentioned that the target is to recover as many battery components as possible (Georgi-Maschler et al. 2012). Moreover, in the laboratory tests, a mixture of LiB cathode chemistries was treated, indicating that this technology intends to recycle more than just LCO chemistry. Traction batteries are also of interest. (Georgi-Maschler et al. 2012). Along with LiBs Accurec recycles NiCd, NiMH and zinc alkaline batteries, but all these battery types are treated distinctively (Accurec n.d.; Vezzini 2014, p. 543). Due to the scope of the present thesis, only the process encompassing LiBs recycling is discussed and represented in Figure 14.

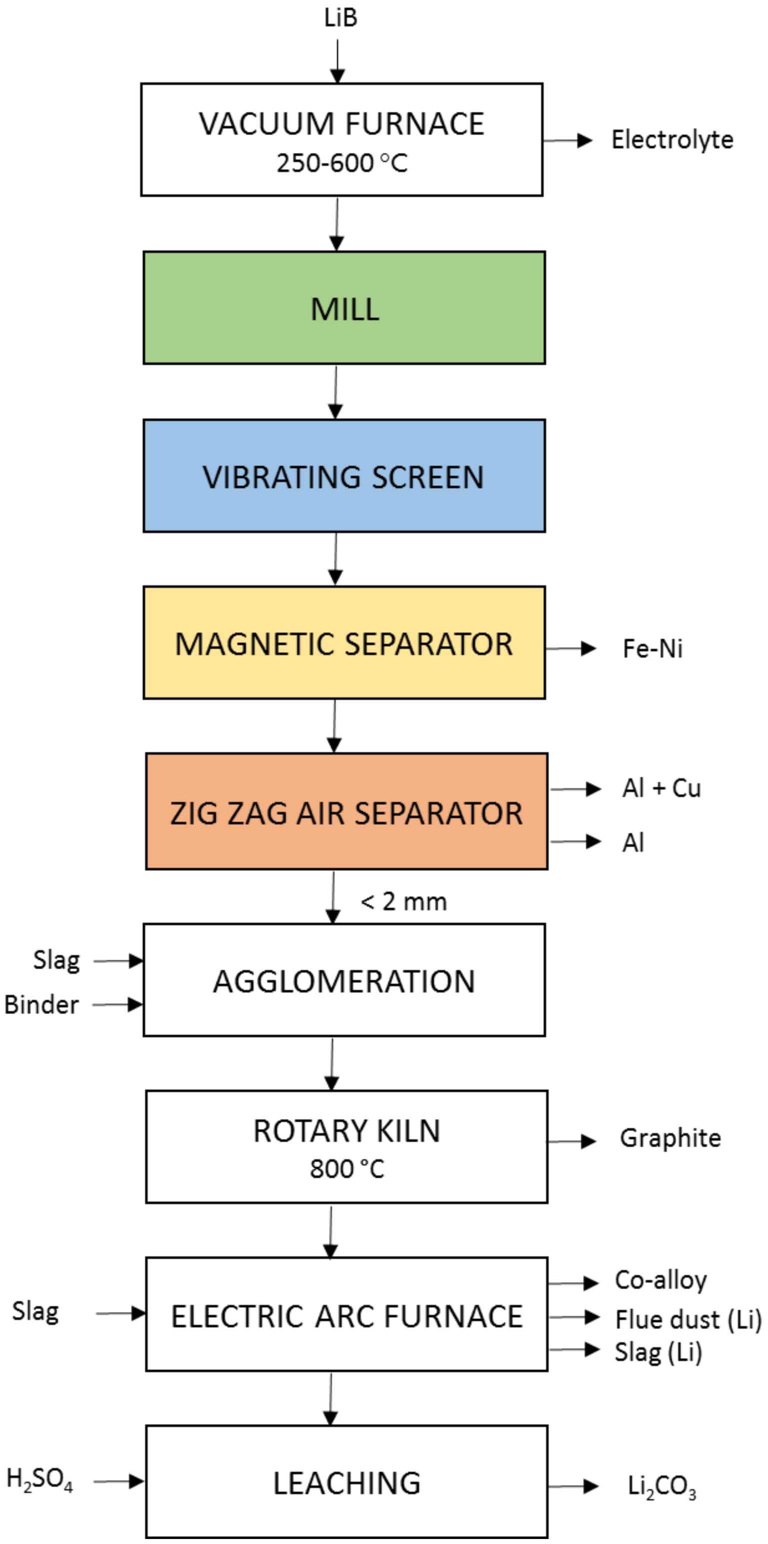

Figure 14 Accurec process for LiBs recycling. Process inputs are marked with arrows on the left side and outputs – recovered or removed items – on the right side. Physical processing steps are indicated with colours: comminution with green, screening with blue, magnetic separation with yellow and density based separation with orange. Particle size range resulting from comminution or screening step is marked below the said step and the other known process parameters such as temperature are expressed within the particular phase. Modified from Georgi-Maschler et al. 2012.

The LiB packs are disassembled manually and plastic casings, electronic devices, steel components and Cu cables are separated from other materials (Georgi-Maschler et al. 2012; Vezzini 2014, p. 543). Due to the Cu content in this manually separated fraction, it is considered as a feasible feed to Cu smelters (Georgi-Maschler et al. 2012). As pointed out in Figure 14, the automated process starts with a thermal treatment that deactivates the cells and evaporates the electrolyte and other organic components. In these first phases, the operation temperature is 250-600 °C. (Georgi-Maschler et al. 2012; Accurec n.d.). Reusing the electrolyte was not considered practical in the tests due to the decomposition products the condensate contains. It was however estimated that after process optimization, an 80% recovery rate of the electrolyte could be achieved (Georgi-Maschler et al. 2012).

In the subsequent step, the cells are comminuted with an unspecified mill. The produced particles are processed with a vibrating screen, magnetic drum separator and a zig zag air classifier to produce a magnetic Fe-Ni fraction, an Al fraction from the casings, an Al and Cu foil fraction and a fine fraction. Details of the exact arrangement of these process steps are not available, thus they are represented as parallel phases in Figure 14. However, the fraction of interest containing metals oxides (Co, Mn, Li) and graphite is < 0.2 mm in size and has to be agglomerated into pellets to ease the following pyrometallurgical handling (Georgi-Maschler et al. 2012; Vezzini 2014, p. 543). In this phase, slag and binder have to be added to the fines to form large enough pellets. Additionally, prior to pyrometallurgical recovery of Co and Li, the graphite content of the fine fraction has to be analysed and adjusted because it affects the appropriate slag-charge-share and the success of the whole process. Reducing graphite content with a thermal treatment can be accomplished either in a separate rotary kiln or in an electric arc furnace. The operation temperature here is approximately 800 °C. (Georgi-Maschler et al. 2012).

In pyrometallurgical treatment in electric arc furnace a trade-off has to be made between the recovery of Co and Mn. Since the same slag composition (input slag in the Figure 14) is not optimal for both of these metals, high recovery of Co is favoured in designing the input slag leading to partial loss of Mn in the slag. Treating the pellets in an electric arc furnace leads to the recovery of Co-based alloy that has a similar content than typical commercial Co-based super-alloys which is therefore a finished product that can be placed on the market, according to the inventors. (Georgi-Maschler et al. 2012).

During the electric arc furnace treatment, part of Li is oxidized and exits the furnace as a flue dust that can have even 5 times higher Li concentration than the original charge. Part of Li is also slagged. Both of these Li-containing fractions can be further treated hydrometallurgically for Li recovery but the flue dust is the more interesting stream because of its higher Li concentration. Additionally, the fine flue dust can be introduced to the leaching process as is, while slag has to be milled approximately to particle size < 100 µm. (Georgi-Maschler et al. 2012). To finalize the process, Li containing materials are leached in H_2SO_4 and Li is precipitated as Li_2CO_3 (Georgi-Maschler et al. 2012; Vezzini 2014, p. 543). According to the developers of the process, over 90% recovery rate of Li could be reached with this method. The qualitative aim is to recover Li_2CO_3 in such a high grade to be used either in battery or glass production. The suitability of the end-product of this process for glass manufacturing has been confirmed by an external glass producer. (Georgi-Maschler et al. 2012).

The authors also claim that other cathodes than LCO are recyclable with this process by adequately adjusting the operating parameters. Nevertheless, they admit that the feasibility of the process depends on the Co price and thus the share of Co in the battery waste. (Georgi-Maschler et al. 2012). Another question that needs to be answered is how deeply the changing battery waste composition affects the several process parameters and products: an optimal slag composition, the grade of the produced alloy and the treating conditions of the flue dust and slag. The Accurec webpage states that the partner in charge of the thermal pre-treatment of the cells is capable of processing all kinds of LiB chemistries (Accurec n.d.), but there is no further information available about the influence of the mixed cathodes to the subsequent process steps, for instance. Finally, it may be justifiable to suspect that only for the purpose of producing a Co alloy and Li salt, Accurec is a relatively a long and probably expensive process.

Accurec has also been a partner in a project called EcoBatRec that focuses on recycling EV, HEV and e-bike batteries. The general outline of the process proposed is similar to the one described above for consumer batteries. However, there are some issues characteristic to traction batteries that have to be addressed. First of all, due to the polymeric foam used as vibration absorber in traction batteries, special attention has to be given to by-product handling during the thermal treatment. (Träger et al. 2015). Another interest of the project is the Li recovery from the electrode active powder fraction that has been generated through subsequent physical separation steps. The methods studied are based on the vapour pressure of Li: they are direct vacuum evaporation and entraining gas evaporation (under N_2). In both methods, the Li compound is thermally decomposed and reduced with graphite to separate a Li phase that can be then selectively volatilized. After vacuum evaporation, elemental Li is produced with distillation, whereas LiO is recovered in entraining gas evaporation. In the preliminary tests with the entraining gas evaporation technique, approximately 75% of the Li content of the feedstock could be recovered at 1650 °C. (Träger et al. 2015). It seems that in terms of process costs, the high operation temperature for Li recovery decreases the feasibility of the complete process. On the other hand, further studies are underway for optimizing and improving the process (Träger et al. 2015).

4.2.2 Gratz "closed loop" process

Gratz et al. (Gratz et al. 2014; Sa et al. 2015; Zou et al. 2013) have, in their own words, developed a "closed loop" recycling process for mixed LiBs targeting high yield of materials and cathode material reuse in batteries. The purpose is especially to preserve the value of the cathode compounds instead of merely the value of the elements they contain (Gratz et al. 2014). According to Heelan et al. (2016) the process is at the moment in commercialization phase. Despite the aim for recycling mixed LiB chemistries, the published work concentrates especially on NMC cathodes. Therefore, the flowsheet depicted in Figure 15 has the focus in NMC cell.

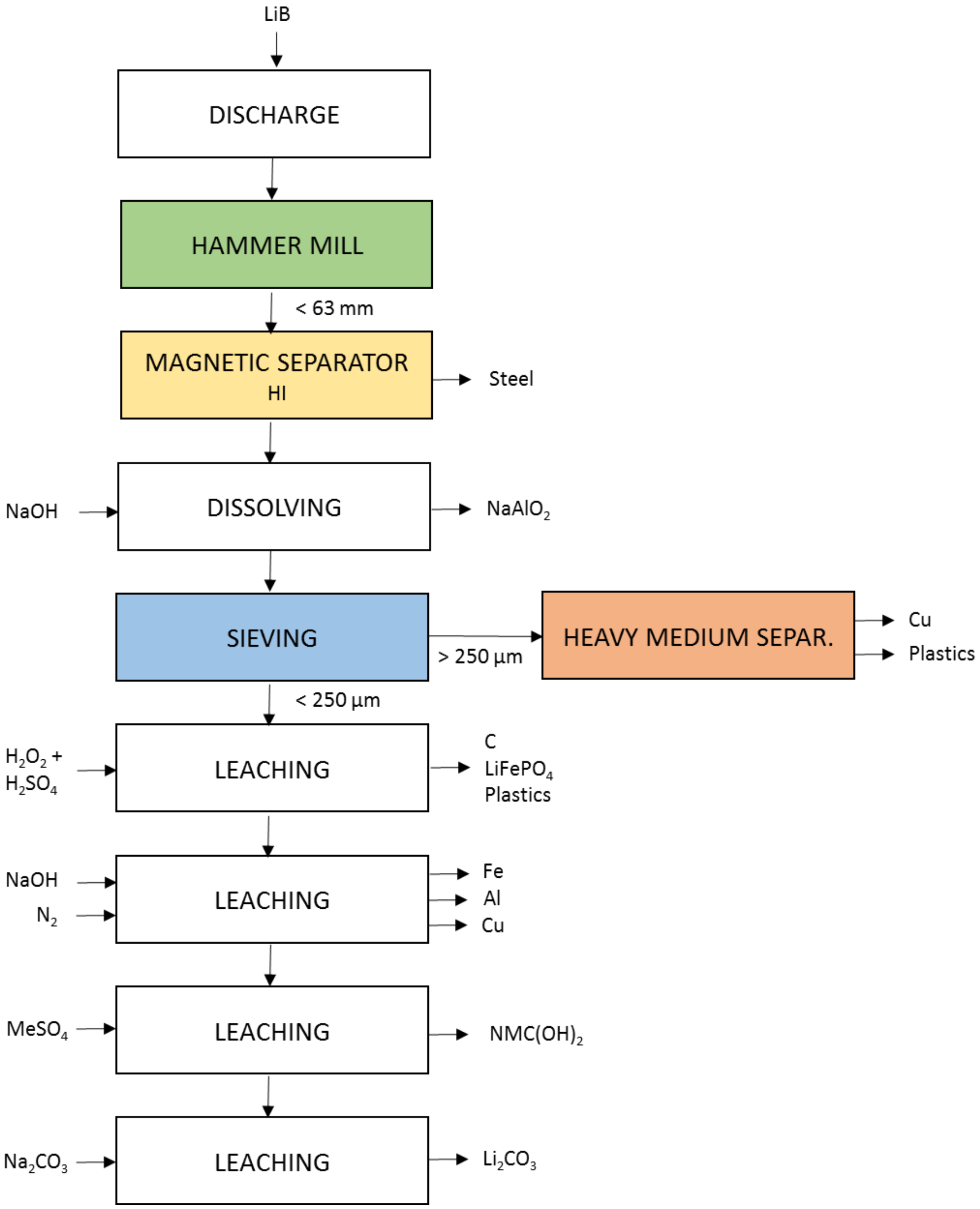

Figure 15 Process developed by Gratz et al. for LiBs recycling with special focus on NMC chemistry. Process inputs are marked with arrows on the left side and outputs – recovered or removed items – on the right side. Physical processing steps are indicated with colours: comminution with green, screening with blue, magnetic separation with yellow and density based separation with orange. Particle size range resulting from comminution or screening step is marked below the said step and the other known process parameters within the particular phase; here e.g. HI for magnetic separation denoting "high intensity". Modified from Gratz et al. 2014 and Sa et al. 2015.

Discharged batteries are first shredded with a hammer mill to under 0.63 cm size. From the resulting particles, the steel case fraction is removed with a rare earth magnet. In the next step, the particles are immersed in NaOH solution in order to separate Al foil from the active powder by dissolving the foil into the solution. As a by-product, $NaAlO_2$ can be recovered. (Gratz et al. 2014). After drying the material, a fine fraction is separated with a 250 µm sieve. The coarse fraction is treated with heavy media density separation procedure: the purpose is mainly to take apart the heavy Cu foil parts from the plastics. The fine fraction and the separated plastics are guided to a leaching process that uses a combination of H_2SO_4 and H_2O_2 as a leachant for improved dissolution of Ni, Mn and Co. By treating the plastics, the cathode powder attached to them can be dissolved and the plastics can then be filtered out from the solution. Additionally, undissolved carbon and residual $LiFePO_4$ – undissolved due to high bonding energy of Fe-P-O – are filtered out. (Zou et al. 2013; Gratz et al. 2014).

As a result of fluctuating LiB waste content, the chemical composition has to be examined in the process to confirm the content of Ni, Co and Mn ion as well as impurities (Sa et al. 2015; Gratz et al. 2014). pH is adjusted with NaOH to get the impurities – Fe, Al, Cu – precipitated out of the solution (Zou et al. 2013) and subsequently, N_2 is introduced to the system to prevent Mn^{2+} ion oxidation (Sa et al. 2015). Ni, Co and Mn ion concentrations of the solution are balanced by adding requisite metal salts, e.g. sulphates as indicated with "$MeSO_4$" in Figure 15, to achieve the desired composition of $Ni_xMn_yCo_z(OH)_2$ co-precipitate that is produced by adjusting pH. Mixing the precipitated $Ni_xMn_yCo_z(OH)_2$ product and Li_2CO_3 (pristine or recycled) a new cathode material can be synthesized and ground into powder to be used in new cathodes (Gratz et al. 2014). There can be a small amount (0.4%) of elemental Li in the precipitated hydroxide, but according to the authors it is not a pressing issue (Sa et al. 2015).

After the co-precipitation step, Li-ions are still in the solution and will be collected in the filtering solution (Sa et al. 2015). In earlier work (Zou et al. 2013), it was described that after precipitating $Ni_{1/3}Mn_{1/3}Co_{1/3}(OH)_2$, Na_2CO_3 was added to the solution and Li_2CO_3 was deposited at 40 °C. It was then used for synthesis of new cathode material with some additional virgin Li_2CO_3. Thus, it has been demonstrated that the authors pursue also producing the other precursor for active cathode material. The recovery of elemental Li will allegedly be studied further in future work (Sa et al. 2015).

The presented process is based on the idea that labour and energy do not need to be consumed for separating hardly separable Ni, Co and Mn, but they are recycled together into a new battery material. Recovery rate for Co, Mn and Ni can reach over 90% with this process. On the other hand, the absolute yield of materials is dependent on the composition of the initial battery waste that has to be determined accurately. (Gratz et al. 2014). Even though the authors call this recycling method a “closed loop” process, it fulfils this definition only for Co, Mn and Ni containing cathodes. However, it seems that recycling NCA and LNO type cathodes is going to be addressed too in the future research (Zou et al. 2015). Fe is considered an impurity implicating that also Fe originating from the $LiFePO_4$ cathode is treated as such (Sa et al. 2015). This could then decrease the recovery rates further, if the share of this particular cathode type was to increase in the waste stream. Hence, the capability of the process to efficiently recycle the entire variety of cathode materials in the waste stream in a “closed loop” process is not yet confirmed – despite the fact that according to authors (Heelan et al. 2016) it is an answer for recycling the changing battery chemistry.

4.2.3 LithoRec

The LithoRec process has been developed for recycling traction battery modules. Compared to LiB cells the feed contains thus additional steel, Al, plastics and Cu originating from the module casing components and electric connectors. Special attention has been given to separation and purity of the active materials, in particular with respect to foil materials. The reason for this is to promote the efficiency of subsequent hydrometallurgical processes aimed at recovering high-grade cathode materials. Potential hazards related to the treatment of electrical and chemical components, along with explosion risks are considered in this method. (Diekmann et al. 2016). There is a demonstration plant of technical scale where this process has been implemented (Diekmann et al. 2017), following the steps included in Figure 16.

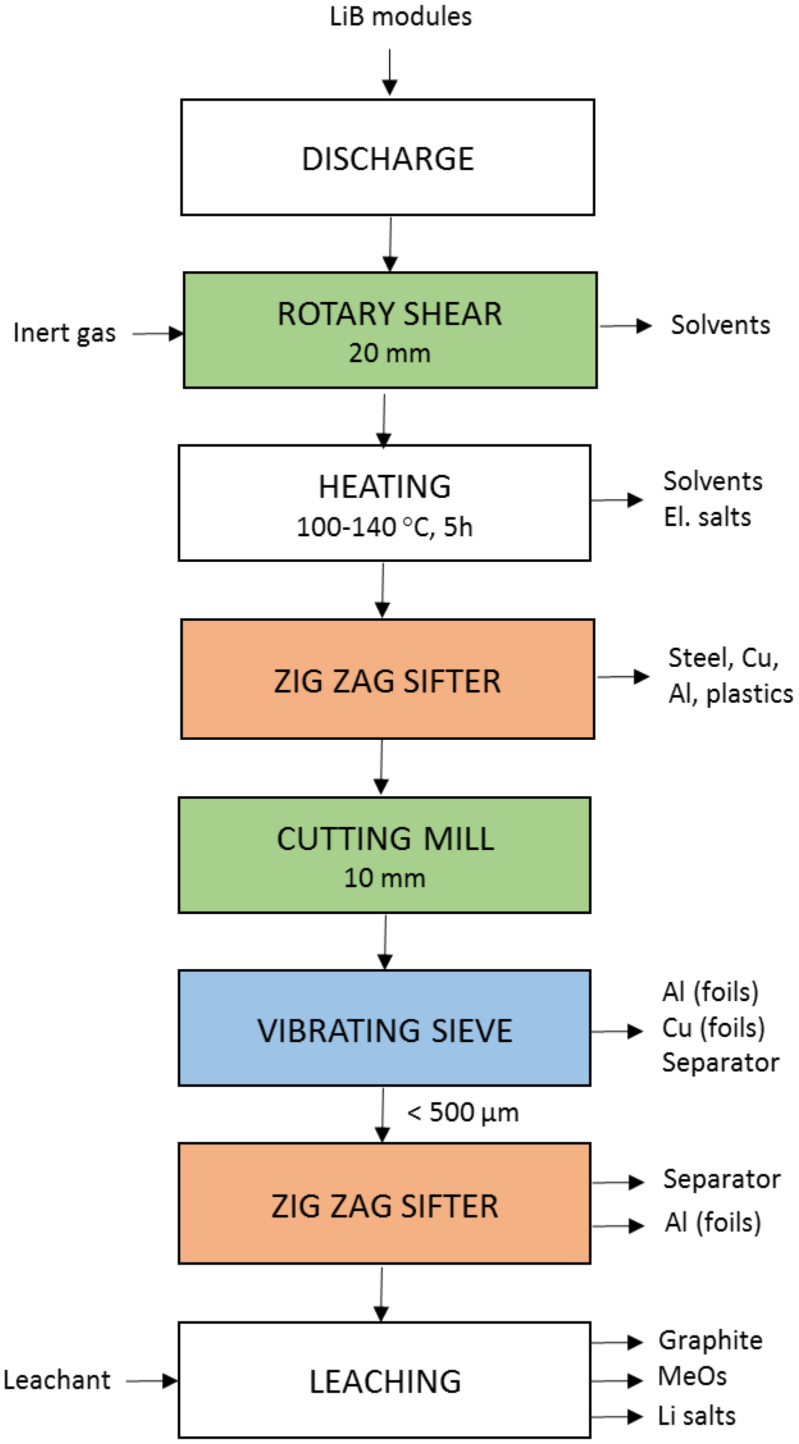

Figure 16 LithoRec process for recycling LiBs. Process inputs are marked with arrows on the left side and outputs – recovered or removed items – on the right side. Physical processing steps are indicated with colours: comminution with green, screening with blue and density based separation with orange. Particle size range resulting from comminution or screening step is marked below the said step and the other known process parameters such as temperature within the particular phase. Modified from Diekmann et al. 2017 and Diekmann et al. 2016

The key of the LithoRec process are the complementary crushing and classification phases. After discharging and disassembling the battery modules, the cells are crushed in an inert atmosphere with rotary shear cutter with a discharge screen with 20 mm opening size. Part of the electrolyte solvents are released already during this first crushing phase, facilitating the later separation of the fragments due to lower adhesion between the particles. The downside is that harmful gases are released, hence treatment using activated carbon filters is required before being released to the atmosphere. In the subsequent drying step, the rest of the electrolyte is removed from the cell. By heating the cells at 100-140 °C for 5 h, the solvents are evaporated and the $LiPF_6$ decomposes producing HF. The solvents can be further condensed for recovery or combusted and the HF by-product is cleaned with a gas scrubber. After this mild thermal treatment step, the cell fragments are set for the first classification step in a zig zag sifter. (Diekmann et al. 2016; Diekmann et al. 2017).

The purpose of the first classification step is to prepare the material for a second, milder crushing by removing the heavy parts – casings, electric conductors, steel parts and plastics – from the softer materials. The separation in the zig zag sifter is brought about by both particle size and density. A disadvantage of this phase is that approximately 2.9 wt.-% of electrode active material, together with Al and Cu, is lost with the heavy fractions because they form inclusions with separators and behave thus as heavy parts in air separation. However, the first air classification is a necessity for protecting the machinery in the second crushing step. (Diekmann et al. 2016; Diekmann et al. 2017).

For an improved yield of black mass (i.e., the mixture of anode and cathode active powder), the battery scrap is treated again with cutting mill. This practice applies cutting stress on the electrode fragments and mitigates the detachment of coating powder from the foil. The effect is based on both the decomposition of the inclusions, formed of active powder, foils and separator, and the reduction of the black mass particle size. During this second crushing step, Diekmann et al. (2017) manage to avoid the increase of Al, Cu and Fe impurities in the fine fraction almost completely because – in their own words – the effect is based on the cutting stress and a 10 mm discharge screen is used. If overmilling occurred, there would be a risk of decreasing the particle size of foils, which would undesirably end up into black mass. (Diekmann et al. 2016; Diekmann et al. 2017)

Prior to the second zig zag sifting of the feed, the fragments are sieved again with 500 µm vibration sieve to separate black mass further from the foil and separator particles. In the second classification phase, the light separator material is detached from the foil materials and separated from the rest of the feed. A slight drawback of this phase is that some Al is lost to the light fraction as well. Nevertheless, the share of Al in the light fraction is lower than it would be in the case of omitting the second crushing. At the end of this phase, the foil, separator and the active powder fractions are separated from each other and the electrode material can be sent to hydrometallurgical treatment. (Diekmann et al. 2016; Diekmann et al. 2017)

The final recovery of electrode materials and Li is accomplished with hydrometallurgical methods about which there are not any specific details available in the open literature. Hence, only a general outline can be provided here. At this point, depicted in Figure 16 with the "final Leaching"-phase, the fine fraction is leached and after removing solid graphite from the solution, Co, Ni and Mn are precipitated as oxides. The remaining Li-containing solution is purified with crystallization and ion-exchange and Li salts are separated with electrochemical processes. The final products i.e. Li salts, hydroxides or carbonates, and metal oxide particles can be calcined together to produce new active materials. (Hanisch 2014)

Hanisch et al., (2015) investigated also the thermal treatment to destroying the binder and thus further separating the active electrode powder from the foils. Thermal treatment under O_2 for 90 min at 500 °C combined with 1 min air impact treatment in an air-jet separator helped to loosen the binding between the foil and the electrode mass, but also the binding forces between the active materials particles. This enabled the use of finer sieve size in further separation and divided Al current collector foil particles and active material more efficiently. (Hanisch et al. 2015). Unfortunately, this resulted also in a higher amount of Cu impurities in the black mass due to Cu corrosion provoked by the O_2 atmosphere (Diekmann et al. 2017). Still, it is not completely clear how notable a problem the presence of Cu in black powder is, since it could be for example cemented with Fe in the beginning of the leaching phase (Wang et al. 2016) and as further discussed, it may not be harmful for the battery performance in small concentrations.

The main focus of the LithoRec process is on the NMC cathodes. For example, the LFP cathode materials cannot be mixed with the NMC powder due to their different precipitation limits (Diekmann et al. 2017). The possibility of processing other common cathode chemistries LCO, LMO or NCA is not discussed in the work related to LithoRec. However, it seems that in this recycling technology, the presumption is to process one battery chemistry at a time, focusing on traction batteries where one pack containing one chemistry cells. Considering the metal contents of LCO and LMO, they could presumably be processed together with NMC. NCA, on the other hand, contains Al that is considered an impurity in the precipitation step and hence might not be suitable to be treated in a mixed waste.

In a more recent follow-up project, namely LithoRec II, also the electrolyte extraction and recycling of graphitic anode have been studied (Rothermel et al. 2016; Grützke et al. 2015). These techniques do not appear to be part of the demonstration plant process (Diekmann et al. 2017), hence they are not discussed in more detail here. However, some of the key findings are discussed in the context of the OnTo recycling process (Section 4.2.4) and in Section 5.4 concerning graphite recycling.

4.2.4 Onto Technology

The OnTo Technology recycling process for LiBs developed in U.S., aims at placing recovered electric vehicle battery materials back to the battery production (Dunn et al. 2012a) and recycling almost any cathode material (Sloop 2014). This recycling process is known in the literature also with the name Eco-Bat or “direct recycling process” (Gaines et al. 2011). There are several innovations and patents related to this technology which according to the main innovator Steven Sloop was in pre-industrial, pilot scale in year 2015 (Sloop 2015). The time span of the patent publications is approximately 10 years. The first patents (Sloop 2007; Sloop 2010; Sloop and Parker 2011) concentrate especially on describing the extraction of the electrolyte from used cells and processing intact cells / damaged cell materials further. In the newer innovations (Sloop 2014; Sloop 2016a; Sloop 2016b; Sloop and Allen 2016), the focus is on refurbishing positive cathode materials. In the following section the focus is on the work concentrating on treating the complete cells; a general outline of the OnTo process is constructed into Figure 17.

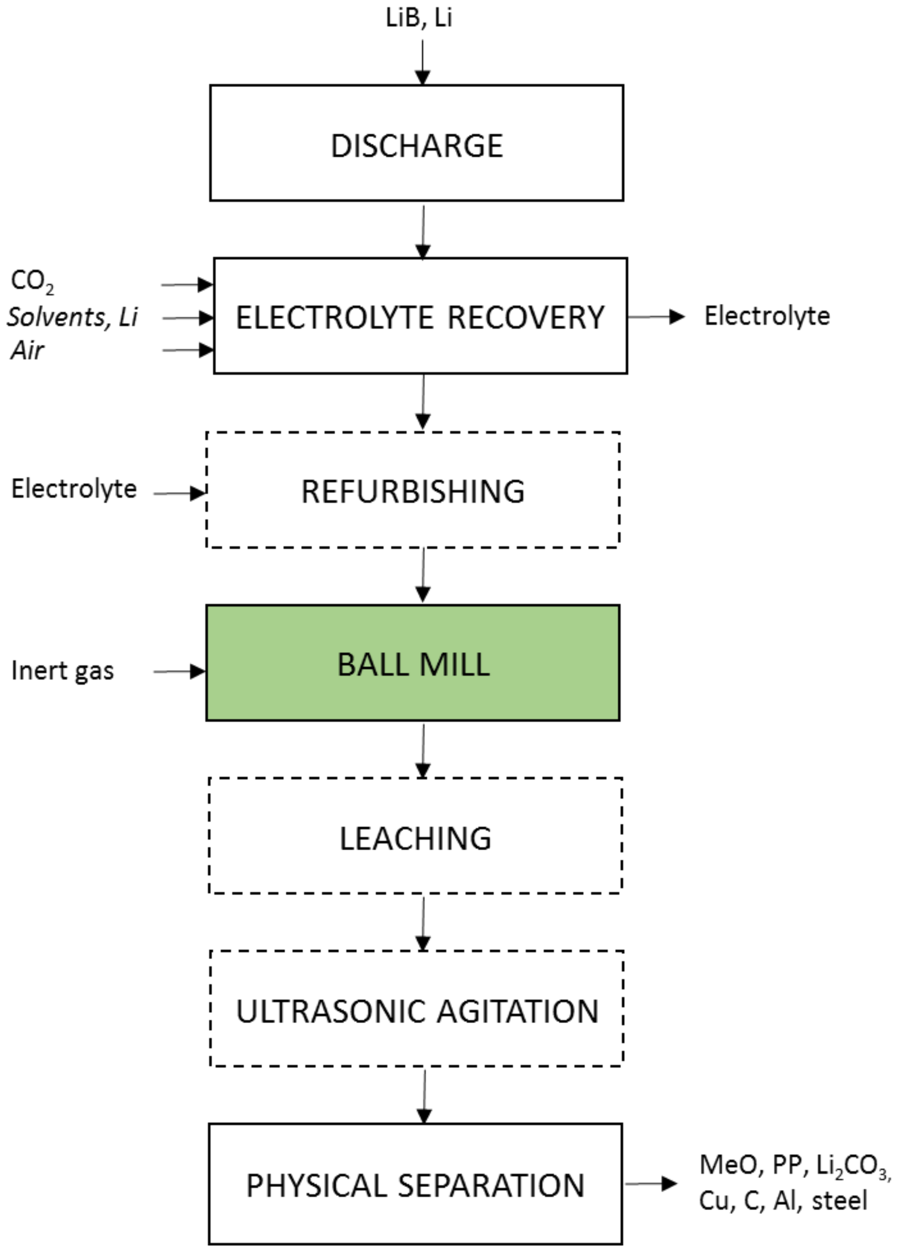

Figure 17 Schematic representation of OnTo process. Optional steps are depicted with dashed line. Refurbishing the cell or processing the materials of a damaged cell starting with ball milling are alternative paths.

After discharging the cells, the process proceeds to the unique phase of OnTo technology, electrolyte recovery, as depicted in Figure 17. The electrolyte recovery is mainly based on the properties of the supercritical CO_2. After discharging and disassembling the battery packs, the exposed cells are fed to a container and CO_2 is added. Temperature and pressure are increased to a point where CO_2 reaches a supercritical phase with a dense gas-like behaviour (approximately 74 bar at 31°C). As the pressure increases, the supercritical fluid is directed to the cells either by the breeched cell walls or alternatively through the possible pressure relief valves or other re-sealable openings. The low surface tension of the fluid improves its contact with the electrolyte, promoting its dissolution. The extraction process could be further improved with solubility enhancers. (Sloop and Parker 2011; Sloop 2010). In fact, a combination of solvents in addition to CO_2 seems necessary for improved electrolyte extraction, especially considering the most valuable part, $LiPF_6$ salt (Grützke et al. 2015). This is due to the different polarity of the electrolyte components: similar polarity of the electrolyte and extraction solvent components improves extraction efficiency (Nowak and Winter 2017). For refurbishing purposes, also a Li-containing solution could be introduced to the cell in this phase. In addition to the electrolyte recovery, this phase enables the removal of the elemental Li possibly present in the cell since it reacts with CO_2 producing Li_2CO_3. To prevent CO formation air can be added to the container. Increasing the pressure up to 138 bar assists the production of Li_2CO_3 further. (Sloop and Parker 2011; Sloop 2010).

The electrolyte is finally recovered in a collection container where the supercritical fluid cools and expands, thus enabling precipitation of the electrolyte solvent and salt. The depicted method is, according to its inventors, capable of removing different kinds of impurities and waste products that have deposited at the SEI layer during the use. (Sloop and Parker 2011; Sloop 2010; Dunn et al. 2012a). As a result of this phase, the cells are devoid of the electrolyte but contain the electrodes and the separator. Now there are two processing options. Refurbishing the cells is the chosen method if the parts are still functional and the casing is intact. The functionality and eligibility of the cells for refurbishment can be determined i.e., with impedance measurements, comparing the capacity of the cell to the original value. In this method, the cells are filled with fresh electrolyte, sealed and recharged in a moisture-free environment (Sloop and Parker 2011; Sloop 2016a; Sloop 2014).

If the refurbishing criteria of the cells is not met, the materials are recycled. The cells are ground e.g. with a ball mill in an environment free of water and O_2 to avoid contamination of the materials. Delamination of the active material powder from the current collector foils could be further improved with an adequate solvent and ultrasonic agitation. As indicated in Figure 17 with the “physical separation” step, separating the ground material is depicted only in a general level. Possible methods according to innovators are e.g. electrostatic method or some density difference-based method such as a cyclone, fluidized bed or solution dispersion, decantation and filtration. (Sloop and Parker 2011; Sloop 2010). The resultant fractions of this phase are transition metal oxides, C, PP, Li_2CO_3 and Cu, Al and steel (Sloop 2010). According to the inventor all the materials recovered can be reused (Sloop and Parker 2011) but detailed information is omitted.

As seen, the main focus of the OnTo technology is in refurbishing the cells and the cathode materials. The separation and processing of cell casings, anode material and the foils are not discussed within this invention. Thus, it cannot be described or deduced what the destination of these other fractions is or how can they be recycled after this process. Recovering the electrolyte is unique for this process which is considered a relevant issue for fulfilling the Battery Directive recycling objective, for example, since the electrolyte forms 10-15% of the cell weight (Nowak and Winter 2017). However, it is not discussed what the quality of the recovered product is and how it would be re-utilized. For example, the use of solubility enhancers with CO_2 might require some further processing of the recovered electrolyte prior to re-use (Dunn et al. 2012a). Additionally, the condition of the electrolyte at the end-of-life should be further studied, considering the possible slow reduction of the electrolyte components due to SEI layer growth (Diekmann et al. 2017; Vetter et al. 2005) and the consumption of Li salt to understand how the electrolyte should be processed in order to be used again.

The effects of high pressure to cell materials need also some consideration in this technology. In the experiments conducted by Rothermel et al., (2016), it was found that the high pressure needed for producing supercritical CO_2 was too harsh for the crystal structure of graphite: the crystallite size of graphite was diminished, which lead to decreased discharge capacity of the cell compared to performance after milder, subcritical CO_2 extraction. An additional disadvantage of supercritical conditions was that electrolyte and SEI layer residuals permeated between the graphite layers. The later could cause graphite delamination upon thermal treatment if the permeated material evaporated or decomposed. Since the cathode material is also a layered or tunnel-like structure that has to enable movement of the Li ions back and forth, it might need further confirmation that this active material was not affected adversely by the high pressure.

Based on the information that was available so far, Dunn et al., (2012a) questioned how the recycled cathode material would perform especially when the PVDF binder was not specifically separated. However, in later work by Sloop (2016b) it is indicated that the measures such as commuting in the basic medium, rinsing the material with acetone and the subsequent grinding contribute to the removal of the binder. Hence, binder removal is considered an issue that has to be solved, but the suggested solutions are limited to the situation of treating solely cathode materials and don’t provide detailed information of these treatments as part of a complete cell recycling procedure. Nevertheless, also the specific capacity obtained when using recycled, re-lithiated and sintered cathode powders as electrode material in a new cells were tested in order to prove the cell performance. The preliminary results demonstrated levels comparable to pristine cathode materials, at least during the first tens of charge-discharge cycles (Sloop and Allen 2016). On the other hand, these results cannot be used to predict the later performance of the cells, since the cell capacity even in new cells can fluctuate drastically after 100 cycles (Harris et al. 2017). Moreover, it seems that in these tests the electrolyte extraction with supercritical CO_2 is omitted, thus also the effects of this procedure on cathode active material structure and performance remain unclear.

There exist some positive results about the recycled anode material after electrolyte extraction. It is expected that the supercritical CO_2 cleans impurities containing carbonate moieties from the electrode surface, and there is also proof that a refurbished cell has an improved initial capacity compared to a new cell (Sloop and Parker 2011). In 100 cycles-long tests conducted by Rothermel et al., (2016) on used graphite that had been cleaned with subcritical CO_2 followed by thermal treatment the recycled material, the recycled material outperformed new synthetic graphite in discharge capacity. Although these results are promising, there is still room for long-term tests.

If the refurbished cells were to be used in traction batteries, also the homogeneity of the cells should be confirmed. Batteries should contain cells of matching capacities within max 3% deviation to minimize the effect of possible capacity retention of individual cells during their useful lifetime, because the lowest performing cell determines the capacity of the total battery (Friel 2011, p. 5.5). When multicell batteries are manufactured from new cells, usually cells from the same lot are used to obtain this criteria (Friel 2011, p. 5.14). Homogeneity of refurbished cells should be similarly verified. However, a more plausible option seems to be reusing the cells in one-cell batteries.

5 Discussion of the processes

In this Chapter, some general observations about the recycling technologies previously described in Chapter 4 are presented. At this point, the discussion is limited on the processes recycling specifically LiBs (with or without primary Li batteries) as gathered in Table 3, while the processes recycling LiBs only as secondary feed (i.e., Batrec, Inmetco and Glencore plc.), are omitted from the analysis.

Table 3 Overview to the recycling processes: battery feed type, discharge methods, the use of mechanical, hydrometallurgical and pyrometallurgical techniques and their external inputs, and the main end products. The year within the technology name is either the publication date of the first patent or the first article identified describing the method.

TECHNOLOGY	FEED	DISCHARGE	MECHANICAL	HYDRO	PYRO	MAIN END PRODUCTS
UMICORE **2005** Cheret and Santén 2007	LiBs and NiMHs	In furnace	-	HCl	Coke Slag formers Air	$CoCl_2$
SUMITOMO-SONY **1998** Cardarelli and Dube 2007	LiB	In furnace	-	Undisc.	Undisc.	CoO
RETRIEV TECHNOLOGIES **1998** McLaughlin and Adams 1999	LiB and Li	In crushing	Brine / N_2	Na_2CO_3 / CO_2	-	MeO-C-cake Li_2CO_3
RECUPYL **2005** Tedjar and Foudraz 2010	LiB and Li	In crushing	Ar/CO_2	H_2O LiOH H_2SO_4 Steel *NaClO* *Li_3PO_4*	-	LCO/$Co(OH)_2$/Co Other cell materials
AKKUSER **2011** Pudas et al. 2015	LiB	In crushing?	Ambient?	-	-	Metal-graphite- powder
ACCUREC **2012** Georgi-Maschler et al. 2012	LiB	In furnace	Ambient?	H_2SO_4	2 slags Binder	Co-alloy Li_2CO_3
GRATZ **2013** Gratz et al. 2014	LiB	Distinct phase	Ambient	NaOH H_2O_2 H_2SO_4 Metal salts Na_2CO_3	-	$NMC(OH)_2$ Li_2CO_3
LITHOREC **2011** Diekmann et al. 2016	LiB	Distinct phase	Inert gas	Undisc.	-	MeOs Li salts
ONTO **2007** Sloop and Parker 2011	LiB and Li	Distinct phase	Inert gas	-	-	Cathode powder /refurbished cell

The processes dedicated especially to LiBs recycling are some of the newest processes – (i.e, AkkuSer, Accurec, Gratz and LithoRec), the exception being Sumitomo-Sony, that was developed as a cooperation between a metal refiner and a LiB manufacturer. In other words, this means that there are at the moment only two industrial-scale technologies dedicated especially to LiBs recycling. As stated already earlier, Retriev and Recupyl processes were initiated for primary Li battery recycling and widened the scope later to encompass LiBs. Moreover, the OnTo process covers both LiBs and primary Li, although its associated patents mainly discuss the treatment of LiBs. Umicore on the other hand, recycles a mixture of LiBs and NiMHs in one process. In general, it can be said that the ability to accept more than one battery type allows the process some flexibility compared to technologies that have been designed to treat only one battery type, or even a single battery chemistry. On the other hand, the processes with more limited feed have the potential to recover the cell materials or original value more extensively. A common aspect of the last four processes in Table 3, representing the emerging technologies, is that they claim to have already transferred from the lab-scale towards to the industrial scale, but the tests and evidence found in the literature seem to originate mainly from lab-scale experiments. Thus, it is likely that some modifications to these processes will still take place in industrial scale.

If the process starts with pyrometallurgical treatment, discharge and deactivation of the cells are not needed, as in the case for Umicore, Sumitomo-Sony and Accurec. Gratz, LithoRec and OnTo on the other hand start the process by discharging the cells, whereas Retriev and Recupyl crush the cells under a protective environment. For Akkuser, neither a discharge phase nor a protective crushing environment is reported, but crushing is executed in a chamber and the gases produced in crushing such as O_2 and H_2 are treated with a cyclonic air mover (Pudas et al. 2015). Despite the fact that in LithoRec and OnTo technologies a discharge step is used, crushing is nonetheless performed under inert gas: to avoid fires due to the release of flammable gases (Diekmann et al. 2016), or to protect the active materials from contamination caused by water or air (Sloop 2010).

Table 3 reveals also that all but two of the processes (i.e., AkkuSer and OnTo) apply hydrometallurgical methods for recovering the valuable materials. In this thesis, processing and filter pressing the slurry in the Retriev technology is also considered as a hydrometallurgical process. Moreover, as mentioned in the previous chapter, the product from the AkkuSer process may undergo hydrometallurgical treatment to recover e.g., Co, although this is not by the AkkuSer company itself. Regarding the OnTo process, the exact method used to refine the final products is unclear, although from the descriptions available, it is not likely that hydrometallurgical methods are not applied (e.g. Sloop 2010; Sloop and Parker 2010).

From the Table 3 it is also evident that the main target in most of the processes is the cathode material. It must be noted, though, that in some of these processes, the main product is deduced rather than stated in the literature. Since the most valuable part of the cell is in most cases the transition metal compound in the cathode, it is a logical main target for recycling. Onto Technology is the only process that proposes direct reuse of cells or cell components as one option, although even in this process some modification to cell materials is needed prior to reuse such as re-lithiation of active materials.

As seen in the process descriptions in Chapter 4 and the discussion above, the processing of LiBs to recover materials with satisfactory grades, complex processes involving mechanical and chemical separation methods are required. Mechanical methods have usually the target of pre-refining the feed for hydrometallurgical treatments, but in some cases the concentrates produced have sufficient value. Hydrometallurgical techniques are usually needed to recover the most valuable materials, particularly when these are found intrinsically attached to other battery components. One of the downsides of hydrometallurgical processes is the required use of solvents that increases the process costs and the environmental burden. For pyrometallurgical methods on the other hand, the costs consist especially of the energy demanded by its high operation temperatures and that sometimes additional components such as slag formers have to be used.

In the following section, the overall trends of the processes to treat specific battery components are discussed in a more detailed manner. It should be noted that electrolyte recovery is excluded as it is attempted only in few processes and was discussed already in the Chapter 4.

5.1 Cathode material recovery

The driving force for LiBs recycling has been cathode material recovery, and especially Co as its most valuable material in the first generation LiBs. The supreme value of Co compared to some other materials used in battery production is clearly shown in Table 4.

Table 4 Prices for some selected battery raw materials. (USGS Mineral commodity summaries 2017)

Raw material prices 2016 USD/kg

Co	Ni	Cu	Mn	Al	Li_2CO_3 (Battery grade)
26.4	9.3	4.9	3.1	1.8	7.4

However, as an inevitable consequence of the commercialization of the new cathode chemistries, new recycling technologies have been developed. In these more recent technologies, the recovery target has been widened to additional metals besides Co. Moreover, the tendency to produce further processed battery-grade material with a more straightforward combination of steps has enforced and the value of compounds or cathode precursor materials in addition to elemental metals is recognized. This tendency is represented schematically in Figure 18.

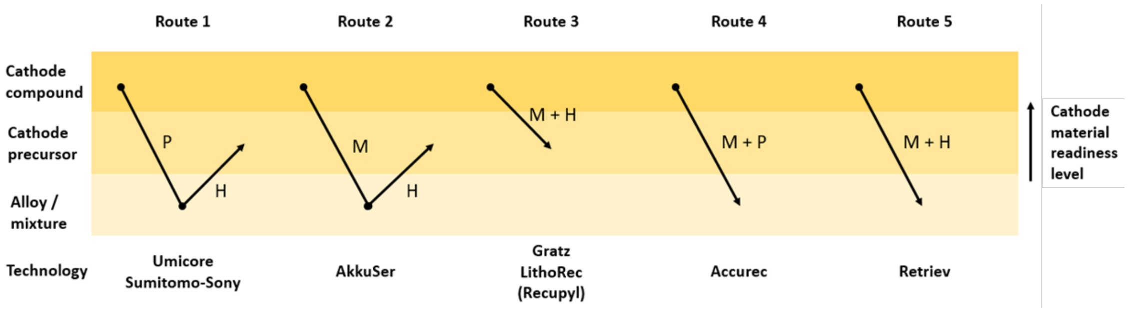

Figure 18 Schematic representation of the cathode compound processing route in relation to cathode material readiness level. Start and interphases are marked with a point and the end level with arrow. P, M and H indicate, whether pyrometallurgical, hydrometallurgical or mechanical techniques are used in processing the material from the one form to another.

In Figure 18 the idea of the levels of recycling is applied to cathode compound. The starting material, cathode compound represents thus the highest level and the initial point of recycling. The subsequent level is a cathode precursor, e.g. transition metal hydroxide or oxide, and the lowest level an alloy or a mixture of materials that cannot be directly used in a cathode compound synthesis. The route of recycling cathode compound is depicted in relation to these steps. For instance, in Umicore process Co contained in the cathode compound is first processed with pyrometallurgical treatment into an alloy that is subsequently processed into cathode precursor material (chloride) with hydrometallurgical treatment. In the LithoRec process, in turn, cathode compound is processed directly into a cathode precursor material (metal oxide) through mechanical and hydrometallurgical steps. One strong incentive to produce a more ready product is the fact that the value of cathode compound material is greater than the value of its elemental components combined (Gaines 2014). Third option is to recycle the cathode compound components into an alloy (Accurec) or a mixture of materials (Retriev) and to use this product as a raw material for some other applications than batteries. OnTo Technology has been omitted from this analysis due to vague information considering the exact cathode recovery methods. For Recupyl, the end product $Co(OH)_2$ is chosen from the three presented options (Tedjar and Foudraz 2010).

It should be further investigated to what extent the compound value of the cathode material can be preserved in the recycling process. Additionally, it should be carefully considered, whether this change brings about benefits considering the goal of circular economy to optimize systems, rather than components (Ellen MacArthur Foundation 2015). In other words: what kind of a recycling process brings about optimized material and value savings. In more direct processes (such as Gratz, LithoRec) the new cathode precursor is produced mainly of the recycled material with just a little refurbishing with virgin material (metal salts). Thus, stricter controlling of the processing environment is needed, and possibly more energy is required for separating impurities to low enough concentrations while keeping the active materials intact because that recycled material has to by itself meet the purity criteria. Moreover, it may be hard to convince the customers that the recycled material quality is competitive. In Umicore and Sumitomo-Sony process, however, in the manufacturing process of the cathode precursor materials more virgin material can be mixed with the recycled metal containing product to meet the purity criteria. Umicore and Sumitomo-Sony represent also companies amongst the ten major active cathode material producers in the world (Watabe and Mori 2011). Hence, also the novel recycling technologies could perhaps benefit from combining the battery component production to the recycling process.

In Table 5 the recycling processes are presented in relation to cathode material recycling with more details about the focus and the end product of the cathode material recovery. In addition, information about binder treatment and foil detachment are provided, because they are relevant issues considering the cathode material reuse.

Table 5 Recycling processes in relation to cathode material recovery.

TECHNOLOGY	FOCUS	CATHODE RECYCLING PRODUCT	END USE	LEVEL VS. CATHODE PRECURSOR	BINDER	FOIL DETACHMENT
UMICORE Cheret and Santén 2007; Dunn et al. 2015b	Co	$CoCl_2$	Cathode material	Ready for hydrothermal synthesis of LCO	In furnace, but not discussed	-
SUMITOMO-SONY Cardarelli and Dube 2007	Co	CoO	Cathode material	Heating and oxidation to Co_3O_4 needed prior to solid state synthesis of LCO	In furnace	-
RETRIEV TECHNOLOGIES McLaughlin and Adams 1999; Gaines and Dunn 2014, p. 499	Co	MeO + C cake	Metal manufacturing	-	Not discussed	Not discussed
RECUPYL Tedjar and Foudraz 2010	Co	LCO/$Co(OH)_2$/Co	unknown	-	Not discussed	Not discussed
AKKUSER Pudas et al. 2015; Ekberg and Petranikova 2015	Co, Ni	Metal+graphite powder	Co product manufacturing, e.g. cathode powder	Requires hydro- or pyrometallurgical processing prior to cathode powder synthesis	Not discussed	Not discussed
ACCUREC Georgi-Maschler et al. 2012	Co	Co-alloy	As such	-	In furnace	Not discussed
GRATZ Gratz et al. 2014	Co containing cathode materials	$NMC(OH)_2$	Cathode powder	Ready for synthesis of new active cath. material	Not discussed	Al dissolved with NaOH
LITHOREC Diekmann et al. 2016	NMC	MeOs	Cathode powder	Ready for synthesis of new active cath. material	Heating + 2-step comminution	Mild heating + 2-step comminution with size control
ONTO Sloop and Parker 2011; Sloop 2016b	All cathode types	Cathode powder/refurbished cell	Cathode material / cell		Multistep procedure suggested in work that concentrates on cathode materials	Not discussed

Based on the present research, the focus of the cathode compound recovery is mainly in Co containing chemistries, LCO and NMC. The emphasis of the more novel technologies, Gratz and LithoRec, is additionally in recovering all the transition metal constituents of the NMC chemistry, not just Co. Even though it is understandable that the most valuable component Co and constantly generalizing compound NMC guide the recycling processes, in practice the LiB waste stream in the coming years will likely still contain all the commercial cathode types. Regarding this variety, only Gratz and OnTo state clearly the target of recycling different chemistries and provide also examples of this, although Gratz seems to be concentrated only on those chemistries containing Co, whereas OnTo mentions also LFP. One major drawback of the OnTo Technology is, however, that the details of the exact methods for obtaining metal oxide fraction are omitted, making the evaluation of the process impossible. Moreover, based on the information available, even Gratz and OnTo Technology appear to process only one chemistry type at a time, or at least are compelled to treat LFP separately.

Undoubtedly the motivation for developing efficient recycling technique for LFP or LMO has been minor, since the constituents of these cathode materials have a distinctly lower commercial value (CEC 2015, p. 32; Boyden et al. 2016). Nonetheless, the larger share of energy demand in production of LFP and LMO cathode materials from virgin materials compared to Co-containing chemistries – 22% and 15% respectively for LFP and LMO compared to around 10% of the Co containing chemistries (Bernhart 2014, p. 559) – could serve as an incentive to develop LFP and LMO recycling further. Especially regarding LFP, it has been estimated that the value would be in the compound and not in the constituent elements (CEC 2015, p. 32). However, an analysis of the production process has shown, that the most energy demanding phase is the cathode material synthesis (Dunn et al. 2015b), a process required whether the raw materials are primary or secondary. In summary, it seems that, along with raw material value, the energy saving potential of recycled LFP or LMO cathode material is quite low and thus, does not provide an economic incentive for recycling.

Whether the materials of LFP and LMO chemistries are recovered or not, they form part of the LiB feed. Considering the challenge of recycling feed consisting of mixed cathode materials, the studied technologies do not provide an answer, not to mention a current lack of discussion in the literature regarding the effects of the possible future chemistries, surface treatments etc. in battery recycling. At this point it is impossible to tell, if this preference is final or if concentrating on one chemistry at a time is just the first step of the very recent technologies. Whatever the case, more research is definitely needed for developing a mixed LiBs recycling process since batteries from consumer electronics form a more heterogeneous mixture than expected.

Ellis et al. (2015) have proposed a procedure in which cathode powders and graphite can be separated either in continuous or batch process with high intensity magnet based on their different response to external magnetic field. The difference is derived from the distinctive valence electron coordination of the transition metal containing compounds and the diamagnetism of graphite. In fact, the compounds with lowest material value and energy saving potential, LFP and LMO have the highest magnetic susceptibility (Ellis et al. 2015) and could thus be separated from the Co-containing powders in the beginning of the process after graphite separation and directed then to a different procedure. On the other hand, it is ambiguous how well different compounds can be separated, e.g., in the case of impurities, and how the separation process can be thus controlled. Moreover, it is not discussed in the literature, how well this technology could be adjusted for the separation of new transition metal compounds that might appear in the feed in future. Nevertheless, this proposal is an important effort to truly handle mixed cathode waste powder.

The challenges regarding the purity of the material recycled to cathode precursor are discussed next in the mechanical-hydrometallurgical route (Route 3 in Figure 18), where attention is needed for separating active material powder from the current collector foils. Cu foil specifically is considered as a concern in hydrometallurgical processing due to the overlapping precipitation pH ranges of Cu and Ni (i.e., Ni precipitation starts at pH 5.16 and Cu precipitation ends at pH 6.65; Zou et al. 2013) and the consequent risk of co-precipitation and loss of Ni. In addition to hydrometallurgical treatment conditions, the impurities should also be considered with respect to the cell performance and safety. Mohanty et al. (2016) introduced large (≤ 2 mm) Al pieces onto the electrode coating artificially during the coating process. This is believed to decrease discharge capacity and especially coulombic efficiency defined as the proportion of discharge current obtained compared to charge applied. One suspected reason was a creation of short circuits via these large metal particles, which on the other hand signify also a safety problem.

Also, in tests related to the LithoRec process, Al was reported to decrease cell capacity. An Al concentration of 0.6 wt.-% in recycled NMC material was estimated to be responsible of a 6-14% capacity loss during 500 cycles with a 1C cycling rate (1C is defined as the current that charges the battery to full capacity within one hour; Krüger et al. 2014). It is though notable that removing Al was not specifically addressed in LithoRec process and, compared to e.g. Gratz et al., (2014) with Al impurity level of approximately 3000 ppm, the Al content in LithoRec cathode precursor was extremely high. On the other hand, a promising result of the aforementioned

LithoRec tests was, that the overall behaviour of the recycled material during the 500 cycles had the same slow decreasing trend as the pristine material, thus there were not any drastic capacity drops. Additionally, Cu impurities, with 1.8 wt.-% concentration (Diekmann et al. 2017), were in turn noted to have also some beneficial effects for the active powder crystal structure: even though Cu defects were considered responsible for a decreased discharge capacity, they also seemed to slow down the capacity retention at least during the first 150 cycles compared to new and pure NMC (Sa et al. 2015).

Overall, it would be worth further examination how the performance of recycled active cathode material is dependent on different impurities that can be detrimental or even beneficial. The detrimental effects should be additionally classified regarding their severity for the cell use, and the thresholds for critical concentrations should be defined. This knowledge would most likely be advantageous also considering future material combinations of cathodes. In the best case, the materials currently considered as an impurity could be turned into a useful component, or at least the thresholds for different impurities in recycled material could be defined. It would also help to recognize whether some impurity is unwanted from the perspective of the cell performance, metal purification processing stages or for both.

5.2 Li recovery

In a used LiB cell, Li is contained both in the electrode active materials and in the electrolyte. Hence, the recovery of Li is a relevant matter in the discussion of materials recycling from LiBs. In Table 6, the recycling processes are compared in terms of their Li recovery method, the chemical form and grade of recovered products, and their targeted use.

Table 6 The status and the methods of Li recovery in different recycling technologies.

PROCESS	LI RECOVERED	PRODUCT	METHOD	RECYCLING EFFICIENCY	GRADE	TARGETED USE OF PRODUCT
UMICORE	No	-	-	-	-	-
SUMITOMO SONY	No	-	-	-	-	-
RETRIEV TECHNOLOGIES McLaughlin and Adams 1999; CEC, p. 40	Yes	Li_2CO_3	Precipitation with Na_2CO_3 / CO_2	90% probably in the presence of primary Li batteries	Technical	Metals manufacturing
RECUPYL Tedjar and Foudraz 2010	Yes	Li_2CO_3 / Li_3PO_4	Precipitation with CO_2	-	-	-
AKKUSER	-	-	-	-	-	-
ACCUREC Georgi-Maschler et al. 2012	Yes	Li_2CO_3	Precipitation	76-90%	> 99%	Glass production / active cathode powder synthesis
GRATZ Zou et al. 2013	Yes	Li_2CO_3	Precipitation with Na_2CO_3	67-80% depending on the cathode type	High purity	Active cathode powder synthesis
LITHOREC Hanisch 2014	Yes	LiOH / Li_2CO_3	Precipitation	85-95% depending on the cathode type	-	Active cathode powder synthesis
ONTO Sloop 2010	Yes	Li_2CO_3 / Complete cathode compound	-	-	-	E.g. battery production

Five processes out of the nine discussed in this thesis proclaim precipitating Li from the leaching solution in the form of Li_2CO_3 or other Li salt with the aid of Na_2CO_3 or CO_2. In the available literature about the OnTo process, the exact Li recovery method is not specified, but Li_2CO_3 is stated as product. A probable reason for the interest on Li recovery by the Retriev and Recupyl processes is their initial feed, i.e., primary Li batteries with a relatively high Li content. The recycling efficiencies claimed by different processes and with different battery chemistries have a wide range, from 67% to 95%. One problem of Li_2CO_3 recovery is that in aqueous solution part can dissolve back and cannot be further recovered with a precipitation method (Gratz et al. 2014). Only three technologies report the Li purity achieved: Retriev Technologies produce technical grade Li_2CO_3, Accurec reports a > 99% purity and Gratz et al. use only the qualitative description of “high purity” about their end product. In most of the processes, Li recovery is the usually the final step of the recycling process and hence the content of the feed material is dependent on all the previous separation phases. If the product of the Li recovery stage is intended for use in the cathode material synthesis, a high content of Al impurity would be detrimental as was previously stated for cathode powder precursor.

With respect to the potential use of the Li salt products, three applications are mentioned. First of all, Retriev Technologies channel their technical grade Li_2CO_3 to metals manufacturing. One possible target of Li_2CO_3 is in Al production as an electrolyte additive (Martin et al. 2017). Accurec, Gratz and LithoRec mention the active cathode powder manufacturing as the intended use for Li salt, although Accurec also mentions glass production as an alternative option. In fact, Li demand in year 2015 was quite similar for battery production and glass and ceramics production, 35% and 32% respectively of the total global demand (Martin et al. 2017). Also OnTo technology names battery production as one option for recovered Li_2CO_3 among other products. Considering the minimum purity of 99.5% required from Li_2CO_3 used in cathode production (Tran and Luong 2015, p. 83), it seems that the only possibility to use the recycled material is to mix with virgin Li_2CO_3. Moreover, it has been stated that the purity requirements for Li_2CO_3 are rising up to 99.9%. (Tran and Luong 2015, p. 118). Hence, it would be worth considering, if some of the various other industrial applications for Li, such as aluminum production or metals casting (Martin et al. 2017), would after all be more appropriate end use of recycled Li.

Considering the existing Li reserves and resources, recycling Li is at the moment not considered imperative, even in high-demand scenarios (Martin et al. 2017). On the other hand, it has been shown that the estimates of Li reserves and resources vary notably between different studies and there are also more pessimistic forecasts about Li sufficiency. Nevertheless, these estimates show that the demand is not expected to exceed the possible production. (Oliveira et al. 2015). Still, if recycling Li does not decrease the feasibility of LiB recycling process as a whole, it would be advisable to recycle Li in order to conserve natural resources. Especially in LMO and LFP cathodes, Li composes one third of the material value (Wang et al. 2014b) and as the price of Li_2CO_3 is expected to rise (Martin et al. 2017), recycling Li will probably become more profitable for other chemistries, as well.

5.3 Casings and current collector foils

In this section, the recycling of the supporting materials of the electrochemical cell such as current collector foils and cell/battery casings is reviewed. Even though the cathode active material is considered the most valuable entity of the cell, the importance of recycling of Al, Cu and Fe of the supporting materials should not be underestimated. In particular, the production of wrought Al manufacturing, the starting material for Al foil production, is very energy intensive hence justifying the recycling of this material (Dunn et al. 2012b). Cu and Fe on the other hand can be recovered to a significant extent with mechanical separation methods, as has been described in the previous chapter. Moreover, removal of Cu and Fe is essential for the success of efficient cathode material recycling with hydrometallurgical methods, thus rendering the recovery of Cu and Fe even more advantageous.

The information gained regarding recycling of casings and foils is gathered in the Table 7. For the sake of discussion, also the cathode material loop level presented already previously has been added to the table. The mechanical processing methods used are gathered in Table 8 and discussed here too, since they are especially relevant to casing and foil material separation.

Table 7 Recycling of foil and casing materials.

PROCESS/TECHNOLOGY	CASINGS	AL AND CU FOILS	CATHODE MATERIAL LOOP
UMICORE Vezzini 2014, p. 546; CECC 2015, p. 45	Fe partly recovered in alloy Al slagged Polymer used as energy	Al slagged Cu recovered in alloy	From cathode to cathode precursor
SUMITOMO SONY Cardarelli and Dube 2007; Al-Thyabat et al. 2013	Fe, steel recovered Al slagged Polymer calcinated	Al slagged, Cu recovered	From cathode to cathode precursor
RETRIEV TECHNOLOGIES Vezzini 2014, p. 545; CEC 2015, p. 39; Smith and Swoffer 2014; Gaines and Dunn 2014, p. 499	Steel, Al and plastics recovered with shaker table	Recovered with shaker table?	From cathode to raw material
RECUPYL Tedjar and Foudraz 2010	Steel recovered with magnetic separator; Al, Cu and plastics with densimetric separator	Recovered with densimetric table Impurity Cu also precipitated	-
AKKUSER Pudas et al. 2015	Plastics recovered with air filtering; Fe with magnetic separator; Al?	Recovered as part of fine powder	From cathode to powder mixture
ACCUREC Georgi-Maschler et al. 2012; Vezzini 2014, p. 543	Polymer evaporated Fe recovered with magnetic separator; Al with air separator	Recovered with air separator	From cathode to alloy
GRATZ Gratz et al. 2014; Heelan et al. 2016	Steel recovered with magnetic separator; plastics with heavy medium separator	Al recovered as $NaAlO_2$ Cu recovered with heavy medium separation Impurity Cu also precipitated	From cathode to cathode precursor
LITHOREC Diekmann et al. 2016; Diekmann et al. 2017	Steel, Al and plastics recovered with air separator	Recovered with multiple sieving and zig zag sifter phases	From cathode to cathode precursor
ONTO Sloop 2010	Steel, Al, plastics recovered	Reused/recovered	From cathode to cathode precursor / from cell to cell

Table 8 Processes using mechanical separation methods and the methods used.

TECHNOLOGY	COMMINUTION	MAGNETIC SEPARATOR	SIZE SEPARATION	GRAVITY SEPARATION	OTHER
RETRIEV TECHNOLOGIES McLaughlin and Adams 1999	Shredder and/or hammer mill	-	Not mentioned	Densimetric table	
RECUPYL Tedjar and Foudraz 2010; Vezzini 2014, p. 548	Rotary shear Impact mill	High intensity	Vibrating screen	Densimetric table	
AKKUSER Pudas et al. 2015	Cutting mill	x	Not mentioned	-	
ACCUREC Georgi-Maschler et al. 2012	Mill	x	Vibrating screen	Zig zag air separator	
GRATZ Gratz et al. 2014	Hammer mill	High intensity	Sieve	Heavy medium density separation	
LITHOREC Diekmann et al. 2016	Rotary shear Cutting mill	-	Vibrating sieve	Zig zag sifter	
ONTO Sloop and Parker 2011; Sloop 2010	e.g. Ball mill	-	Not mentioned	Cyclone/fluidized bed/solution dispersion	Electrostatic method, e.g. capacitor plate

The processes applying pyrometallurgical methods (i.e., Umicore, Sumitomo-Sony and Accurec), lose part of the casing and foil materials during processing, a typical occurrence in this kind of high temperature operations. All three processes lose polymer casings, while Umicore and Sumitomo-Sony also lose Al in the slag. However, steel, Fe and Cu are recovered in all of these processes, although their methods differ. The Accurec process uses mechanical methods such as magnetic separation and zig zag air separation thus it additionally can recover Fe based on the magnetic properties and Al and Cu based on their density difference. Umicore states partial recovery of Fe/steel while part is slagged. It is hence reasonable to assume that this is also true for Sumitomo-Sony.

In the rest of the processes, the main separation methods for casings and foils are some form of density difference-based technique, preceded possibly by magnetic separation for ferrous materials. In the Retriev Technologies process, only shaker tables are used for separating the materials in question, which is quite logical considering the intended application is in the metals manufacturing: obtaining highly pure, separated material fractions is not relevant. Only LithoRec claims to separate steel without magnetic separation, although in a follow-up project, this step was added to the process (Rothermel et al. 2016; Grützke et al. 2015). A particular case is the AkkuSer process, where plastics are recovered by filtering the off-gases prior to magnetic separation and not with a density separation method. Detailed information about the exact methods Onto Technology implements for casing and foil separation is unavailable, but different types of density-based methods are mentioned as suggestions. As can be seen, casing and foil materials can be recovered with physical methods but for the sake of further refining and purifying, additional methods such as leaching and precipitation might be needed for separating foils from the fines.

A two-step comminution is used in three processes: Recupyl, AkkuSer and LithoRec. In the two first processes, the incentive for this seems to be related to a safe and controlled processing of the active cells. In the Recupyl process, this is particularly due to the presence of primary Li cells. In the context of LithoRec, the two-step comminution is discussed in more detail and the mild cutting stress conditions are chosen for improving separation efficiency. Even though in the context of AkkuSer process the comminution parameters are not discussed in relation to separation efficiency, it is notable that in this process a cutting mill was specifically chosen out of all available comminution options. There is thus some indication that cutting stress is required when good comminution and separation results of LiBs are targeted by mechanical processing. Still, considering the special behaviour of the cells in comminution there is surprisingly little discussion about this issue.

5.4 Graphite

In this section the recycling technologies are discussed with respect to graphite recovery. The description of graphite handling is gathered in Table 9.

Table 9 Treating of graphite in different technologies.

PROCESS	GRAPHITE
UMICORE Cheret and Santén 2007; Georgi-Maschler et al. 2012	Used as reducing agent in furnace.
SUMITOMO SONY Cardarelli and Dube 2007	Calcinated.
RETRIEV TECHNOLOGIES CEC 2015, p. 39; Gaines and Dunn 2014, p. 499	Recovered in MeO+C filter cake.
RECUPYL Tedjar and Foudraz 2010	Filtered off in leaching step.
AKKUSER	Part of black powder.
ACCUREC Georgi-Maschler et al. 2012	Partly burnt, partly used in carbo-reductive melting; finally slagged.
GRATZ Heelan et al. 2016	Recovered, details undisclosed.
LITHOREC Diekmann et al. 2016 AND 2017	Separated in leaching step, not recovered.
ONTO Sloop 2010	Recovered, details undisclosed.

As shown in Table 9, the details of the graphite recovery are scarce. It is also necessary to emphasize that in most cases the real recovery of graphite remains uncertain. Indeed, graphite is extracted from the feed but the subsequent phases are not discussed. In processes that use high-temperature methods, like Umicore, Sumitomo Sony and Accurec, graphite is used as energy or reduction agent or simply calcined. Retriev recovers graphite in an elemental form in a MeO+C filter cake. The AkkuSer process seems to recover graphite as part of the black mass containing also cathode active material. In Recupyl and LithoRec processes carbon/graphite is removed from the solution at the beginning of the leaching step. However, it is expressed that utilizing such recovered graphite is not feasible at the moment (Diekmann et al. 2017), even though it has been proven technically possible to produce battery-grade graphite with subcritical CO_2 cleaning combined with thermal treatment (Rothermel et al. 2016). Gratz and OnTo state that they recover graphite, but the details of the exact method are not provided. Nevertheless, the electrolyte recovery step with supercritical CO_2 is even capable of removing reactive functional groups from the graphite surface (Sloop 2010). Moradi et al. (2016) stated that, to separate graphite with hydrometallurgical methods, the anode has to be treated separately from the cathode, suggesting that pre-separation would be required for graphite recovery. Overall it seems that recycling graphite is not a subject of interest, at least in the recycling processes discussed.

A couple of issues have to be discussed in the context of graphite recycling. Compared to the cathode and the other cell components, graphite production constitutes only a small share of the total energy consumption of the cell materials during their life cycle (Dunn et al. 2012b). Furthermore as was previously discussed, a SEI layer is formed on the surface of graphite during usage. Even though there exists proof of good performance of recycled graphite after CO_2-cleaning and thermal treatments (Rothermel et al. 2016), the economics of this procedure require further studies. According to Moradi et al. (2016) it might not be economically viable to remove SEI, binder and conductive carbon from the graphite surface to enable re-use in cell, at least with the present anode materials and their tendency to degrade. However, other principles such as resource efficiency or self-sufficiency in battery manufacturing, might render the target of reusing graphite favourable.

6 Conclusions

From to the large amount of produced LiBs, at the moment only a small share is recycled at their end-of-life. In other words, only a small fraction of the valuable materials contained in the cells are recovered and utilized. Regarding the material efficiency and the need to preserve natural resources for future generations, some actions should hence be taken. Even though the full recycling chain consists of several interconnected processes and actors, the key to successful recovery of materials is the existence of efficient and feasible recycling technologies. To evaluate the status of LiBs recycling from the technical point, the existing industrial and emerging pilot scale recycling technologies for LiBs were studied. As a result of the research performed in this thesis, several interesting and important issues were discovered as summarized next.

Since the first LiBs were introduced in the beginning of 1990's there has been tremendous technical progress associated with them. The application of rechargeable Li cells has diversified from one cell batteries to serve the requirements of variety of consumer electronics and into their use as traction batteries. As a consequence, the construction and active materials of LiBs have been developed to meet increasingly demanding and specific demands. Meanwhile, the recycling technologies for LiBs have been evolving more slowly: since the introduction of LiBs, several recycling technologies have been introduced, but so far only few industrial technologies dedicated especially to LiBs recycling exist.

Part of the industrial recycling technologies have been in fact initially invented for the needs of recycling Li primary batteries having their specific material and safety requirements and then later broadened to encompass LiBs. Moreover, in one existing process, LiBs are processed together with NiMH batteries. The advantage of these processes is the flexibility and readiness to accept different kinds of chemistries, although with the limitation that not all materials having potential reuse value can be recovered. In contrast, most of the newer technologies are dedicated to recycling LiBs and their constituent materials with varying scope.

Co is the most valuable element in LiBs and, at first, LCO was the only cathode material in LiBs. Thus, designing up the first recycling process around Co was natural. In the newly produced cells, NMC seems to be the major chemistry due to its wide application area, but other chemistries such as LMO or LFP can also be found regularly. Among the new recycling technologies, Co containing NMC seems to be in the centre of interest. Despite the fact that NMC chemistry includes Co, the share in this cathode compound and amongst the entire mixed LiB waste is decreasing as the new types of cells reach their end of life. In addition, higher energy densities are pursued with material modifications (Berhart 2014, p. 556) which gradually lead to a further decreasing of active material amounts in the battery waste feed. Probably as a one method to control the changing conditions of recycling, in some of the new recycling technologies (LithoRec, Gratz, Onto) there is an attempt to recover the value of the cathode compound rather than the constituent elements separately. In the newer technologies, the target is additionally to recover the hydroxides or oxides with such a high grade that they could be directly used for synthesis of new active cathode material. The difference compared to the older technologies such as Umicore or Sumitomo-Sony that also produce a battery grade material, is that their product is generated in a more complex process and furthermore, energy intensive pyrometallurgical methods are used. In addition, a larger variety of materials are lost in the course of these traditional processes since their original focus was on Co recovery.

Targeting high grade material to be reused in cells has of course both advantages and drawbacks. Trying to preserve the energy and quality once invested into the materials is advisable, but reaching this goal should be possible within realistic boundaries. For instance, producing battery precursor materials almost exclusively from the secondary materials might prove to be challenging regarding the high purity and homogenous quality requirements placed to the battery materials. Materials might have gone through structural changes during use and have different kinds of side-products deposited on them due to reactions taking place in the cell. Additionally, despite the separations steps some mixing of materials is inevitable in the recycling process which could be detrimental for the battery materials even in small impurity levels. If the recycled material cannot be mixed with a virgin material by the recycling company itself, it might be challenging to find a customer to a product that has usually high grade requirements. Since there are indications of integration of the different parties in the cell production chain, especially considering the cathode material, it would be expected that this cooperation would extend also to recycling process. This progress would advance the principles of circular economy and the shared knowledge would also help taking the challenges of recycling into consideration from such early stages as the battery designing and manufacturing phase. Additionally, this would support the research of the recycled materials and their possibilities and limitations considering the cell performance.

The importance of mechanical processing methods in the studied technologies evidently lies in the need of breaking up and separating the outer parts of the cells – casings and electrode composite constructions. Successful accomplishment of these steps is a requirement for the exposal of the cathode powders that usually are later processed with hydrometallurgical methods in order to recover the valuable materials. Since materials such as Fe, Al and Cu are also valuable, especially considering their proportional value in lower cost cathode chemistries such as LMO and LFP, mechanical processing is further relevant as it is capable of recovering these materials with an acceptable degree of purity. Additionally, without appropriate comminution and separation steps prior to the hydrometallurgical treatment, the recovery of valuable cathode materials would not succeed, especially when pure battery grade materials are pursued. Considering how crucial step comminution is for the further success of recovery processes, the parameters and choices related to it are surprisingly discussed with minimum detail. Perhaps there is a need for further studies about the comminution and liberation behaviour of LiB materials with different equipment and parameters.

Considering the mixed LiB feed, the LFP chemistry seems to be challenging even for the newer recycling technologies. It also seems that a proven technology capable of recycling a mixture of cathode chemistries has not yet been developed into practice. Treating one chemistry at a time might be a feasible option regarding traction batteries that contain usually hundreds or at least tens of cells with the same chemistry but when processing mixed feed originating from consumer electronics that is not possible. Thus, the recycling system should be robust enough to handle the different types of chemistries, possibly on the cost of recovery (grade or yield), or the mixed feed should be sorted by chemistry in advance of recycling, which would demand a more specific labelling system for cells.

A question remains if there can be a reliable recycling route for all the present LiBs considering that the most valuable materials per cathode material vary and new types of materials are constantly developed. If the materials of the different LiB chemistries were to be recovered, it would require sorting the cells to different processes, at minimum removing LFP from the rest of the feed. To accomplish this prerequisite feasibly, it would demand a more detailed labelling of the LiBs denoting the cathode chemistry as mentioned above. Meanwhile, it seems inevitable that some materials will be lost, unless substantial manual sorting work is used or computer assisted sorting based on probabilities and constantly expanding knowledge base.

Graphite and electrolyte recovery have been studied and tested in few technologies. Promising results have been obtained with supercritical or subcritical CO_2. Especially graphite could be cleaned and treated up to a condition that would even surpass the performance of new, synthetic graphite. Although this method is regarded technically possible, it is not considered economically feasible. What comes to electrolyte recovery, it has also been conceptually proven, but it is not clear how the used electrolyte could be reutilized and what procedures would be needed to refurbish the electrolyte considering the typical decomposition during use.

It would be advantageous to construct a consistent analysis of the materials of the different types of LiBs and compare the elemental, compound and component values. Experts should also evaluate with proper criteria what is the real potential of the recycled cathode compound materials for manufacturing new batteries. This knowledge could be used in estimating the possibility of integrating the recycling process to the battery manufacturing chain. Additionally, acknowledging the different levels of material value and the possible risks included in them from an economical perspective would help to design a reasonable recycling process with a feasible business case. Finally, the environmental impact of the recycling process should be included to this analysis.

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