

Recovery Concept of Value Metals from Automotive Lithium-Ion Batteries

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A recycling process for automotive lithium-ion batteries was developed. The process combines a mechanical pretreatment with pyrometallurgical recycling process step to recover all battery components, and realize cost-neutral and sustainable recycling. The focus of the research work is the development of a pyrometallurgical process step to recover especially Li out of electrode mass powder which is the fine fraction extracted mechanically from spent Li-ion batteries. Two metallurgical treatment technologies were investigated: direct vacuum evaporation of Li and recovery of metallic Li by distillation, and a selective entraining gas evaporation of Li and recovery of lithium oxide.

Keywords: Lithium, Li-ion batteries, Pyrometallurgy, Recycling

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1 Introduction

Battery recycling in Germany has only become a systematic necessity with the introduction of the battery enactment in 1998 [1]. In September 2006, the EU-Directive 2006/66/EC was adopted, which defines in all EU countries uniform regulations of the battery manufacturer for collection and the recycling of batteries with description of minimum recycling efficiencies for the battery recycling processes. The disposal in landfills or by incineration is prohibited. The required recycling efficiencies shall be determined depending on the Best Available Technology (BAT), but must be at least 50 wt % [2]. However, the recycling efficiency refers to the single cells not on the modules or the entire battery. This rules out any possibility of deposition or energy recovery of the batteries and enforces the development of recycling processes, which correspond to the upcoming demands for utilization and recycling efficiency. At the same time the recycling process has to be economically and ecologically sustainable [1, 2].

Due to the growing interest in the battery recycling from the public, politics and industry, the IME Process Metallurgy and Metal Recycling Institute and Chair of the RWTH Aachen University has systematically developed optimal pyrometallurgical and hydrometallurgical recycling concepts for all standard battery systems. In this context, recycling processes for nickel-cadmium batteries, nickel-metal hydride batteries, primary batteries and portable Li-ion batter-

ies were developed in cooperation with the industrial partner Accurec Recycling GmbH. Some of these methods have already been implemented industrially and have been rated as BAT.

2 Recycling of Lithium-Ion Batteries

2.1 Lithium-Ion Consumer Batteries

Within the last two decades the technical requirements for batteries in the market of mobile energy storages have increased and have become more complex. Lithium-ion batteries are considered to be the most promising energy source for mobile applications because they have several advantages over other accumulator systems. Lithium-ion batteries (LIBs) are very popular recently in the field of electronic appliance such as cellphones, laptops, power tools, and especially for electrical vehicles. And with increasing demand and consumption of the lithium-ion batteries, large quantities of valuable metals have to be recycled after the failure of the LIBs. The recycling of lithium-ion batteries will play an increasingly and important role in the future, because the proportion of Li-ion batteries will continue to rise in the coming years. So the return current of batteries that can be recycled will increase (see Fig. 1) [3].

A portable Li-ion battery for consumer applications normally contains just a single cell. This cell consists of an anode, a cathode, separator, electrolyte, and the cell body. The anode is usually composed by coating a carbon material on a copper foil as negative electrode. The cathode consists of aluminum foil-coated lithium-containing metal compounds and is set as a positive electrode plate. In order to prevent a short circuit between these two electrodes, a separator is located between the anode and cathode as a barrier. An

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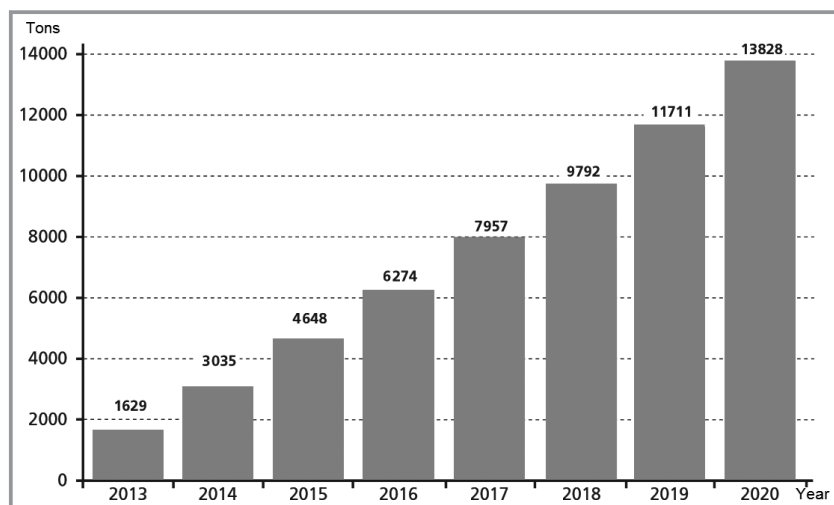


Figure 1. Forecast of the return quantity of Li-ion batteries for recycling in the EU [3].

electrolyte solution that allows the lithium ionic movement is injected into the battery and fully contacts with the electrode. The electrolyte is usually a solution of a lithium salt in an organic solvent. The housing of the battery is typically an iron or aluminum can body [5, 6]. A Li-ion battery cell for consumer applications is shown in Fig. 2 [4].

2.2 Automotive Lithium-Ion Batteries for Electro Mobility

Another big field of application for lithium-ion systems is electro mobility. LIBs are used as traction batteries for energy storage in electric bicycles, electric vehicles (EV) and hybrid electric vehicles (HEV). Different from single portable Li-ion batteries for consumer applications, LIBs for automotive applications contain a set of cells. Usually, a certain number of cells are packed together into a unit so-called module. Hence, the battery is composed out of several mod-

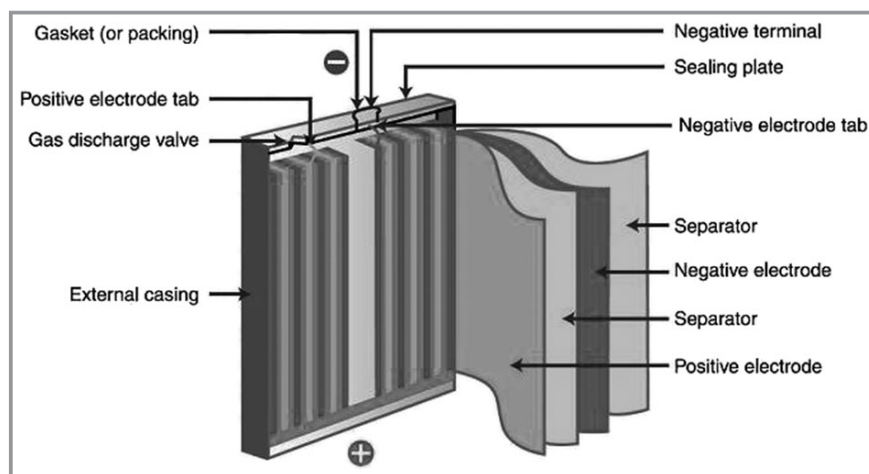


Figure 2. Composition of a single Li-ion consumer cell [4].

ules. This requires additional electrical components to manage the modules and cells differently. Due to safety reasons, cooling equipment is also installed and the voltage and temperature of each cell are monitored and controlled to avoid overheating and a thermal runaway of the cells and modules. Therefore, the structure of automotive LIBs is more complex than of the portable Li-ion batteries [7, 10].

According to EU-Directive 2006/66/EC automotive Li-ion batteries should be recycled, at least with a recycling efficiency of 50 wt % [2]. Fig. 3 [7] shows the contents of components and metals in a spent HEV Li-ion battery (complete battery, including cells and electrode powder).

The entire battery contains up to 63 wt % of cells [7]. These cells contain mainly aluminum. The aluminum has a larger proportion than copper, because not only the foil but also the casings of the cells are made of it. Furthermore, the cells contain organic electrolyte and the most valuable part of cells the electrode powder, which comes from the coated cathode and anode. The composition of the electrode powder is strongly depending on the Li-ion cell type and the used cathode material. In addition to the recyclable metals copper, aluminum and steel that can be found in every type of battery, the active electrode mass also contains valuable materials such as cobalt, nickel and manganese – depending on the type of battery. These metals are typical products of the recycling process. The theoretically maximum possible tonnage of high-value materials are listed in Tab. 1 [3, 7, 10].

The recycling of LIBs has an enormous potential for economically strategic industrial metals. However, there is a growing amount of diverse lithium-ion subsystems, operating with different metals and lithium

compounds in the cathode material. The Li-ion battery is named after the used cathode material such as LCO (lithium cobalt oxide), NCM (lithium nickel manganese cobalt oxide), NCA (lithium nickel cobalt aluminum oxide) and LFP (lithium iron phosphate). As a result of missing industrial agreement on standards it is not possible to distinct these systems visually. This severely complicates the efficient recycling processes. The recycling processes for Li-ion batteries that are currently operated at industrial scale can be divided into three types: pyrometallurgy, hydrometallurgy and pure mechanical

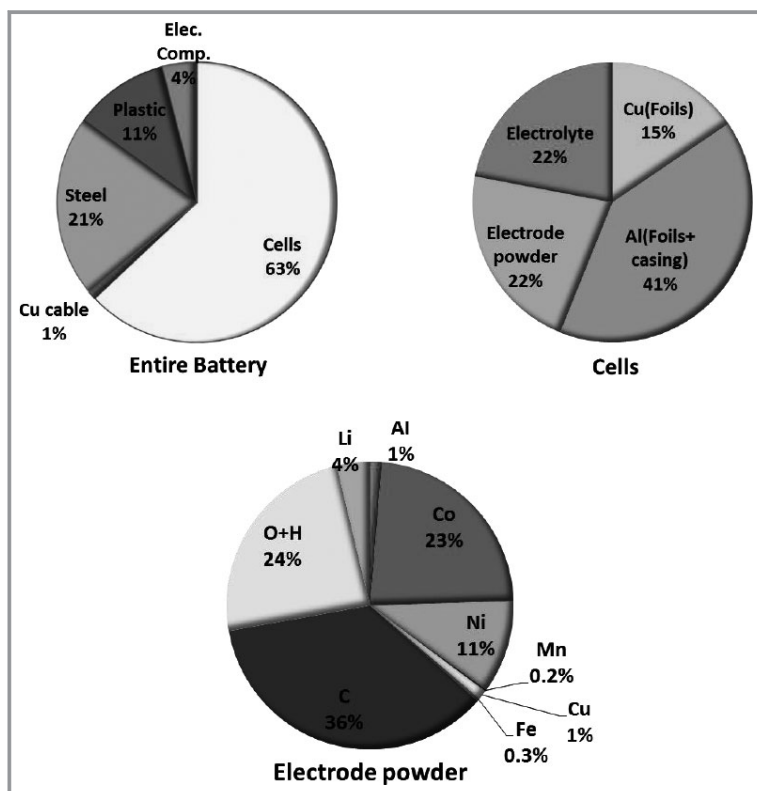


Figure 3. Composition of a (H)EV Li-ion battery with cells and electrode powder [7].

treatment. The current industrial recycling of Li-ion batteries recovers only the profitable value metals Co, Cu, Fe, and Ni as a cost-effective recycling method. Lithium out of LIBs is not recycled on an industrial scale as apparent from Tabs. 1 and 2. Furthermore the statutory recycling efficiency of at least 50 wt % is not met [7, 10, 11].

In order to lower the cost of the battery production and at the end to lower the cost of electric vehicles, the automobile industry uses electrode materials with low or no portion of Co and Ni. So used (H)EV battery supplies already consist of different lithium-ion subtypes which are either not

suitable for the existing recycling operations, cause high costs or are not accepted by the recipient. The automobile industry has to finance net cost arising from collection and recycling of LIBs and has to consider future recycling cost at the earliest stage of life cycle already now. Electric vehicles are still in front of their broad market introduction, so there are not many experiences for the recycling of lithium-ion traction batteries. There were some studies of individual process steps, such as the hydrometallurgical recovery of lithium from the active electrode material, but in total there is still no closed circuit process for the recycling of Li-ion batteries from the automotive sector.

This is a significant advantage for battery manufacturers and automotive companies. So the TCO gap (total cost of ownership) is lowered for electric vehicles compared to conventional vehicles. The eventual selling price of electric vehicles, and thus the sales success depends largely on the cost of the battery module. The raw material cost share is set to increase in proportion to the mass production of cells. The dependence on raw materials and other cost increases can only be prevented by the closure of domestic material cycles. The automotive Li-ion battery recycling is also an ecological goal for waste management and to the strategic

accessibility of raw materials for battery production in Germany [7].

3 EcoBatRec Recycling Project

For electric vehicles, the selling price is significantly influenced by the cost of production of the battery modules. As part of the responsibility of the product manufacturer, currently about 7 % of the module costs account for the disposal. In consequence of the growing demand of strategic raw materials, commodity dependence and an increase in costs is expected in this sector. This development needs to be counteracted by the exploitation of domestic material cycles. The statutory required recycling rate for batteries is a minimum ratio of 50 % [2]. Currently, the recycling efficiency of industrial treatment plants, however, is about 30 % (see Tab. 2), and does not cover costs and profit. Furthermore current recycling processes are fully aligned for the recovery of the valuable metals cobalt

Table 1. Theoretically available value metals for recycling out of Li-ion batteries [3].

Year	2013	2014	2015	2016	2017	2018	2019	2020
Cu [t]	212	395	604	816	1034	1273	1522	1798
Al [t]	114	212	325	439	557	685	820	968
Steel [t]	309	577	883	1192	1512	1861	2225	2627
Electrode mass	635	1184	1813	2447	3103	3819	4567	5393
Co [t]	147	280	410	512	608	680	735	780
Mn [t]	48	84	133	193	261	349	449	565
Ni [t]	22	44	78	124	181	256	341	438
P [t]	7	12	19	29	36	46	58	73

Table 2. Comparison of industrial LIBs depending of the different cathode materials [3].

	Li-ion subtype	LCO	NMC	NCA	LFP
Company A (Canada, industrial scale)	Permitted input	+	+	+	-
	Recycled metals	Co, Cu	Co, Cu, Ni	Co, Cu, Ni	
	Not recycled metals	Li, C, Fe, Al	Li, C, Fe, Al, Mn	Li, C, Fe, Al	
	Recycling efficiency (RE)	< 30 %	< 30 %	< 30 %	
	Comply with Bat. Dir. EU/66/2006	-	-	-	
Company B (Belgium, industrial scale)	Permitted input	+	+	+	+
	Recycled metals	Co, Cu	Co, Cu, Ni, Fe	Co, Cu, Ni, Fe	Fe
	Not recycled metals	Li, C, Al	Li, C, Fe, Al, Mn	Li, C, Al	Li, C, Al, P
	Recycling efficiency (RE)	< 30 %	< 30 %	< 30 %	< 10 %
	Comply with Bat. Dir. EU/66/2006	-	-	-	-
	Credit or cost for scrap batteries	Credit	Cost	Cost	Cost

and nickel [3]. So the existing recycling processes are not suitable for the disposing of Li-ion (H)EV batteries and

recycling process removes the electronics, cables and plastics which are then separated from the battery scrap. At this

unprofitable due to the low content of cobalt and nickel [3, 8, 10].

The research project EcoBat-Rec is promoted by the German Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety. The main objective is the testing of commercially viable technologies for recycling of LIBs. Furthermore, it aims for the development of a demonstration plant for a cost-neutral, resource-efficient processing of spent Li-ion batteries of (H)EV. Within the project the whole recycling process is subject to observation, starting with the characterization of the batteries, to the disassembling, the mechanical crushing and classification of different materials, up to the development of new processes for lithium recovery. Fig. 4 [3, 8] shows schematic the process of the EcoBatRec project.

Mechanical preparation and disassembling prior to the recycling

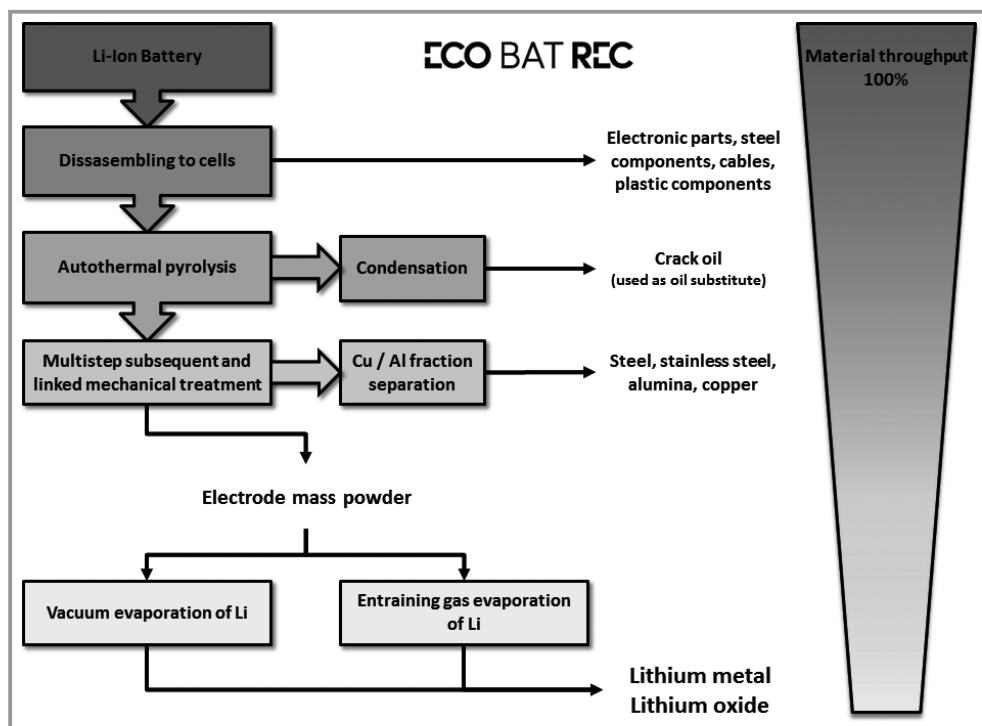


Figure 4. Process scheme and material throughput of the EcoBatRec project [3, 8].

point the first high-value, marketable products are generated. In the further course of the EcoBatRec recycling process a characterization, dismantling and disassembling of the automotive batteries to module level takes place. The disassembling alone can already reduce the mass flow by up to 50 %. After dismantling a thermal deactivation and discharge of the modules takes place. The flammable electrolyte, decomposed organics and products of the separator layer can be removed via a vacuum- or atmospheric thermal treatment by an autothermic pyrolysis.

Due to security measures, the modules are often fixed with polymeric foam or epoxy resin, cushioning the vibrations during the vehicle operation. Thus, more organic by-products are produced during the thermal treatment. The following condenser unit and the exhaust treatment have to handle these by-products and have to be adapted appropriately. After the vacuum thermal treatment, the deactivated cells are crushed, shredded, and sieved in a subsequent, highly complex mechanical treatment. At this point, by classification of different material fractions clear metallic fractions like copper, aluminum, steel are generated from the cell residues and are separated from the electrode powder. An early integration of these out-coming fractions to standard industrial routes should be considered for an optimized economic evaluation.

The concentrated electrode mass powder contains graphite and lithium-compounds of the cathodes. To recycle lithium from this generated electrode mass powder two metallurgical treatment technologies are investigated scientifically [3].

- Direct vacuum evaporation of Li and recovery of metallic Li by distillation
- Selective entraining gas evaporation of Li and recovery of lithiumoxide

With the approach of a hybrid method of thermal and mechanical treatment the presented EcoBatRec process provides an alternative to the conventional recycling routes. The patented thermal treatment process ensures exceptional flexibility, security and an eco-friendly access to the included battery materials. Simultaneously high recycling rates with marketable products can be achieved by using an adaptive, advanced and cost-effective mechanical treatment process.

The main objective is the design of a recycling operation that is economically advantageous and has a maximum recovery rate for the valuable materials. Additionally, there is a further objective in creating an ecological balance to prove the advantages for the environment compared to processes using primary resources. Overall, it is the goal of the project EcoBatRec to obtain positive revenues for the different recycled material fractions by the low process and treatment costs.

The EcoBatRec project will implement:

- a significant increase of recovered recyclables with positive market revenue,

- ensuring the legal minimum rate of > 50 % for recovered metals,
- lowering the cost of treatment,
- a high robustness of the method against interference and impurities (e.g., state of charge attachments etc.),
- a high level of flexibility and usability for all current and future Li-Ion cell types and chemistries,
- lowest possible emissions.

3.1 Current Research on the Recovery of Lithium

In the following only a brief overview of the current state of research is given. The electrode powder used for the experiments was generated out of spent Li-ion traction batteries in accordance with the EcoBatRec process. The chemical composition is shown in Tab.3, analyzed by ICP-OES method.

Table 3. Chemical Composition of the used battery electrode powder.

Element	Contents [wt %]
C	24.40
Li	4.04
Cu	2.42
Al	7.42
Mn	4.89
Co	16.39
Ni	4.00

Carbon with 24 % is the largest proportion of the material because it is used as an anode material. The remaining elements also correspond to a conventional composition of (H)EV Li-ion batteries. For recovery of the lithium out of the powder by volatilization it is important to know the vapor pressures of Li and the accompanying elements. The vapor pressure curves of the metals contained in the feedstock were created using the software FactSage™ 6.4 and are shown in Fig.5 (only the vapor pressures of the pure phases were calculated).

In Fig. 5 the pressure is plotted logarithmically against the temperature. Based on the vapor pressure curves it can be seen that lithium at 1 bar ambient pressure evaporates already at 1342 °C. This is consistent with literature values [9].

Since lithium is present as a compound in the cathode material it needs to be converted into the pure phase for selective volatilization. This is done by thermal decomposition and by carbothermal reduction with the graphite contained in the electrode mass powder. In the experiments described below, the same feedstock is heated under vacuum and under inert gas used as carrier gas.

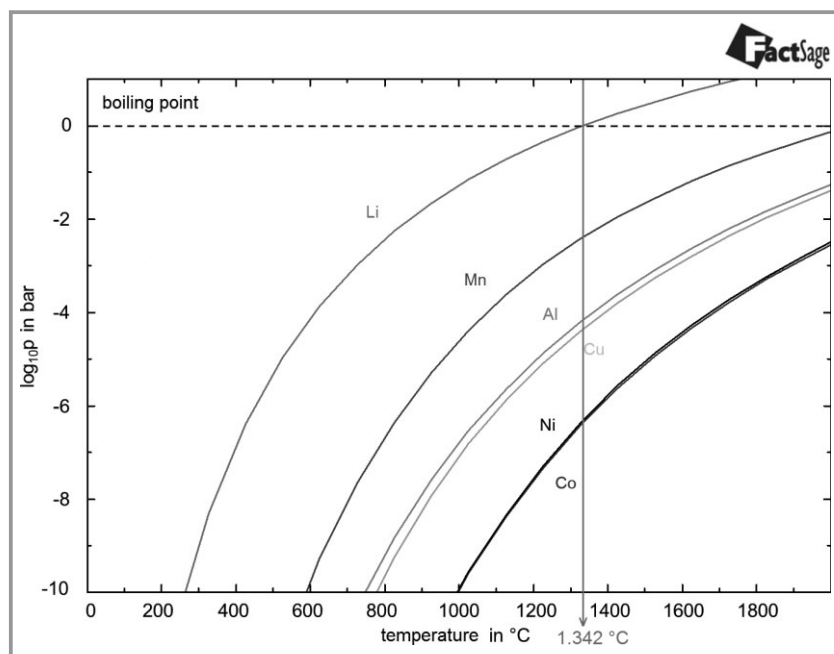


Figure 5. FactSage™ vapor pressure curves for the metals contained in the feedstock.

3.1.1 Direct Vacuum Evaporation

For the entire test series the electrode mass powder was placed in graphite crucibles in a vacuum induction furnace. Via a riser the steam jet was directed into a condenser and the metals should condense there. The complete experimental setup incl. the riser and condenser was within the closed vacuum furnace. The feedstock was heated under vacuum over a period of about 120 min to a temperature of about 1400 °C. During this time the temperatures of the powders in the crucibles, the steam jet and the condenser were measured continuously with thermocouples. Fig. 6 illustrates the temperature profile over time. It is a representation with averaged values of several same trials.

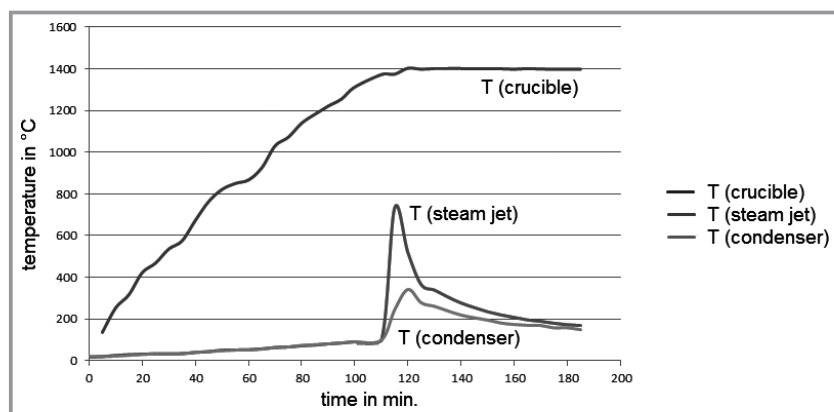


Figure 6. Temperature gradients of the crucible, the vapor stream and the condenser under vacuum.

It can be seen that from a crucible temperature of about 1300 °C an incipient steam jet is observed. This suggests that massive volatilization for about 20 min occurs. Tab. 4 shows the composition of the feedstock after the treatments (considering the mass balance calculated values based on the input mass).

In a comparison with the output levels (see Tab. 3) in the electrode mass powder a decrease can be observed, especially the lithium content. The carbon loss is due to the carbothermal reduction. The lithium content in the condensate is between 14.4 wt % and 26.0 wt %. The contents of the other elements considered lies between 0.05 wt % and 3.0 wt %. But the chemical analyses of the condensate of the test series show large fluctuations. So the composition of the condensate is not representative. This is partly due to the fact that a precipitate has formed already in the riser. Furthermore, partially en-

Table 4. Chemical composition of the feedstock after the trials (vacuum atmosphere, 1400 °C).

Element	Contents [wt %]
C	18.80
Li	2.46
Cu	2.06
Al	8.36
Mn	2.87
Co	15.43
Ni	3.32

trained flue dust was found in the condenser. In principle, however, a selective vacuum evaporation of lithium is feasible.

3.1.2 Entraining Gas Evaporation

For this test series a resistance heated furnace and Al₂O₃ crucibles were used. The steam jet and the carrier gas, respectively, could leave the furnace via a riser. A baffle plate was mounted above the riser so that vaporous lithium was able to oxidize to LiO₂ under normal air atmosphere. The feedstock was heated under nitrogen atmosphere over a period of about 120 min to a temperature of about

1400 °C. The temperature of the furnace at the crucible and the temperature at the end of the riser were measured. In comparison to the experiments of the vacuum test series, in this nitrogen test series no change in temperature of the vapor stream was observed. This is explained by the fact that the N₂ was the protective inert gas inside the furnace and at the same time the outgoing entraining gas with the same exhaust temperature, constant at about 480 °C. Tab. 5 shows the composition of the feedstock after the treatments (considering the mass balance calculated values based on the input mass).

Table 5. Chemical composition of the feedstock after the trials (nitrogen atmosphere, 1400 °C).

Element	Contents [wt %]
C	16.11
Li	3.13
Cu	2.27
Al	8.15
Mn	4.74
Co	16.24
Ni	4.07

Similar to the direct vacuum evaporation experiments the output levels (see Tab. 3) in the electrode mass powder decrease, especially the lithium content. Compared to the experiments in vacuum, the lithium content is not so much reduced in the feedstock (see Tab. 4). As expected, the evaporation rates under vacuum and nitrogen are similar under the same experimental conditions.

In a second test series, the same input material was heated under nitrogen atmosphere with a higher heating rate over a period of about 120 min to a temperature of about 1650 °C. Again, no change in temperature of the vapor stream was observed. The exhaust temperature was constant at about 540 °C. Tab. 6 shows the composition of

Table 6. Chemical composition of the feedstock after the trials (nitrogen atmosphere, 1650 °C).

Element	Contents [wt %]
C	12.84
Li	0.94
Cu	2.15
Al	6.22
Mn	4.09
Co	14.21
Ni	3.79

the feedstock after the treatments (considering the mass balance calculated values based on the input mass).

The lithium content has fallen to less than 1 wt % in the output material. This is a reduction of 76.73 % compared to the input material (see Tab. 3). The carbon content was also once again slightly reduced. This means that the lithium compounds of the cathode materials were almost completely decomposed or reduced. However, the kinetics increases with increasing treatment temperature. This also means that the volatilization of lithium content increases with increasing treatment temperature [12, 13]. So, a selective volatilization of lithium is technically possible.

A gray-black colored condensate has formed on the baffle plate. The analysis is shown in Tab. 7 (considering the mass balance calculated values based on the input mass from test series with 1650 °C.)

Table 7. Chemical composition of the condensate after the trials (nitrogen atmosphere, 1650 °C).

Element	Contents [wt %]
Li	18.2
Cu	0.27
Al	0.14
Mn	0.58
Co	0.062
Ni	0.05

As compared to the test series under vacuum, these results are reproducible. In comparison to the experiments under vacuum with lithium contents between 14.4 wt % and 26.0 wt % in the condensate, the lithium content in the condensate is with 18.2 wt % at a similar level under nitrogen atmosphere. Some samples of the condensate were dissolved in deionized water. The chemical analysis gave an average lithium content of 947 mg L⁻¹ (Fig. 7) [12, 13].

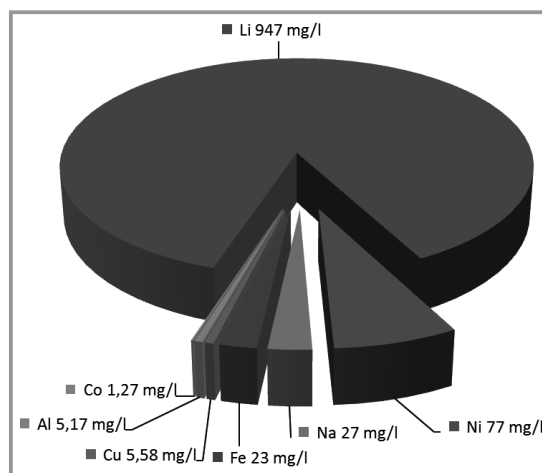


Figure 7. Composition of solubilized condensate in solution.

4 Summary

The lithium-ion accumulator and its subsystems will dominate the future market. Therefore intelligent, material specific and economically optimized processing techniques have to be developed, especially for the recycling of lithium. In the years ahead, newly developed recycling processes will be validated and expanded in economic aspects and industrial applications. With the unpredictable amount and time scale for the rate of return, as well as with decreasing metal value contained in lithium-ion batteries, comes an incalculable investment risk for the recycling industry. The introduction of EU-wide obligations for collection and utilization of used batteries creates additional requirements – in quantity and quality – for future recycling processes. Recycling the metals from the Li-ion batteries out of the automotive sector not only has the economic benefit but also relieves the environmental burdens.

The EcoBatRec project shows that an almost completely cost-neutral and sustainable recycling is possible. In the experimental work it was examined whether and how it is possible to separate lithium from the other electrode materials selectively to regain it. The results show that a pyrometallurgical recovery of lithium from lithium-ion traction batteries is possible. The underlying decomposition and evaporation reactions take place under vacuum and under nitrogen atmosphere. They start already at about 1400 °C and are accelerated at a higher temperature. The mechanisms for the decomposition and evaporation of lithium compounds from automotive Li-ion batteries are currently being researched in more detail in order to obtain a higher selectivity. From these results a further step for the recycling process should be developed.

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