

Process for Recycling Battery Materials By Way of Reductive, Pyrometallurgical Treatment

The present invention relates to a recycling method for battery materials, in particular lithium-ion/polymer batteries, and the further use of the valuable materials recovered by the method according to the invention.

Electromobility is considered as a central component of a sustainable and climate-friendly transport system based on renewable energies and belongs to the global megatrend "Advanced Mobility", which is discussed intensively not only in society and politics, but is now also present in the industry. Electromobility includes all types of electric vehicles: electric bicycles, motorcycles, forklifts, ferries and sport boats, hybrid cars, plug-in cars and fully electric cars up to electric buses and hybrid or fully electric trucks. For the time being, batteries, in particular the so-called lithium-ion/polymer accumulators (hereinafter referred to as LIB), have become established as energy storage in this context.

With the increasing demand for electric vehicles, not only the need for corresponding drive and energy storage systems increases. The question also arises as to how these systems can be integrated into a clean and circular economy, which will certainly continue to gain importance in the future from the perspective of sustainability. Therefore, the strategic relevance of the recycling of these systems is an essential component in the entire value chain of the global megatrend of mobility and thus an indispensable part of international efforts to achieve climate goals. Therefore, it is absolutely necessary to be able to provide key materials for electromobility as quickly as possible through environmentally friendly, energy and cost-efficient and socially compatible recycling processes. The emancipation from the classic primary raw material recovery of battery-relevant materials towards the sustainable and nevertheless economical handling

of them through the development and large-scale implementation of innovative recycling processes will increasingly come to the fore globally.

Typical elements, that are used in LIB in metallic form or in the form of their compounds, are iron (Fe), aluminum (Al) and copper (Cu), manganese (Mn), nickel (Ni) and cobalt (Co), lithium (Li) as well as graphite in various modifications, which mainly make up parts of the housing, the electrical supply lines, but also especially the electrode materials and, depending on the battery type, battery model and battery design, can occur in a wide variety of proportions in addition to the minor electrolyte and separator materials. Some of these raw materials are often recovered under precarious conditions that are associated with far-reaching social and environmental impacts. In this context, it should pay attention to, for example, the existence of child labor e.g. in the manual mining of cobalt or the extremely dubious influence of lithium recovery on the water balance in desert areas and plateaus from an environmental point of view. In view of the massive social and ecological impacts associated with the steadily increasing demand for these strategic raw materials, the recycling of LIBs and related systems plays a key role in the sustainable transition to alternative energy storage systems, as explained above. Due to the complexity of the material compositions and the use of substances and mixtures classified as carcinogenic and their electrical and chemical energy content, the recycling of LIBs is not only a purely technological challenge, but also associated with a number of health, safety and environmental risks to be controlled.

Initial attempts to establish a closed cycle for LIBs resulted in various recycling processes that have so far only been implemented in a few industrial plants around the world. All of these methods are characterized by long and costly process chains and based on a combination of mechanical and/or thermal and/or pyrometallurgical and hydrometallurgical process steps. An overview of the common processes is provided by L. Brückner *et al* in their review article: "*Industrial Recycling of Lithium-Ion Batteries - A Critical Review of Metallurgical Process Routes*", published in *Metals* **2020**, 10, 1107.

Within the framework of the following statements and the present invention, no distinction is made between the systems lithium batteries, rechargeable lithium batteries and lithium accumulators, rechargeable lithium-ion batteries and

lithium-ion accumulators and rechargeable lithium-polymer batteries and lithium-polymer accumulators. All systems are hereby considered to be synonymous with one another and summarized under the designation "LIB", unless expressly stated otherwise.

Currently, two variants for recycling LIBs have been established, the first based on a combination of pyrometallurgical and hydrometallurgical treatments, whereas the second is based on mechanical treatment, possibly with an upstream or downstream thermal stage, prior to the actual hydrometallurgical further processing.

In the case of a pyrometallurgical treatment of used LIBs or residues from battery production, as it is carried out in the first variant described, molten alloys containing Co, Cu and Ni (metallic phase), a liquid slag containing Al, Mn and Li and fly ash appear. The metallic phases and the slag can then be further treated hydrometallurgically in order to obtain the individual metals using known methods via multi-stage processes.

Within the framework of the second variant described, the LIBs are first treated mechanically, whereby typically magnetic and non-magnetic metal concentrates such as Al and Cu concentrates as well as a fraction appear, that contains the active electrode materials, the so-called black mass. The mechanical treatment can optionally be preceded by a thermal treatment in order to reduce the energy content in a controlled manner and to remove organic components and halides in a targeted manner. Particularly with larger traction batteries, an upstream electrical residual discharge of the LIBs can also be advantageous for safety reasons. The black mass resulting from these processes can then either be fed to a pyrometallurgical treatment, in accordance with the first variant described, or, which is preferred, be subjected directly to a hydrometallurgical treatment. Depending on the composition of the black mass and the upstream treatment procedure practiced in each case, a thermal treatment can now also be advantageous in order to remove organic components and halides present at this point and to increase the metal content. During the hydrometallurgical treatment, Co, Li, Mn, Ni and, if available, graphite can be recovered.

The following is an example of the processing of used LIBs based on the second variant, as known in the state of the technology:

The mechanical treatment of the disused LIBs usually begins with a crushing in order to release the components of the LIBs. With large batteries from electric drives, an electrical deep discharge is advantageous. The components can then be sorted by their physical properties, such as by particle size, shape, density and electrical and magnetic properties. Usually, the crushing process produces concentrates for further metallurgical processes.

Pyrometallurgy includes high-temperature processes such as roasting or melting for the separation, recovery and refinement of metals. The term roasting is generally understood to mean processes such as gas-solid reactions, with which ores or secondary raw materials can be converted into other, more easily processed chemical substances or mixtures, whereby some of the undesirable components can often be removed in gaseous form. During smelting, the metal is extracted from the ore or the secondary raw material with the help of heat and chemical reducing agents, whereby the ore or the secondary raw material is decomposed and other elements are expelled in the form of gas or captured or accumulated in slag in order to get alloys or, in the best case, pure metal.

The hydrometallurgy refers to the entirety of the methods in metal recovery and refining, which, in contrast to pyrometallurgy, take place at comparatively low temperatures in solution. Hydrometallurgical methods usually involve several steps. In a first step, the metal is first brought into solution by leaching, usually with the help of acids, bases or salts. In a subsequent step, cleaning takes place, for example with the help of liquid/solid reactions such as ion exchange reactions and precipitation or liquid/liquid reactions such as solvent extraction. In a final step, the valuable material element initially in solution is precipitated, either directly as a metal or as a chemical compound, often in salt form, for example by crystallization, ionic precipitation, reduction with gases, electrochemical reduction or electrolytic reduction.

Like other battery types, LIBs are usually made up of a cathode, an anode, an electrolyte and a separator, whereby the components can vary depending on the

battery type and manufacturer and therefore have a large influence on possible recycling processes.

Commercially high-performance cathode materials in LIBs are typically LiCo oxides (LCO), Li (Co/Ni) oxides (LCNO), Li (Ni/Co/Mn) oxides (LNCMO), Li (Ni/Co/Al) oxides (LNCAO) or Li (Ni/Al) oxides (LNAO) in the form of LiMO_2 layer structures (with $M = \text{Ni, Co and/or Mn}$), which can optionally be doped with Al for stabilization, or Li (Ni/Mn) oxides in the form of LiM_2O_4 spinel structures, whereby only the main components essential for recovery from a supply engineering and economic point of view are mentioned here. There is also a variety of other doping elements, which, depending on the battery or cathode material manufacturer and the respective uses of the rechargeable batteries, extend over various other subgroup metals, including the rare earth elements, but also main group elements of the periodic system.

Furthermore, Li-metal-phosphates of the structure LiMPO_4 ($M = \text{Fe, Mn, Co, Ni}$), also in variously doped form, can be used, but due to their usually high content of less valuable iron and phosphorus, the main component LiFePO_4 in the desired recycling processes play a subordinate role.

The most common cathode materials known from the literature are as layer structures LCO (LiCoO_2), NMC ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ with $x + y + z = 1$), NCA ($\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ with $x + y + z = 1$, especially $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$) as well as spinel LiMn_2O_4 and LFP (LiFePO_4), which has an olivine structure, whereby the places of the SiO_4 tetrahedra in the olivine ($(\text{Mg, Fe})_2\text{SiO}_4$) are occupied by PO_4 tetrahedra.

Due to their high content of aluminum, which comes mainly from the housing, and significant amounts of lithium and organic compounds only to a limited extent as starting material for classic smelting processes as they are used for the recovery of Co, Ni or Cu, so-called end-of-life LIBs to be recycled or waste from LIB production (off-spec) are suitable, as in particular lithium is known to attack the furnaces. Another problem is that the established processes concentrate on the recovery of Co, Cu and Ni and that lithium, together with aluminum and manganese only occurs in low concentrations in the form of slag, from which it is difficult to remove.

In order to address these problems, a number of processes have been developed that focus specifically on the treatment of LIBs. These processes allow lithium to accumulate in the slag and use special furnaces that are designed for highly corrosive materials.

In this context, US 7,169,206 describes a method for the recovery of Co or Ni, in which a metallurgical charge of iron, slag formers and a workload, which contains either nickel or cobalt or both, is brought into a shaft furnace and melted, whereby a Co/Ni alloy, a ferrous slag and a gas phase occur. The workload comprises at least 30% by weight of batteries or their scrap, and the redox potential of the shaft furnace is selected in such a way that the slag contains at least 20% by weight of iron and a maximum of 20% by weight of the nickel and/or cobalt of the workload. Although LIBs are mentioned as suitable starting materials, no further details are given as to whether and in what amount lithium could be recovered.

EP 2 480 697 also describes a method for the recovery of Co from Li-ion batteries, which also contain Al and C, comprising the steps: Providing a bath furnace which is equipped with means for injecting O₂; Providing a metallurgical charge comprising Li-ion batteries and at least 15% by weight of a slag former; Supplying the metallurgical charge to the furnace with injection of O₂, whereby at least a part of the Co in a metallic phase is reduced and collected; Separating the slag from the metallic phase, whereby the process is carried out under autogenous conditions by adding the proportion of Li-ion batteries, expressed in % by weight of the metallurgical load, equal to or greater than $153\% - 3.5 (Al\% + 0.6 C\%)$, whereby Al% and C% are the % by weight of Al and C in the batteries. It can be seen from the examples that the slag obtained also contained Li, but no further treatment of the slag to isolate the lithium is described.

WO 2011/141297 describes a method for the production of lithium-containing concrete, in which lithium-containing metal scrap is melted to obtain a metallic phase and a lithium-containing slag, the slag is separated from the metallic phase, the slag is solidified by cooling and then the slag is processed into a powder with a particle size D₉₀ of less than 1 mm. The pulverized slag is then added to concrete or mortar in order to prevent undesirable ASR (alkali-silica reactions), whereby the lithium is finally extracted from the material cycle.

Further investigations have shown that the lithium content of the slag recovered is comparable to that of spodumene concentrates, which, in addition to lithium-containing brine, are the largest commercial lithium source in the field of primary raw materials containing lithium. Within the framework of various research work, methods for the extraction of lithium from slags of different compositions have been developed. In a first step, the slag was ground to a powder on a micrometer scale and then leached with H_2SO_4 or HCl at 80°C , whereby an acid concentration of around 10 g/L has proven advantageous. In order to separate aluminum, the pH value of the leaching solution was then adjusted to pH 5 and aluminum hydroxide precipitated. After filtration and concentration of the lithium content in the leaching solution, the lithium was then precipitated as lithium carbonate at pH 9 to 10 with the help of Na_2CO_3 . Under optimized conditions, a lithium yield of 60 to 70% could be achieved. However, the method shows the disadvantage that the low lithium content in the slag results in a high proportion of waste and the Li_2CO_3 obtained has a high level of impurities.

An alternative recycling method for LIBs is based on a combination of mechanical treatment and pyrometallurgical and/or hydrometallurgical treatment, in which a certain fraction, the so-called black mass, is in the foreground. In an optional pretreatment, the LIBs are subjected to thermal treatment, for example pyrolysis, in order to reduce the energy content in a controlled manner and to remove organic components. After the material obtained has been crushed, it can be separated by sieving, sorting or magnetically, whereby as typical fractions, Al/Cu foils, non-magnetic metals such as aluminum or copper in pieces or powder form, magnetic metals and a fraction known as black mass, which are essentially made of the active materials of the batteries, i.e. the cathode material with the main components Ni, Co, Mn, Al and Li as well as optionally graphite from the anode material, can be isolated. With the exception of the black mass, all fractions obtained can be fed to conventional treatment processes.

Due to its already reduced aluminum content, the black mass is better suited for conventional pyrometallurgical processes than LIBs. Due to the corrosive properties of lithium and the costly reprocessing of the lithium-containing slag and the high losses of lithium during the reprocessing, the problem of efficient recovery of lithium in this way remains unsolved.

WO 2017/121663 relates to a lithium-containing slag, which shows 3 to 20% by weight of Li_2O , 1 to 7% by weight of MnO , 38 to 65% by weight of Al_2O_3 , less than 55% by weight of CaO and less than 45% by weight of SiO_2 . The lithium-containing slag can be obtained by melting battery materials, in which it is obtained together with a metallic phase. For this purpose, used lithium-ion batteries are added into a furnace together with limestone (CaCO_3) and sand (SiO_2) in the presence of oxygen. Due to the high content of metallic aluminum and carbon in the batteries, a temperature of 1400 to 1700°C is reached. The resulting alloy melt and the slag are separated and the lithium is isolated from the slag. Although more than 50% of the lithium should accumulate in the slag, it could not be prevented that part of the lithium is discharged together with the exhaust gases. According to the amounts of battery material used according to the examples, the expert would expect a content of 12.42% Li_2O in the slag, but in fact table 1 only gives a content of recovered lithium of 8.4%, so that a loss of 32.4% of the lithium used is to be booked.

On the hydrometallurgy side, the focus is currently on two alternatives. The first alternative attempts to obtain intermediate products by leaching and precipitation, in which Ni/Co and manganese and lithium can then be purified separately from one another in existing refineries. The second alternative provides for a direct production of more complex products. Both methods provide for a step-by-step separation of the elements, in which manganese, cobalt and nickel are separated one after the other and in a last step lithium is isolated in the form of Li_2CO_3 . Figures 1 and 2 show an overview of the two methods.

WO 2018/184876 describes a method for the recovery of lithium from a lithium- and aluminum-containing metallurgical composition, comprising the steps: Leaching the metallurgical composition by bringing it into contact with an aqueous sulfuric acid solution at a pH of 3 or less, thereby obtaining a residue containing insoluble compounds, and a first leachate comprising lithium and aluminum; Optionally neutralizing the first leachate comprising lithium and aluminum to a pH of 2 to 4, thereby precipitating a residue comprising a first part of the aluminum and obtaining a second leachate comprising lithium; Adding a phosphate ion source to the first leachate comprising lithium and aluminum, or, with the proviso that the optional neutralization of the first leachate is carried out, to the second leachate comprising lithium and aluminum, thereby

precipitating a residue comprising the second part of the aluminum and obtaining a third leachate comprising lithium; Optionally neutralizing the third leachate comprising lithium and aluminum to a pH of 3 to 4, thereby precipitating a residue comprising a third part of the aluminum and obtaining a fourth leachate comprising lithium; and separating the residue comprising the second part of the aluminum from the third leachate by filtration, or, with the proviso that the optional neutralization of the third leachate is carried out, separating the residue comprising the third part of the aluminum from the fourth leachate by filtration. The lithium can then be obtained in the form of Li_2CO_3 with the help of known methods such as classic carbonate precipitation. In this way, a better separation of aluminum and lithium is to be achieved and the content of recovered lithium is to be increased.

WO 2019/149698 relates to a method for the recycling of lithium batteries, with the steps (a) digesting material to be crushed, which contains crushed components of electrodes of lithium batteries, with concentrated sulfuric acid at a digestion temperature (AT) of at least 100°C , so that an exhaust gas and a digestion material arise, (b) removal of the exhaust gas and (c) at least a wet chemical extraction of at least one metallic component of the digestion material.

WO 2020/011765 discloses a process for the recovery of transition metal from spent lithium ion batteries containing nickel, wherein said process comprises the steps of (a) heating a lithium containing transition metal oxide material, which is derived from lithium-ion batteries and contains fluorine compounds and/or compounds of phosphorus as contaminants, to a temperature in the range of from 200 to 900°C in the presence of H_2 , (b) treatment of the product obtained in step (a) with an aqueous medium, (c) solid-solid separation for the removal of Ni from the solid residue of step (b), (d) recovery of Li as hydroxide or salt from the solution obtained in step (b), (e) extraction of Ni and, if applicable, Co from the solid Ni-concentrate obtained in step (c).

In their article "A promising approach for the recovery of high value-added metals from spent lithium-ion batteries", issued in the Journal of Power Sources, 351 (2017), 192-199, J. Hu et al. describe an approach for the recycling of metals having a high added value from the cathode materials of used LIBs by reductive roasting to degrade $\text{LiNi}_x\text{Co}_y\text{Mn}_2\text{O}_2$ into simpler compounds or metals.

CN 108539309 relates to a method for recycling a waste lithium-nickel-cobalt-manganese oxide cathode material, in which the material is freeze-dried and sieved at first, the sieved material obtained is placed into a reducing furnace, and hydrogen is supplied for reduction under specific conditions. The thus obtained raw material is stored in a storing box filled with nitrogen, then washed by adding hot pure water, and admixed with carbon dioxide to obtain a lithium hydrogen carbonate solution and aluminum hydroxide precipitates. The cobalt, nickel and manganese residues are mixed with hydrazine, converted to their metallic form, and then separated magnetically.

WO 2020/212587 discloses a process for the production of battery precursors with recovery of metals M from a Li-containing starting material, wherein M comprises Ni and Co, comprising the steps of: Step 1: Providing said starting material comprising Li-ion batteries or their derived products; Step 2: Removing Li in an amount of more than the maximum of (1) 30% of the Li present in said starting material, and (2) a percentage of the Li present in said starting material determined to obtain a Li:M ratio of 0.70 or less in a subsequent acidic leaching step using either one or more of the following methods: (a) a pyrometallurgical smelting process using slag-formers, thereby producing one or more of a Li-bearing slag phase and Li-fumes, and a Li-depleted Ni-Co-bearing phase susceptible to be acid-leached; (b) a thermal treatment process using a reducing agent, thereby producing a Ni-Co-bearing residue containing at least one water-soluble Li-compound, and selectively removing said at least one Li-compound by washing with an aqueous solution, thereby obtaining a Li-depleted Ni-Co-bearing residue susceptible to be acid-leached; (c) a hydrometallurgical leaching process using an aqueous or acidic solution, thereby selectively leaching Li from said starting material, wherein Ni and Co are at least partially insoluble, and solid-liquid separation, thereby obtaining a Li-depleted Ni-Co-bearing residue susceptible to be acid-leached; Step 3: Subsequent leaching using relative amounts of Li-depleted, Ni-Co-bearing product obtained in step 2, and a mineral acid, thereby obtaining a Ni-and Co-bearing solution; and, Step 4: Crystallization of Ni, Co, and optionally Mn.

CN 109652655 describes a method for recovering lithium in a lithium battery recycling process, in which a lithium-rich solution is obtained from the lithium batteries by treatment with CO₂ followed by pyrolysis.

CN 107324392 proposes a method for recycling lithium manganese oxide materials under reducing conditions, in which the material is heated in the presence of hydrogen, followed by aqueous processing to obtain a lithium hydroxide solution.

In "Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: A comprehensive review", Hydrometallurgy 150 (2014), 192-208, P. Meshram proposes different methods and processes for extracting lithium from primary and secondary sources.

The methods described in the state of the technology show the disadvantage that the proportion of recovered lithium has so far been relatively low and the lithium is only separated as the last element, which on the one hand results in high losses and on the other hand, interferences from the lithium in the preceding method steps cannot be ruled out. An earlier extraction of lithium from the black mass is therefore of great interest.

In addition, there are currently no large-scale methods available that allow the efficient recovery of lithium from LIBs.

Conventional pyrometallurgical processes achieve high yields for Co, Cu and Ni in the alloy melts. However, lithium can only be recovered in special methods that require lithium to be concentrated in the slag. As a result, plants for the recovery of the valuable metals nickel, copper and especially cobalt, as they are currently used, have major disadvantages, if a certain recovery rate for lithium is prescribed by law, as expected after the reform of Directive 2006/66/EC, which regulates the legal foundations for the recycling of LIBs.

In hydrometallurgical processes, only small losses are observed for Co, Cu and Ni, but corresponding processes are not available for lithium. In the literature, possible recovery rates for Li from the slag are given with approximately 90%, but the total Li recovery is likely to be lower, as it is assumed that lithium is partially smoked in pyrometallurgy, as also described in WO 2017/121663.

Against this background, the present invention is based on the task of providing a method for recycling LIBs, which allows better recovery of the elements, in

particular the active cathode material and in particular the lithium used. In particular, the method according to the invention should enable lithium to be separated off at the beginning of the reprocessing process, so that it does not have to be carried through the entire process chain.

Surprisingly, the present invention has shown that the previous problems in the recovery of lithium from LIBs can be overcome for the most part by separating lithium as one of the first elements, in contrast to the conventional methods, by means of a reductive treatment of a Li(I)-containing composition, without the formation of the usual melt phases.

Instead of dragging the lithium along through the entire processing and separation process, the method according to the invention provides for the separation of the lithium from the other metals nickel, cobalt and manganese at the beginning of the process chain. This could be achieved by the fact that a Li(I)-containing composition, unlike usual, is not subjected to a conventional pyrometallurgical treatment, which usually requires temperatures well above 1000°C and provides liquid metal phases and liquid slag, but a reductive treatment in the solid state without the addition of slag formers. In this respect, the method according to the invention is distinguished in that a solid Li(I)-containing composition, for example in powder form, is subjected to a reductive treatment, whereby a lithium(I)-containing solution and again a solid, the reduced material, are obtained. In this way, the amount of lithium recovered could be increased significantly.

Therefore, a first object of the present invention is a method for the recycling of LIB materials, comprising the following steps:

- a) washing a lithium (I)-containing composition, wherein said lithium(I)-containing composition is obtained from used lithium-ion batteries;
- b) heating a lithium (I)-containing composition in the presence of a reducing agent,

c) suspending the product obtained in step b) in an aqueous or organic suspension medium to obtain a solid reduced material and a lithium (I)-containing solution and

d) separating the solid reduced material from the lithium (I)-containing solution.

Within the framework of the present invention, it has surprisingly been found that the reducing treatment can accumulate the lithium compounds contained in the composition in the suspension medium, whereas other components of the LIBs such as nickel, manganese and cobalt remain in the solid reduced material. The lithium(I)-containing solution and the reduced material can then be separated and reprocessed separately from one another. Therefore, the method according to the invention offers the possibility of separating lithium from the other components at the beginning of the recycling process, instead of carrying it along through the entire separation process of nickel, cobalt and manganese, as described in the state of the technology.

Within the framework of the present invention, a composition is understood to mean a lithium(I)-containing composition, unless stated otherwise.

Within the meaning of the present invention, reducing agent is understood to mean a substance or a compound, which can reduce other substances by donating electrons and is itself oxidized in the process, i.e. its oxidation number increases.

Within the framework of the present invention, element as well as the general designation lithium, nickel, cobalt, manganese, etc. are understood as the general generic designation, which includes the elements in all of their oxidation numbers occurring within the framework of the method according to the invention, unless otherwise stated. For example, the term "nickel" includes nickel in the oxidation state + III, as it occurs, for example, in $\text{Li}(\text{Ni}, \text{Co}, \text{Mn})\text{O}_2$, nickel in the oxidation state + II, as it occurs, for example, in NiO or $\text{Ni}(\text{OH})_2$ and Nickel in the oxidation state 0, as it is in the form of nickel metal.

In the method according to the invention, unlike conventional methods, no liquid phases in the form of slag and alloy melt are formed. Rather, the method according to the invention is characterized in that both the composition used as the starting material and the reduced material obtained are in the form of powder, which significantly simplifies their handling. Therefore, in a preferred embodiment, the composition and/or the reduced material, in particular the reduced material, is in the form of a powder, preferably with a particle size of less than 500 μm , preferably less than 250 μm , more preferably less than 200 μm , especially less than 100 μm , determined in accordance with ASTM B822.

Further, within the framework of the method according to the invention, the use of slag formers or fluxes, as used in conventional methods, can advantageously be dispensed with. A preferred embodiment is therefore characterized in that the method is carried out without the addition of slag formers and/or fluxes.

The method according to the invention is distinguished in particular by the fact that the lithium is separated off first. The elements nickel, cobalt, manganese and optionally aluminum are only subjected to further separation into groups and finally into pure compounds of the individual elements only after they have been separated from the lithium. Therefore, an embodiment is preferred, in which the lithium is separated off from the composition before separating the nickel, cobalt, manganese and optionally aluminum. The lithium is preferably separated off from a suspension, which contains at least one of the elements nickel, manganese and cobalt as solid components.

The method according to the invention was developed primarily for the recycling of LIBs, both from corresponding end-of-life batteries and from off-spec materials, by-products and waste from the actual battery production. Therefore, an embodiment is preferred, in which the composition of used LIBs, production waste and secondary yields arising in the production of LIBs, in particular in the production of the electrode materials, are obtained or consist of these.

In a further preferred embodiment, the composition is obtained from used LIBs. In a particularly preferred embodiment, the composition is lithium cathode materials, production waste from the production of lithium cathode materials and

production waste from the production of lithium batteries/accumulators, in particular lithium-ion/polymer batteries.

In a further preferred embodiment, the composition is black mass.

Within the framework of the present invention, black mass is understood to mean the fraction, that is obtained in the mechanical and possibly pyrolytic reprocessing of used LIBs, especially lithium batteries/accumulators, in particular lithium-ion/polymer batteries, waste from LIB production or raw material components and essentially contains the cathode materials, i.e. usually compounds of lithium with Co, Ni and/or manganese and their pyrolysis products, as well as graphite as anode material base. Typical compositions of the cathode materials are LiCo oxides (LCO), Li(Co/Ni) oxides (LCNO), Li(Ni/Co/Mn) oxides (LNCMO), Li(Ni/Co/Al) oxides (LNCAO), or Li(Ni/Al) oxides (LNAO) in the form of LiMO_2 layer structures with $M = \text{e.g. Ni, Co and/or Mn}$, optionally doped with Al, or Li(Ni/Mn) oxides in the form of LiM_2O_4 spinel structures or Li-metal phosphates LiMPO_4 ($M = \text{Fe, Mn, Co, Ni}$). Particularly common cathode materials are LCO (LiCoO_2), NMC ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ with $x + y + z = 1$), NCA (with $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ with $x + y + z = 1$, especially $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$) and LiMn_2O_4 as spinel and LFP (LiFePO_4), which has an olivine structure.

In a preferred embodiment, the composition contains lithium or at least one of its compounds in an amount of 1 to 20% by weight, preferably 2 to 20% by weight, more preferably 2 to 15% by weight, especially 3 to 15% by weight, based on the total weight of the composition. The lithium is preferably in the oxidation state + I in the composition.

In addition, an embodiment is also preferred, in which the composition has at least one of the other elements in addition to lithium:

- Aluminum, preferably in the oxidation state + III;
- Cobalt, preferably in the oxidation state + II and/or + III;
- Manganese, preferably in the oxidation state + II and/or + III;
- Nickel, preferably in the oxidation state + II and/or + III;

whereby the elements are present in the form of their oxides and/or in the form of mixed oxides among one another.

In a preferred embodiment, the composition has at least 1% by weight, preferably at least 3% by weight, more preferably at least 8% by weight, of cobalt, preferably in the oxidation state + III, based on the total weight of the composition.

In a preferred embodiment, the composition has at least 1% by weight, preferably at least 10% by weight, more preferably at least 15% by weight, of nickel, preferably in the oxidation state + III, based on the total weight of the composition.

In a preferred embodiment, the composition has at least 1% by weight, preferably at least 3% by weight, more preferably at least 8% by weight, of manganese, preferably in the oxidation state + III, based on the total weight of the composition.

In particular, the composition used according to the invention contains, or is obtained, preferably by pyrolysis, from, at least one of the compounds selected from the group consisting of LiMO_2 layer structures with preferably $M = \text{Ni, Co, Mn and/or Al}$, in particular LiCo oxides (LCO), Li(Ni/Co) oxides (LNCO), Li(Ni/Co/Mn) oxides (LNCMO), Li(Ni/Co/Al) oxides (LNCAO), Li(Ni/Al) oxides (LNAO), Li(Ni/Mn) oxides (LNMO), or LiM_2O_4 spinel structures with preferably $M = \text{Ni, Co and/or Mn}$, optionally with Al doping, or pure or doped LiFe phosphates, or any mixtures thereof.

The composition particularly preferably contains or is obtained from at least one of the compounds, which is selected from the group consisting of LCOs, in particular LiCoO_2 , NMCs, in particular $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ with $x + y + z = 1$, NCAs with $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ with $x + y + z = 1$, especially $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, as well as LiMn_2O_4 spinels and LFP, especially LiFePO_4 .

In a preferred embodiment, the composition also contains graphite, preferably in an amount of not more than 60% by weight, more preferably not more than

45% by weight, especially from 10 to 45% by weight, particularly preferably from 20 to 40% by weight, each based on the total weight of the composition.

In an alternatively preferred embodiment, the composition is essentially free of graphite, whereby the proportion of graphite in the composition is preferably less than 5% by weight, particularly preferably less than 2% by weight and in particular less than 1% by weight, each based on the total weight of the composition.

In the battery technology, there are a number of doping elements that, depending on the intended use, extend over various elements of the main and subgroups of the periodic system. Therefore, an embodiment is preferred, in which the composition also has doping elements, in particular those from the group of alkaline earth metals (magnesium, calcium, strontium, barium), scandium, yttrium, the titanium group (titanium, zirconium, hafnium), the vanadium group (vanadium, niobium, tantalum), the group of lanthanoids or combinations thereof.

According to the invention, it is provided that the composition is subjected to a washing step before the reductive treatment. In this way, not only can the electrolyte solution be removed, in particular, but it has also been found that the amount of recovered lithium can be increased by this upstream washing step. Therefore, an embodiment is particularly preferred in which the method according to the invention provides the following steps in the given order:

- a) washing a lithium (I)-containing composition, wherein said lithium(I)-containing composition is obtained from used lithium-ion batteries;
- b) heating the washed lithium (I)-containing composition in the presence of a reducing agent,
- c) suspending the product obtained in step b) in an aqueous or organic suspension medium to obtain a solid reduced material and a lithium (I)-containing solution and

d) separating the solid reduced material from the lithium (I)-containing solution.

Preferably, water or an aqueous solution is used as the washing medium for washing the lithium (I)-containing composition. Basic washing has proven particularly efficient. Therefore, preferably a basic aqueous solution is used, wherein the pH of the washing medium is preferably adjusted by adding a basically reacting inorganic compound, preferably alkali and/or alkaline earth hydroxides, and more preferably sodium hydroxide, lithium hydroxide, or ammonia.

The washing medium preferably has a pH of more than 5, more preferably the pH of the washing medium ranges from 5 to 14. The washing is preferably performed at a temperature of 10 to 120°C, more preferably 10 to 70°C.

In an also preferred embodiment, the washing is followed by a drying step, preferably at a temperature of 60 to 200°C, more preferably 80 to 150°C. In another preferred embodiment, the drying may be combined with said heating the lithium (I)-containing composition in the presence of a reducing agent in step b).

In a preferred embodiment, the washed composition is essentially free, preferably free, of fluorine-containing compounds and/or compounds of phosphorus. Preferably, the content of fluorine-containing compounds in the composition is less than 2% by weight, more preferably less than 1% by weight, especially less than 0.5% by weight, respectively based on the total weight of the composition. In a further preferred embodiment, the content of compounds of phosphorus in the composition is less than 0.2% by weight, preferably less than 0.1% by weight, respectively based on the total weight of the composition.

In a preferred embodiment, the composition is essentially free, preferably free, of non-aqueous aprotic solvents as usually employed in LIBs. Such solvents may be, for example, ethylene carbonate, dimethyl carbonate, or propylene carbonate. Preferably, the content of such compounds in the composition is less than 5% by weight, more preferably less than 2% by weight, especially less than

0.5% by weight, specifically less than 0.1% by weight, respectively based on the total weight of the composition.

Within the scope of the method according to the invention, the lithium (I)-containing composition may be subjected to further treatments, which may, for example, be performed before the washing step, subsequent to it, or may be combined with it. In this way, for example, electrolyte residues or graphite residues can be removed. The pretreatment is preferably heating, drying, crushing, grinding, sorting, sieving, classifying, oxidizing, sedimenting, floating, washing and filtering or combinations thereof.

In a further preferred embodiment, the pretreatment consists of an oxidative treatment. In particular, graphite contained in the composition can be removed in this way. Alternatively or additionally, graphite can also be separated from the composition by flotation and/or sedimentation. Therefore, a further embodiment is preferred, in which the method according to the invention includes a flotation and/or sedimentation, which are preferably performed before the washing, or may be combined with it. In this case, an embodiment is particularly preferred in which the sedimentation, i.e., the separation of the graphite and cathode active material, is performed by using a heavy liquid having a density that is between those of the graphite and cathode active material to be separated, wherein the cathode active material is sedimented, and the graphite can be skimmed from the surface of the heavy liquid. The heavy liquid is preferably selected from the group consisting of tungstate solutions.

The composition is preferably in the form of a powder. In order to achieve a desired particle size, the composition may be ground, preferably said grinding being performed before the washing step a) of the method according to the invention. Accordingly, an embodiment is preferred in which the composition is ground, preferably to a particle size of less than 200 μm , particularly preferably less than 100 μm , determined in accordance with ASTM B822.

Within the framework of the method according to the invention, the composition is heated in the presence of a reducing agent. The reduction is preferably carried out in an oven suitable for wet, dry or pre-dried materials. This oven is preferably a static or moving bed oven. One furnace selected from the group

consisting of rotary kilns, fluidized bed furnaces, shelf furnaces, roller hearth furnaces, tunnel furnaces, hearth furnaces, converters, pusher-type kilns and conveyor furnaces is particularly preferred as a suitable furnace for the thermal treatment.

In a preferred embodiment, the reduction is carried out in a rotary kiln.

In an alternatively preferred embodiment, the reduction is carried out in a fluidized bed furnace.

In an alternatively preferred embodiment, the reduction is carried out in a shelf furnace.

In an alternative preferred embodiment, the reduction is carried out in a roller hearth furnace.

In an alternatively preferred embodiment, the reduction is carried out in a conveyor furnace.

In an alternatively preferred embodiment, the reduction is carried out in a tunnel furnace.

In an alternatively preferred embodiment, the reduction is carried out in a hearth furnace.

In an alternatively preferred embodiment, the reduction is carried out in a converter.

The furnace can be operated continuously or in batch mode.

It has proven advantageous within the framework of the method according to the invention to carry out the reduction at no more than 1000°C. Therefore, an embodiment is preferred in which the reduction is carried out at temperatures from 300°C to 1200°C, preferably from 350°C to 600°C, more preferably from 350°C to 450°C.

In particular, gases with a reducing effect can be used as reducing agents. In a preferred embodiment, the reducing agent is selected from the group consisting of hydrogen, carbon monoxide, carbon, methane, SO_2 , NH_3 and chemically compatible mixtures thereof.

Hydrogen has proven to be particularly effective, so that an embodiment is particularly preferred, in which the reducing agent is hydrogen. The reduction may be performed in a hydrogen atmosphere, wherein the fraction of hydrogen is preferably from 0.1 to 100% by volume, based on the atmosphere. In a preferred embodiment, the atmosphere comprises at least 50% by volume, especially at least 80% by volume, specifically at least 90% by volume, of hydrogen, wherein the other gases contained are preferably those selected from the group consisting of nitrogen, argon, water vapor, carbon monoxide, carbon dioxide, and mixtures thereof. In a particularly preferred embodiment, step b) of the method according to the invention is carried out in a rotary kiln or shelf furnace with hydrogen as the reducing agent.

In a preferred embodiment, carbon monoxide (CO) is used as the reducing agent.

In a preferred embodiment, sulfur dioxide (SO_2) is used as the reducing agent.

In a preferred embodiment, ammonia (NH_3) is used as the reducing agent.

In a preferred embodiment, carbon is used as the reducing agent.

In a preferred embodiment, methane is used as the reducing agent.

In an alternatively preferred embodiment, the reducing agent is generated *in situ*. This is particularly preferred in cases where the composition contains graphite. In this way, for example, carbon monoxide can be generated *in situ* as a reducing agent by introducing oxygen.

By reducing the composition according to the invention, the lithium from the lithium compounds contained in the composition are effectively converted to compounds soluble in the suspension medium, while other components of the

LIBs, such as nickel, manganese and cobalt, remain as insoluble components in the solid reduced material.

In a next step, the product obtained after the reductive treatment in step b) of the method according to the invention is converted to a suspension, wherein an organic or aqueous suspension medium is used. In particular, alcohols are preferred as an organic suspension medium. More preferably, water is used.

According to the method of the invention, a solid reduced material and a lithium(I)-containing solution are obtained, which can be processed separately in the further process. Therefore, the method according to the invention further comprises a separation step in which a liquid phase containing dissolved lithium and a solid filtration residue are obtained.

Preferably, said separation step is a filtration, centrifugation, or a method based on sedimentation, in which a liquid phase containing lithium dissolved therein and a solid residue are obtained.

In a preferred embodiment, the solid reduced material contains one or more of the compounds that are selected from the group consisting of nickel metal, cobalt metal, Ni(II) compounds, Co(II) compounds and/or Mn(II) compounds, wherein additionally aluminum oxide and/or aluminum hydroxide can be included.

Therefore, the method according to the invention offers the advantage that the lithium compounds can be further processed separately from the remaining residue, so that relatively high concentrations of the lithium-containing compound can be achieved, whereby on the one hand, the recovery of the lithium can be operated very economically and on the other hand, the lithium is not dragged along through the entire subsequent method steps for cleaning and separating the residue.

In the following, the separate reprocessing of the liquid phase and the residue will be discussed in more detail.

i) Liquid phase

The lithium is preferably present in the liquid phase in the form of a water-soluble compound, in particular in a form selected from the group consisting of lithium hydroxide, lithium hydrogen carbonate and lithium sulfate.

Depending on the composition and method used, the liquid phase can contain aluminum compounds soluble in the liquid phase, in addition to the lithium compounds. Therefore, an embodiment is preferred, in which the liquid phase also contains aluminum compounds.

In a preferred embodiment, the liquid phase is subjected to a further treatment to isolate the lithium. The lithium is preferably extracted from the liquid phase by precipitation, preferably by means of carbonation. The carbonation is preferably carried out by reaction with Na_2CO_3 or CO_2 .

Any aluminum compounds present in the liquid phase are preferably precipitated in the form of aluminum hydroxide by adjusting the pH accordingly.

In a preferred embodiment, lithium and aluminum dissolved in the liquid phase are separated from one another by treatment with CO_2 .

In a preferred embodiment, the lithium is at least partially in the form of its hydroxide and any aluminum present as lithium aluminate. In these cases, lithium and aluminum are preferably separated by treating the liquid phase with CO_2 . In this way, if the method is carried out appropriately, the aluminum can be precipitated in the form of aluminum hydroxide in a first step, whereas the lithium remains in solution in the form of lithium hydrogen carbonate. This can then be isolated in a subsequent step in the form of lithium carbonate. Surprisingly, the separation could be carried out in this way without any significant losses of Li_2CO_3 being observed.

In an alternatively preferred embodiment, the lithium is at least partially in the form of a salt of a mineral acid, preferably as sulfate, and any aluminum present as $\text{Al}_2(\text{SO}_4)_3$. In these cases, the aluminum is preferably first precipitated as $\text{Al}(\text{OH})_3$ by partial neutralization or appropriate adjustment of the pH value, then separated off and washed and separated from the lithium in this way.

ii) Solid residue

In particular, the elements cobalt, nickel, manganese and possibly aluminum remain as solid residues. Therefore, an embodiment is preferred, in which the residue contains one or more of the elements selected from the group consisting of nickel, cobalt, manganese, their alloys, their oxides and their hydroxides and mixtures thereof, whereby the elements can also be in the form of mixed oxides or mixed hydroxides.

In order to isolate the elements remaining in the residue, in a preferred embodiment, the residue is subjected to further separation processes in order to separate it into its components. The further reprocessing depends on the form, in which the elements are present in the residue, whereby various methods can also be combined with one another. The expert is aware that the residue is not limited to the embodiments described below and that these are only intended to provide the expert with an advantageous teaching on how the elements nickel, cobalt, manganese and possibly aluminum remaining in the residue can be extracted.

In a preferred embodiment, the residue contains one or more of the elements selected from the group consisting of nickel, cobalt, manganese, their alloys, their oxides, their hydroxides or mixtures thereof.

In a preferred embodiment, the residue comprises the following:

- Nickel in the oxidation state + II and/or 0, particularly preferably in the oxidation state 0;
- Cobalt in the oxidation state + II and/or 0, particularly preferably in the oxidation state 0;
- Manganese in oxidation state + II
- if necessary, aluminum in the oxidation state + III.

In a further preferred embodiment, the residue preferably has less than 5% by weight of lithium, particularly preferably less than 1% by weight of lithium and in particular less than 0.5% by weight of lithium and very particularly less than 0.1% by weight of lithium, each based on the total weight of the residue.

In a particularly preferred embodiment, the residue contains or consists of nickel and cobalt in metallic form and manganese in the form of its oxide and/or hydroxide.

In a preferred embodiment, the residue is further processed with the help of at least one of the methods selected from the group consisting of treatment with mineral acids, magnetic separation methods, sedimentation, filtration, solvent extraction or pH-controlled precipitation.

In a preferred embodiment, the method according to the invention can dispense with a solid-solid separation step for the removal of nickel and/or cobalt from the filtering residue.

Further, it has proven advantageous to treat the residue with mineral acids. In this way, the elements can be brought into solution in the form of their corresponding salts and thus extracted. Mineral acids are preferably hydrochloric acid or sulfuric acid. Therefore, an embodiment is preferred, in which the filtration residue is treated with mineral acids. From the solution thus obtained, aluminum can be precipitated and separated in the form of its hydroxide by adjusting the pH accordingly, whereas the other elements nickel, cobalt and manganese remain in the solution. The remaining elements can then be separated e.g. by means of solvent extraction. Therefore, an embodiment is preferred, in which the residue is treated with a mineral acid, the solution obtained is preferably adjusted to a pH of 2 to 5, in particular 3 to 4, in order to precipitate aluminum in the form of its hydroxide, the precipitate obtained is separated off and the remaining liquid phase is subjected to a solvent extraction.

In an alternatively preferred embodiment, the liquid phase obtained is further treated with an oxidizing agent, preferably H_2O_2 , while observing the pH value. In this way, the manganese contained in the liquid phase can be separated, whereas the elements nickel and cobalt remain in solution. The elements nickel and cobalt remaining after separating the manganese can be separated in further steps and used to produce pure nickel and cobalt compounds or used to precipitate hydroxidic or carbonate precursors for the production of cathode material for lithium batteries, especially LIBs. Therefore, an embodiment is preferred, in which the residue is treated with a mineral acid, the solution

obtained is preferably adjusted to a pH of 2 to 5, in particular 3 to 4, in order to precipitate aluminum in the form of its hydroxide, the precipitate obtained is separated off and the remaining liquid phase is treated with an oxidizing agent, preferably H_2O_2 , while observing the pH value, in order to separate manganese, the precipitate obtained is separated off and the remaining liquid phase is further processed for further separation of nickel and cobalt.

For those cases, in which the elements nickel and cobalt are present in the residue in their metallic form and manganese and aluminum in the form of their oxides and/or hydroxides, it has proven advantageous to convert the residue into a preferably aqueous suspension, from which the elements nickel and cobalt are separated in metallic form from the Al- and Mn-containing solution. The elements manganese and aluminum remaining in solution can then be extracted using known methods. Therefore, an embodiment is preferred, in which the residue is converted into a preferably aqueous suspension by treatment with mineral acid and the elements nickel and cobalt remain in the filtering residue in a metallic form, and are subsequently dissolved completely in mineral acids under more strongly acidic conditions.

For those cases, in which aluminum is present in the residue in the form of its hydroxide, it has proven advantageous to extract the aluminum by alkali leaching and to separate off the metals. Therefore, an embodiment is preferred, in which the residue is subjected to an alkaline leaching.

The method according to the invention gives lithium in the form of its salt or hydroxide, which can be present in highly concentrated solutions. Correspondingly, the lithium obtained with the help of the method according to the invention can be fed into the material cycle for further use. Therefore, the present invention also provides the use of the lithium obtained according to the invention in the production of lithium batteries, rechargeable lithium batteries and lithium accumulators, rechargeable lithium-ion batteries and lithium-ion accumulators and/or rechargeable lithium polymer batteries and lithium polymer batteries and other lithium containing electrochemical cells.

The use of the lithium obtained with the help of the method according to the invention for the production of lithium metal and/or lithium oxide is also preferred.

Another preferred use of the lithium obtained with the help of the method according to the invention is its use in the glass and ceramic industry, as a melt additive in aluminum production and/or as a flux in enamel production as well as in the production of antidepressants.

The present invention is to be illustrated using the following examples and the following figures, whereby these are in no way to be understood as a restriction of the invention concept.

Within the scope of the following examples, the following analytical methods are employed as stated:

Inductively coupled plasma optical emission spectrometry: Li

Pyrohydrolysis, potentiometry: F

Combustion analysis: C

Carrier gas hot extraction: O

X-ray fluorescence analysis: Al, Co, Cu, Fe, Mn, Ni, P

Example 1:

1000 g of an exemplary metallurgical composition $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ in powder form were heated in a furnace in the presence of hydrogen. After the end of the reaction, the reduced material was cooled and suspended in water. The suspension was stirred, until lithium was completely in solution. The results are summarized in Table 1. For comparison, the "conventional" column on the right in Table 1 shows the values obtained with the help of a conventional method, as shown for example in Figure 1. The values in brackets denote the insoluble residue in each case, denoted by $M = \text{Ni}, \text{Co}, \text{Mn}$.

Table 1

according to the invention	conventional
----------------------------	--------------

Suspension	1.7 l	Suspension	-
Solid	379 g/l	Solid	-
(M)	346 g/l	(M)	-
LiOH	144 g/l	LiOH	-
Li ₂ SO ₄	-	Li ₂ SO ₄	-
Solution	1.6 l	Solution	10.4 l
MeSO ₄	-	MeSO ₄	154 g/l
(M)	-	(M)	58 g/l
LiOH	152 g/l	LiOH	-
Li ₂ SO ₄	-	Li ₂ SO ₄	55 g/l
(Li)	44.2 g/l	(Li)	6.9 g/l

The comparison in the table shows the clear improvement that the method according to the invention achieves over the conventional method. It can thus be clearly seen that, according to the conventional method, the transition metals are in solution together with lithium, whereas the method according to the invention allows the transition metals to be separated off in the form of solids, whereas lithium remains in solution. The table also shows the increased Li concentration achieved with the method according to the invention. In the conventional method, the Li concentration is lower by a factor of 6.4 and naturally the transition metals are present in a molar ratio of 1 to 1 in relation to Li, corresponding to the starting compound.

Example 2:

Step a): Washing

500 g of a black mass having the composition

Li (3.21% by weight), Al (1.02% by weight), Co (3.34% by weight), Cu (1.27% by weight), Fe (<0.1% by weight), Mn (1.95% by weight), Ni (20.6% by weight), P (0.24% by weight), F (2.41% by weight), O (19.2% by weight), C (46.84% by weight), based on the total weight of the composition,

was suspended in 1 liter of fully desalted water with stirring for 30 minutes, filtered, and dried at 80°C. In this way, 450.9 g of dried washed black mass was obtained.

Step b): Reductive treatment

40 g of the washed black mass obtained in step a) was placed in an alsint boat in a tube furnace, and after flushing with nitrogen, it was heated at 400°C under a flow of pure hydrogen (240 L/h). The temperature was kept constant for 360 minutes, and thereafter, the furnace was allowed to cool at room temperature under a flow of hydrogen to obtain 36.8 g of reduced material.

Step c): Suspending

With stirring, 20 g of the reduced material obtained in step b) was suspended in 50 ml of fully desalted water.

Step d): Separating the solid reduced material

The suspension obtained in step c) was filtered, and the filtering residue was washed several times with a total of 450 ml of fully desalted water until the washing solution was no longer alkaline. 17.8 g of dry residue and 500 ml of filtrate solution were obtained, in which the residue contained 0.16% by weight of Li, and the filtrate solution contained 0.67% by weight of Li. This corresponds to an Li recovery rate of 95.9%, based on the Li content in the residue, or 96.0% according to the Li content in the filtrate solution, based on the original amount of lithium in the black mass employed. The good agreement of the yields according to the two determination methods verifies the analytical methods employed, and thereby confirms the effective recovery of lithium by the method according to the invention.

Example 3:

Step a): Washing

400 g of a black mass having the composition

Li (3.21% by weight), Al (1.02% by weight), Co (3.34% by weight), Cu (1.27% by weight), Fe (<0.1% by weight), Mn (1.95% by weight), Ni (20.6% by weight), P (0.24% by weight), F (2.41% by weight), O (19.2% by weight), C (46.84% by weight), based on the total weight of the composition,

was heated at 50°C in 3.3 L of aqueous sodium hydroxide solution with a concentration of 200 g/L with stirring, and stirred for 2 hours at a constant temperature. Subsequently, the black mass was filtered, washed with 3.7 L of fully desalted water, and dried at 50°C. 366.1 g of dried washed black mass was obtained.

Step b): Reductive treatment

40 g of the washed black mass obtained in step a) was placed in an alsint boat in a tube furnace, and after flushing with nitrogen, it was heated at 400°C under a flow of pure hydrogen (240 L/h). The temperature was kept constant for 360 minutes, and thereafter, the furnace was allowed to cool at room temperature under a flow of hydrogen to obtain 37.1 g of product.

Step c): Suspending

With stirring, 36 g of the product obtained in step b) was suspended in 100 ml of fully desalted water.

Step d): Separating the solid reduced material

The suspension obtained in step c) was filtered, and the filtering residue was washed several times with a total of 1.9 L of fully desalted water until the washing solution was no longer alkaline. 32.4 g of dry residue and 2000 ml of filtrate solution were obtained, in which the residue contained 0.16% by weight of Li, and the filtrate solution contained 1.24 g of Li. This corresponds to an Li recovery rate of 95.9% according to the Li content in the residue, or 99.4% according to the Li content in the filtrate solution, based on the original amount of lithium in the black mass employed. The good agreement of the yields according to the different determination methods verifies the analytical methods

employed, and thereby confirms the effective recovery of lithium by the method according to the invention.

Example 4 (Comparative Example):

Step a): Washing

40 g of a black mass having the composition

Li (3.21% by weight), Al (1.02% by weight), Co (3.34% by weight), Cu (1.27% by weight), Fe (<0.1% by weight), Mn (1.95% by weight), Ni (20.6% by weight), P (0.24% by weight), F (2.41% by weight), O (19.2% by weight), C (46.84% by weight), based on the total weight of the composition,

was heated under reducing conditions without previous washing.

Thus, the black mass was placed in an alsint boat in a tube furnace, and after flushing with nitrogen, it was heated at 400°C under a flow of pure hydrogen (240 L/h). The temperature was kept constant for 360 minutes, and thereafter, the furnace was allowed to cool at room temperature under a flow of hydrogen to obtain 34.5 g of product.

With stirring, 20 g of this product obtained in step b) was suspended in 50 ml of fully desalted water, and the suspension obtained was filtered, and the filtering residue was washed several times with a total of 450 ml of fully desalted water until the washing solution was no longer alkaline. 18.1 g of dry residue and 500 ml of filtrate solution were obtained, in which the residue contained 1.08% by weight of Li, and the filtrate solution contained 0.52 g of Li. This corresponds to an Li recovery rate of 73.8% according to the Li content in the residue, or 69.6% according to the Li content in the filtrate solution, based on the original amount of lithium in the black mass employed. The good agreement of the yields verifies the analytical methods employed.

As shown by a comparison of the data from Examples 2 and 3 according to the invention with those of Comparative Example 4, the yield of recovered lithium from the battery waste could be significantly increased by the method according

to the invention. Thus, the method according to the invention is an effective means for processing used LIBs, allowing the valuable raw materials to be recycled in a sustainable cycle of valuable materials.

Description of the figures:

Figure 1 shows the schematic sequence of a conventional separation method, as it is used in the reprocessing of battery waste, in particular for the recovery of the elements cobalt, nickel, manganese and lithium. First, a metallurgical composition is brought into solution by acidic digestion with H_2SO_4 and the elements are precipitated one after the other. As can be seen in the overview, the elements cobalt and nickel are extracted in a joint precipitation, followed by manganese and lithium. The method has the disadvantage that lithium is separated off as the last element and is thus present as an interfering element in the previous precipitations.

Figure 2 shows the schematic sequence of a conventional separation method, as it is used in the reprocessing of battery waste, in particular for the recovery of the elements cobalt, nickel, manganese and lithium. First, a metallurgical composition is brought into solution by acid digestion with H_2SO_4 and the elements manganese, cobalt and nickel are separated by successive solvent extractions. Here, lithium is also extracted from the residue of the previous reactions, which leads to a significant loss in yield.

Figure 3 shows a schematic overview of an exemplary embodiment of the method according to the invention, in which an exemplary composition is heated in a furnace in the presence of hydrogen as the reducing agent. The reduced material is cooled and suspended in water. Filtration of the solid gives a residue I, which contains nickel, cobalt and manganese, and a filtrate I, which contains the dissolved LiOH . This is precipitated in the form of its carbonate by adding CO_2 . After separating the lithium, the further processing and separation of nickel, cobalt and manganese can take place without the disruptive effects of lithium.

The method according to the invention, as described in figure 3, offers various starting points, at which the valuable materials can be returned to the material cycle. For example, the lithium sulfate solution (filtrate II) can be electrolytically

broken down into LiOH lye and dilute sulfuric acid at a Li producer. The Li producer then extracts solid $\text{LiOH} \cdot \text{H}_2\text{O}$ from the LiOH lye for reuse in the production of cathode materials, in particular NCA cathode materials, and returns the sulfuric acid to the processors of transition metals. In this way, a sustainable cycle can be established.

Figure 4 shows an exemplary reprocessing of the aqueous filtrate obtained after leaching, in which lithium is present in the form of its hydroxide and aluminum in the form of lithium aluminate (filtrate I), as is obtained, for example, in the process described in Figure 4. The filtrate I is mixed with a suitable amount of CO_2 in deficit and the lithium carbonate formed is separated off (residue II), whereby a filtrate II is obtained. By adding more CO_2 , lithium hydroxide and lithium aluminate remaining in filtrate II are separated, whereby the addition is controlled in such a way that the aluminate is precipitated in the form of its hydroxide and then filtered off (residue III), whereas lithium remains in solution in the form of lithium hydrogen carbonate (filtrate III), which is converted into lithium carbonate by heating and thus precipitated. The resulting CO_2 can be fed back into the cycle. In this way, an efficient and simple separation of lithium and aluminum from the filtrate I is achieved.

Figure 5 shows an alternative extraction of aluminum and lithium from the filtrate I obtained according to the invention. The filtrate I is mixed with excess CO_2 , so that aluminum is precipitated in the form of its hydroxide (residue II), whereas the lithium remains in solution in the form of lithium hydrogen carbonate (filtrate II). After the aluminum hydroxide has been filtered off, the remaining solution can be heated, through which the lithium hydrogen carbonate changes into lithium carbonate and precipitates. The resulting CO_2 can be fed back into the cycle.

As clearly shown in the figures, the method according to the invention offers a simple and sustainable way of recovering the various valuable materials from the active materials of used batteries. Costly handling of liquid metallic phases and slag is therefore no longer necessary.

C l a i m s :

1. A method of recycling LIB materials, comprising the following steps:
 - a) washing a lithium(I)-containing composition, wherein said lithium(I)-containing composition is obtained from used lithium-ion batteries;
 - b) heating a lithium(I)-containing composition in the presence of a reducing agent,
 - c) suspending the product obtained in step a) in an aqueous or organic suspension medium to obtain a solid reduced material and a lithium(I)-containing solution and
 - c) separating the solid reduced material from the lithium(I)-containing solution.
2. The method according to claim 1, characterized in that water or an aqueous solution is used as the washing medium in step a).
3. The method according to claim 2, characterized in that the aqueous solution employed is a basic aqueous solution.
4. The method according to claim 3, characterized in that the pH of the washing medium is adjusted by adding a basically reacting inorganic compound, preferably alkali and/or alkaline earth hydroxides, and more preferably sodium hydroxide, lithium hydroxide, or ammonia.
5. The method according to at least one of the preceding claims, characterized in that step b) is carried out at a temperature of 300 to 1200°C, preferably 400 to 700°C.
6. The method according to at least one of the preceding claims, characterized in that the composition and/or the reduced material, in particular the reduced material, is in the form of a powder.

7. The method according to at least one of the preceding claims, characterized in that the composition is obtained from or consists of used LIBs, production waste and secondary yields that arise in the production of LIBs, in particular in the production of the electrode materials.
8. The method according to at least one of the preceding claims, characterized in that the composition is black mass.
9. The method according to at least one of the preceding claims, characterized in that the composition contains lithium in an amount of 1 to 20% by weight, preferably 2 to 20% by weight, more preferably 2 to 15% by weight, especially 3 to 15% by weight, based on the total weight of the composition.
10. The method according to at least one of the preceding claims, characterized in that the composition contains, or is obtained, preferably by pyrolysis, from, at least one of the compounds selected from the group consisting of LiMO_2 layer structures with preferably $M = \text{Ni, Co, Mn and/or Al}$, especially LiCo oxides (LCO), Li(Ni/Co) oxides (LNCO), Li(Ni/Co/Mn) oxides (LNCMO), Li(Ni/Co/Al) Oxides (LNCAO), Li(Ni/Al) oxides (LNAO), Li(Ni/Mn) oxides (LNMO) or LiM_2O_4 spinel structures with preferably $M = \text{Ni, Co and/or Mn}$, optionally with Al doping, or pure or doped LiFe phosphates, or any mixtures thereof.
11. The method according to at least one of the preceding claims, characterized in that the composition contains or is obtained from at least one of the compounds selected from the group consisting of LCOs, in particular LiCoO_2 , NMCs, in particular $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ with $x + y + z = 1$, NCAs with $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ with $x + y + z = 1$, especially $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ as well as LiMn_2O_4 spinels and LFP, especially LiFePO_4 .
12. The method according to at least one of the preceding claims, characterized in that the reduction is carried out in a furnace with a static or moving bed.

13. The method according to claim 12, characterized in that the reduction is carried out in a furnace selected from the group consisting of rotary kilns, fluidized bed furnaces, shelf furnaces, roller hearth furnaces, tunnel furnaces, hearth furnaces, pusher-type furnaces, converters and conveyor furnaces.
14. The method according to claim 12, characterized in that the reduction is carried out in a rotary kiln or shelf furnace.
15. The method according to at least one of the preceding claims, characterized in that the reducing agent is selected from the group consisting of hydrogen, carbon monoxide, carbon, methane, SO_2 , NH_3 or mixtures thereof.
16. The method according to claim 15, characterized in that the reducing agent is hydrogen.
17. The method according to claim 15, characterized in that the reducing agent is carbon monoxide (CO).
18. The method according to claim 15, characterized in that the reducing agent is sulfur dioxide (SO_2).
19. The method according to claim 15, characterized in that the reducing agent is ammonia (NH_3).
20. The method according to claim 15, characterized in that the reducing agent is carbon.
21. The method according to claim 15, characterized in that the reducing agent is methane.
22. The method according to at least one of the preceding claims, characterized in that the solid reduced material contains one or more of the compounds selected from the group consisting of nickel metal, cobalt metal, Ni(II) compounds, Co(II) compounds and/or Mn(II) compounds,

wherein aluminum oxide and/or aluminum hydroxide can be additionally included.

23. The method according to at least one of the preceding claims, characterized in that the separation step d) is a filtration, centrifugation or a method based on sedimentation, in which a liquid phase containing lithium dissolved therein and a solid residue are obtained.
24. The method according to claim 23, characterized in that the lithium is extracted from the liquid phase by precipitation, preferably by carbonation.
25. The method according to at least one of claims 23 or 24, characterized in that lithium and aluminum dissolved in the liquid phase are separated from one another by treatment with CO₂.
26. The method according to at least one of claims 23 to 25, characterized in that the solid residue contains one or more of the elements selected from the group consisting of nickel, cobalt, manganese, their alloys, their oxides, their hydroxides or mixtures of these, whereby the elements can also be present in the form of mixed oxides and mixed hydroxides.
27. The method according to at least one of claims 23 to 26, characterized in that the solid residue comprises the following:

nickel in the oxidation state + II and/or 0, preferably in the oxidation state 0;

cobalt in the oxidation state + II and/or 0, preferably in the oxidation state 0;

manganese in oxidation state + II;

if necessary, aluminum in the oxidation state + III.

28. The method according to at least one of claims 23 to 27, characterized in that the residue contains or consists of nickel and cobalt in metallic form and manganese in the form of its oxide and/or hydroxide.
29. The method according to at least one of claims 23 to 28, characterized in that the residue is further processed by means of at least one of the methods selected from the group consisting of treatment with mineral acids, magnetic separation methods, sedimentation, filtration, solvent extraction or pH-controlled precipitation.
30. The method according to claim 29, characterized in that the residue is treated with a mineral acid, the solution obtained is preferably adjusted to a pH of 2 to 5, in particular 3 to 4, in order to precipitate aluminum in the form of its hydroxide, the precipitate obtained is separated off and the remaining liquid phase is subjected to a solvent extraction.
31. The method according to claim 29, characterized in that the residue is treated with a mineral acid, the solution obtained is preferably adjusted to a pH of 2 to 5, in particular 3 to 4, in order to precipitate aluminum in the form of its hydroxide, the precipitate obtained is separated off and the liquid phase is treated with an oxidizing agent, preferably H_2O_2 , while maintaining the pH value, in order to separate manganese, the precipitate obtained is separated off and the liquid phase obtained is further processed for further separation of nickel and cobalt.
32. The method according to claim 23, characterized in that the residue is converted into a preferably aqueous suspension by treatment with mineral acid and the elements nickel and cobalt are separated off in the form of their metals.
33. The method according to claim 23, characterized in that the residue is subjected to alkaline leaching.
34. Use of lithium obtained by a method according to claim 1 in the production of lithium batteries, rechargeable lithium batteries and accumulators, rechargeable lithium-ion batteries and lithium-ion accumulators and/or

rechargeable lithium-polymer batteries and lithium-polymer accumulators and other lithium-containing electrochemical cells.

35. The use according to claim 34, characterized in that the lithium is used to produce lithium metal and/or lithium oxide.
36. The use according to at least one of claims 34 or 35, characterized in that the lithium is used in the glass and ceramic industry, as melt additive in aluminum production, as a flux in enamel production and/or in the production of antidepressants.