

Method for extracting residual metallic lithium from a set of one or more electrical energy storage cells

- [0001]** The present invention relates to a method for extracting residual lithium from an assembly of one or more electrical energy storage cells, in particular an electric battery, comprising residual solid metallic lithium, in a secure manner, as well as an integral method for extracting lithium from an assembly of one or more electrical energy storage cells, in particular an electric battery, comprising solid metallic lithium implementing said method for extracting residual lithium. It also relates to a unit for extracting residual lithium implementing said method for extracting residual lithium.
- [0002]** The field of the invention is the field of batteries based on solid lithium metal, and in particular Lithium-Metal-Polymer batteries, and even more particularly the field of recycling these batteries.
- Prior art**
- [0003]** Batteries based on solid metallic lithium, such as for example Lithium-Metal-Polymer batteries (LMP[®]), are known. Safer and more energy-dense, these batteries are increasingly used, for example, in the electric mobility and renewable energy storage sectors. As a result, the number of solid metallic lithium batteries has been rising steadily for several years, as has the number of batteries reaching end-of-life. However, even at the end of its life, a battery still comprises solid metallic lithium, which can be reused in other batteries or in other fields, and is of considerable value.
- [0004]** Today, the processing of end-of-life lithium batteries has become a regulatory obligation. The new European regulation on batteries calls for the recycling of at least 65% of the battery's weight by 2026, and the recovery of at least 50% of the lithium contained in these batteries.
- [0005]** Thus, recycling the valuable metals contained in these batteries, notably metallic lithium, has become economically attractive due to the soaring price of these metals. This price increase is due to strong demand from the battery market for these energy transition metals.
- [0006]** In this context, there are currently very few techniques for recovering metallic lithium from an all-solid-state battery (that is to say recovering the zero-oxidation lithium present in an all-solid-state battery, particularly in the negative electrode). These rare techniques provide for heating the battery to a temperature greater than or equal to the melting temperature of the metallic lithium to recover the lithium in the liquid state. Other techniques involve grinding the battery in a controlled atmosphere (CO₂, Ar, etc.) or under cryogenic conditions (for example -150°C) to prevent the metallic lithium from reacting during grinding. However, these techniques present a risk of battery fire, and the processing conditions are costly and restrictive from an industrial point of view. Other methods are described for separating various metals

(including lithium) present in positive electrode active materials of lithium-ion batteries. However, these methods are long and complex, and involve lithium-ion batteries which have very different structures/materials and behaviors from those of metallic lithium batteries. In particular, metallic lithium in all-solid-state batteries
 5 behaves differently from lithium ion in lithium-ion batteries.

[0007] Known from international application WO2020/161339 A1 is a method for recovering metallic lithium from an assembly of at least one electric battery cell comprising solid metallic lithium, said method comprising an extraction phase comprising the following steps: positioning said assembly in an orientation in which a
 10 first edge of said assembly, from which one or more negative electrodes protrude, is below a second edge of said assembly, opposite said first edge, and from which one or more positive electrodes protrude; and heating said assembly to a temperature, referred to as the processing temperature, greater than or equal to the melting temperature of said solid metallic lithium. Once the metallic lithium has melted, all or
 15 part of it drains naturally from each cell, under the effect of gravity.

[0008] This solution is not entirely satisfactory, however, as the extraction of metallic lithium is not optimized. In particular, the batteries obtained comprise lithium residues which remain stuck to the battery components at the end of this operation. As a result, the battery cells produced by this method cannot be processed by conventional battery
 20 recycling methods, and the cathode contained in the cells cannot be recovered.

[0009] One purpose of the present invention is to remedy this shortcoming.

[0010] Another aim of the invention is to provide a simple method for recovering residual solid metallic lithium in an assembly of at least one electrical energy storage cell.

25 **[0011]** Another aim of the invention is to provide an efficient method for recovering residual solid metallic lithium in an assembly of at least one electrical energy storage cell while limiting and controlling the effect of potential short-circuits during recycling.

[0012] Another aim of the invention is to provide a method for recovering residual solid metallic lithium in an assembly of at least one electrical energy storage cell, while
 30 guaranteeing recycling of all or part of the liquids and solids used in said method.

Disclosure of the invention

[0013] The invention has as its first object a method for extracting residual lithium from an assembly of one or more electrical energy storage cells comprising residual solid metallic lithium, said method comprising at least the following steps:

- 35 i) immersing said assembly in an aqueous composition,
 ii) separating the solids (and/or solid residues) from the aqueous composition,

- iii) adding at least one acid or precursor thereof capable of forming at least one lithium salt that is insoluble in the aqueous composition, and
- iv) recovering lithium salt.

[0014] The method according to the invention proposes to recover residual solid
 5 metallic lithium from an assembly of one or more electrical energy storage cells, by treating the cell(s) of said assembly individually or together.

[0015] In the present invention, "solid metallic lithium" or "solid lithium metal" means solid lithium in the zero oxidation state.

[0016] Furthermore, the method according to the invention proposes to recover, in the
 10 form of at least one salt, the residual solid metallic lithium from an assembly of one or more electrical storage cells, by immersing said assembly in an aqueous composition in order to dissolve the residual solid metallic lithium, then reacting said dissolved lithium with an acid to form a salt that is insoluble in the aqueous composition which can then be easily recovered.

[0017] Thus, the method according to the invention allows a simple and uncomplicated
 15 recovery of the residual solid metallic lithium.

[0018] Additionally, the method according to the invention offers reuse of the aqueous composition for one or more subsequent closed-loop residual solid metallic lithium recovery processes.

[0019] In the present application, each electrical energy storage cell of the assembly of
 20 one or more cells preferentially comprises residual solid metallic lithium.

[0020] In the present application, the expression "each cell comprises residual solid metallic lithium" means that each electrical energy storage cell implemented in step i) is delithiated at least in part.

[0021] According to a preferred embodiment, each electrical energy storage cell
 25 comprises:

- residual solid metallic lithium, in the form of a layer and/or debris, in particular from the negative electrode,
- a positive electrode, in particular in the form of a layer,
- 30 - a solid or quasi-solid electrolyte comprising a lithium salt, in particular in the form of a layer, said solid or quasi-solid electrolyte being arranged on the side of the positive electrode, and
- a current collector associated with and/or on the side of the positive electrode.

In other words, said assembly preferably comprises residual solid metallic lithium (from
 35 a plurality of films or layers of negative electrodes), and a plurality of films or layers of solid or quasi-solid electrolytes, positive electrodes, and current collectors.

[0022] In the present application, "residual solid metallic lithium" may comprise: residual pure metallic lithium; or at least one residual metallic lithium alloy; or a combination of residual pure metallic lithium and at least one residual metallic lithium alloy.

5 **[0023]** The assembly implemented in step i) may comprise a single or unique electrical energy storage cell or a plurality of electrical energy storage cells.

[0024] When the assembly comprises a plurality of cells (for example at least two cells), they are preferentially assembled, or in particular stacked, along an assembly direction. The assembly direction can be perpendicular to the plane formed by each
10 electrical energy storage cell.

[0025] The assembly implemented in step i) is preferably an electric battery, and particularly preferably one in which a plurality of cells are connected in series.

[0026] The assembly used in step i) comprises residual solid metallic lithium. According to a preferred embodiment of the invention, residual solid metallic lithium in the
15 assembly of one or more cells implemented in step i) represents at most 20% by mass, preferably at most 15% by mass, and particularly preferably at most about 10% by mass, with respect to the total mass of solid metallic lithium present in a non-delithiated assembly of one or more cells.

[0027] Step i): immersing said assembly in an aqueous composition

20 **[0028]** This step dissolves residual solid metallic lithium in the aqueous composition. This is also referred to as the residual solid metallic lithium dissolution step.

[0029] The whole assembly is immersed in the aqueous composition. In other words, the amount of aqueous composition is such that it completely covers said assembly. When the assembly comprises a plurality of electrical energy storage cells, all the cells
25 are preferably immersed in the aqueous composition.

[0030] The aqueous composition preferably comprises at least 90% by weight of water, and particularly preferably at least 95% by weight of water, with respect to the total weight of the aqueous composition. More particularly preferred, the aqueous composition consists solely of water.

30 **[0031]** The aqueous composition before immersion (that is to say before step i)) preferably has a neutral pH, that is to say ranging from 6.5 to 7.5, and particularly preferably is close to 7.

[0032] Step i) can be carried out using a vessel or soaking tank containing the aqueous composition. In step i), the assembly of one or more electrical storage cells is then in
35 the soaking tank or vessel, and covered by the aqueous composition.

[0033] Step i) preferentially takes at least 30 min, and preferably 1 to 2 hours. The duration of step i) will depend on the number of cells in the assembly and/or the size

of the cells, and in particular on the presence or absence of prior cell cutting and/or grinding steps as described below. Dissolution is favored when the size of the cells used in the aqueous composition is reduced.

[0034] The method may further comprise stirring the aqueous composition during step i). This improves delithiation kinetics. Mechanical stirring can also be used. Step i) can be carried out with one or more stirring means, such as a shaft equipped with a mechanical stirrer.

[0035] The method may further comprise heating the aqueous composition during step i). This improves delithiation kinetics. Step i) can be carried out with one or more heating means, such as a reactor equipped with a double wall through which a fluid circulates to heat the aqueous composition. Heating can be carried out at a temperature ranging from about 40°C to about 70°C. Heating can be started before the assembly is immersed, that is to say before step i).

[0036] Step i) preferentially leads to delamination of the solid or quasi-solid electrolyte, positive electrode and current collector film(s)/layer(s). In other words, this step i) also allows delamination of the layers or films of the individual cells forming the assembly. In this way, the layers or films of the individual cells forming the assembly are separated in step i).

[0037] Step ii) solid/liquid separation

[0038] Between steps i) and iii), the method comprises a step ii) for separating solids (and/or solid residues) from the aqueous composition. This step ii) avoids over-consumption of acid in the following step iii). Furthermore, at the end of step i), the positive electrode of the cell is not soluble in the aqueous composition and must be separated from the aqueous composition before step iii) in order to avoid contaminating the lithium salts with positive electrode residues and complicating the recovery of the lithium salts in step iv).

[0039] In step ii), solids (and/or solid residues) are separated from the aqueous composition, in particular solids (and/or solid residues) are removed or discharged from the soaking tank or vessel. Step ii) can be implemented with one or more means for separating solids and/or solid residues from the aqueous composition, such as filtration, for example using a filter press, or centrifugation, for example using a centrifuge.

[0040] Step ii) may comprise or be followed by a step ii') of washing said solids (and/or solid residues), preferably with water. Washing ii') is preferentially carried out above the aqueous composition, and in particular above the soaking tank or vessel. This improves the method's yield of recovered lithium salts. Alternatively, the washing step ii') can be carried out by injecting clean water during filtration, in particular into the filter press. Step ii') can therefore be concomitant with step ii).

- [0041]** Indeed, at the end of step i), the aqueous composition comprises particles and/or solid elements which are insoluble (referred to as solids and/or solid residues) in the aqueous composition (positive electrode active material, current collector, etc.). Step ii) then removes these solids. These solids are preferably positive electrode active materials and/or current collectors. In other words, in step ii), at least the positive electrode active materials and/or current collectors (also known as "black mass") are separated as solids from the aqueous composition. The resulting aqueous composition then comprises dissolved residual lithium and optionally one or more polymers of the dissolved electrolyte.
- 10 **[0042]** Step ii) (and step ii') if present) thus provides a solids-free aqueous composition, and ensures that all residual lithium is present in said aqueous composition.
- [0043]** Step iii): adding at least one acid or precursor thereof capable of forming at least one lithium salt that is insoluble in the aqueous composition
- 15 **[0044]** Step iii) involves reacting residual solid metallic lithium dissolved in the aqueous composition with said acid to form a lithium salt which is insoluble in the aqueous composition. This step iii) thus facilitates the subsequent lithium salt recovery step iv).
- [0045]** Preferably, the acid or one of its precursors is chosen from mineral acids, such as phosphoric acid or carbonic acid, carboxylic acids, such as acetic acid, and mixtures thereof.
- 20 **[0046]** In step i), immersing the assembly in the aqueous composition leads to dissolution of the lithium and an increase in the pH of the aqueous composition (which can reach a pH greater than or equal to 13). In step iii), the pH of the aqueous composition decreases. Preferably, the acid or one of its precursors is added in quantities sufficient to precipitate all the lithium present in the aqueous composition.
- 25 **[0047]** According to one preferred embodiment of the invention, the aqueous composition at the end of step iii) has a neutral pH, that is to say ranging from 6.4 to 7.6, and particularly preferably from 6.5 to 7.5, and more particularly preferably close to 7. This allows the aqueous composition to be reused for soaking a new assembly of cells. The aqueous composition can thus be used in a closed loop.
- 30 **[0048]** In step iii), the aqueous composition is analyzed, for example by ICP-AES, to measure the mass concentration of Li (in g/L). The mass concentration of Li in the aqueous composition is adjusted. It can range from 2 to 30 g/L (depending on the quantity of cells immersed), and preferably from 5 to 20 g/L.
- 35 **[0049]** The acid or its precursor is added to the aqueous composition at a rate of at least 10 g/L, and particularly preferably from 10 g/L to 500 g/L of aqueous composition (depending on the acid used).

[0050] Step iii) preferentially lasts at least 10 min, and preferably from 10 to 60 minutes. The duration of step iii) will depend on the amount of residual lithium to be reacted with the acid or its precursor, the acid used, the volume of the aqueous composition and/or the temperature of the mixture.

5 **[0051]** The method may further comprise stirring the aqueous composition during step iii). This improves the kinetics of lithium salt formation. Mechanical stirring can also be used. The stirring means may be those described for step i).

[0052] The method may further comprise heating the aqueous composition during step iii). This improves lithium salt formation kinetics and salt recovery yield. Heating
10 can be started before adding the acid or its precursor, that is to say before step iii). Heating can be carried out using a reactor as described for step i) above. In particular, heating reduces the solubility of Li salts in the aqueous composition, thereby improving the recovery yield of dissolved Li.

[0053] Heating can be carried out at a temperature ranging from about 50°C to about
15 100°C, and preferably between 70°C and 90°C.

[0054] At the end of step iii), the aqueous composition comprises at least one lithium salt which is insoluble therein. In other words, the lithium salt is in solid form in the aqueous composition (that is to say in the form of solid particles dispersed in the aqueous composition). The solid appearance can be detected visually or by a
20 spectroscopic method such as UV-Visible light absorption.

[0055] Step iv): recovering one or more lithium salts

[0056] Step iv) can be carried out by filtration or centrifugation. At the end of step iv), the lithium salts are separated from the aqueous composition.

[0057] Step iv) can be implemented with one or more solid/liquid separation means,
25 such as a filter press or centrifuge.

[0058] By virtue of steps i), ii), iii) and iv), it is possible to recover the residual solid metallic lithium initially present in the assembly of one or more cells, in the form of salts. Furthermore, at the end of step iv), the lithium salt(s) are separated from the aqueous composition, allowing the aqueous composition to be reused in a new process
30 for extracting residual solid metallic lithium, in particular in a new step i).

[0059] Step v): washing the lithium salts

[0060] The method may further comprise a step v) for washing the one or more lithium salts obtained in step iv). Rinsing or washing can be carried out with water. Washing is preferentially carried out above the aqueous composition, and in particular above the
35 soaking tank or vessel. Alternatively, the washing step v) can be carried out by injecting clean water during filtration, in particular into the filter press. In particular, step v) improves the purity of the lithium salts obtained.

[0061] Step vi): drying the lithium salts

[0062] The method may further comprise a step vi) for drying the one or more lithium salts obtained in step iv) or v). Drying can be carried out at a temperature ranging from about 60°C to about 100°C. Step vi) can be carried out with one or more means for drying lithium salts, such as an oven or a heating tunnel.

[0063] Steps a) and b): cutting and grinding cells prior to step i)

[0064] Prior to step i), the method can further comprise a step a) for cutting the assembly of one or more cells, preferably all the cells in the assembly. This reduces the lithium dissolution time in step i) and improves the subsequent step ii) of separating the solids from the aqueous composition. According to this embodiment, step i) is then carried out with an assembly of cut cell(s) or with one or more cut cells. Step a) can be implemented with one or more cutting means, such as a metal guillotine, a laser cutting machine, or an ultrasonic cutting machine. Cutting step a) is a dry cutting step.

[0065] Prior to step i), the method can further comprise a step b) for grinding the assembly of one or more cells, preferably all the cells in the assembly. This reduces the lithium dissolution time in step i) and improves the subsequent step ii) of separating the solids from the aqueous composition. According to this embodiment, step i) is then carried out with an assembly of ground cell(s) or with one or more ground cells. Step b) can be implemented with one or more grinding means, such as a jaw grinder or a disc grinder. The grinding means can be equipped with a cooling system to prevent the material from heating up during grinding, thereby reducing industrial risk. Grinding step b) is a dry grinding step.

[0066] Step b) is preferentially carried out after step a). According to this embodiment, step i) is then carried out with an assembly of cut and ground cell(s) or with one or more cut and ground cells.

[0067] Step c): oxidizing residual lithium from cells prior to step i)

[0068] Prior to step i), the method may further comprise a step c) of oxidizing residual lithium to lithium oxide (Li_2O). This avoids generating too much hydrogen in step i). In particular, step c) reduces the reactivity of the lithium prior to step i), thereby reducing the industrial risk.

[0069] Step c) can be carried out by heating the assembly of one or more cells, preferably to a temperature ranging from about 300°C to about 400°C. Step c) can be carried out with one or more heating means, such as an oven, a furnace or a heating tunnel.

[0070] Step c) can take from about 30 min to about 2 hours.

[0071] Step c) can be carried out without prior steps a) and/or b), or in conjunction with steps a) and/or b). Preferentially, step c) is carried out after a grinding step b), in particular to accelerate metallic lithium oxidation kinetics.

5 **[0072]** The method, and in particular steps i), i'), ii), ii'), iii) and iv), can be repeated with other assemblies of one or more cells, preferably with the aqueous composition from step iv) of the previous method. This means it can be recycled. The method is preferentially carried out at atmospheric pressure and in ambient air. In other words, inert atmosphere conditions are not required.

[0073] Step d): purifying the aqueous composition

10 **[0074]** The method may further comprise a step d) in which the aqueous composition comprising dissolved lithium is purified. In this way, all compounds soluble in the aqueous composition from step ii) or ii') are removed, except lithium. These soluble compounds include solid or quasi-solid electrolyte or its derivatives. In particular, at the end of step ii) or ii'), the solid or quasi-solid electrolyte is at least partly dissolved in the
15 aqueous composition. The result is an aqueous composition comprising the solid electrolyte or one of its derivatives, and residual lithium.

[0075] Step d) is preferably carried out by solid/liquid separation. Particularly preferably, step d) is carried out by hot filtration or hot centrifugation, and more particularly preferably at a temperature ranging from about 70°C to about 90°C. In step
20 d), the solid or quasi-solid electrolyte becomes insoluble in the aqueous composition when hot, and can be easily separated by filtration from the lithium which is still soluble in the aqueous composition. Step d) can be implemented with one or more solid/liquid separation means, such as a filter press or centrifuge.

25 **[0076]** Step d) avoids overconsumption of acid or one of its precursors in step iii), and also improves the purity of the salts obtained in step iv).

[0077] The method may further comprise, after step i) and before step ii), a step i') of adding at least one anti-foaming agent to the aqueous composition. Indeed, immersion step i) can lead to the formation of a thick foam, which in turn can lead to liquid overflow and necessitate stopping step i). The use of an anti-foaming agent prevents
30 this. Different types of anti-foaming agents can be used, such as alcohol and fatty acid-based anti-foaming agents like the anti-foaming agent marketed under the reference "RM 761" (manufactured by Karcher) or polydimethylsiloxane-based anti-foaming agents like the anti-foaming agents marketed under the references "CQ-232", "CQ-233", "CQ-234" (manufactured by NANHUI NEW MATERIAL CO., LTD).

35 **[0078]** The invention has as its second object a method for the integral extraction of lithium from an assembly of one or more electrical energy storage cells comprising solid metallic lithium, said method comprising:

A) a first method for extracting lithium from an assembly of one or more electrical energy storage cells, each cell comprising a negative electrode containing solid metallic lithium, a positive electrode, a solid or quasi-solid electrolyte, and optionally a current collector,

- 5 said assembly of one or more cells including a first edge from which the one or more negative electrodes of said one or more cells protrude and a second edge, opposite said first edge, and from which the one or more positive electrodes protrude, said method comprising an extraction phase comprising the following steps:
- positioning said assembly in an orientation in which one of said first and second
 - 10 edges is below the other one of said first and second edges, and
 - heating said assembly to a temperature, referred to as processing temperature, greater than or equal to the melting temperature of said solid metallic lithium,
- said first extraction method leading to an assembly of one or more electrical energy storage cells comprising residual solid metallic lithium, and
- 15 B) a second method for extracting residual lithium in accordance with the first object of the invention.

[0079] The first method according to A)

- [0080]** When the assembly comprises a plurality of cells (that is to say at least two cells), each cell comprises a positive electrode, a negative electrode containing solid
- 20 metallic lithium, a solid or quasi-solid electrolyte, and optionally a current collector, said assembly comprising a first edge from which the negative electrodes of said cells protrude and a second edge, opposite said first edge, and from which the positive electrodes protrude. In this embodiment, said first method preferentially further comprises a step for cutting the electrical connection between the positive electrodes
- 25 of at least two, and in particular all, of the cells of said assembly.

[0081] Each electrical energy storage cell preferentially comprises:

- a negative electrode containing solid metallic lithium, in particular in the form of a layer,
- a positive electrode, in particular in the form of a layer,
- 30 - a solid or quasi-solid electrolyte comprising a lithium salt, in particular in the form of a layer, said solid electrolyte being arranged between the positive electrode and the negative electrode, and
- a current collector associated with and/or on the side of the positive electrode.

- [0082]** In the first method according to A), the "solid metallic lithium" may comprise:
- 35 pure metallic lithium; or at least one metallic lithium alloy; or a combination of pure metallic lithium and at least one metallic lithium alloy.

[0083] The assembly used may comprise a single or unique electrical energy storage cell or a plurality of electrical energy storage cells, preferably assembled, or in particular stacked, along an assembly direction. The assembly direction can be perpendicular to the plane formed by each electrical energy storage cell.

- 5 **[0084]** According to a preferred embodiment of the invention, the assembly corresponds to an electric battery, and particularly preferably one in which the cells are connected in series.

- 10 **[0085]** The assembly used in the method according to A) comprises solid metallic lithium. According to a preferred embodiment of the invention, in the assembly of one or more cells used in the method according to A), solid metallic lithium represents at least 80% by mass, preferably at least 85% by mass, and particularly preferably at least about 90% by mass, with respect to the total mass of solid metallic lithium present in an assembly of one or more non-delithiated cells.

- 15 **[0086]** The first method according to A) removes the vast majority of solid metallic lithium from the assembly of one or more cells, leaving only residual solid metallic lithium. The second method according to B) is in line with the first object of the invention and allows all residual solid metallic lithium to be extracted.

- 20 **[0087]** When the “solid metallic lithium” comprises a combination of different forms of lithium, such as those indicated above, having different melting temperatures, then the heating step of the assembly of one or more cells is carried out at a processing temperature greater than or equal to:

- the lowest of said different melting temperatures; and
- preferentially, the highest of said different melting temperatures.

- 25 **[0088]** Thus, the first method according to A) proposes recovering solid metallic lithium from an assembly by heating said assembly to a processing temperature greater than or equal to the melting temperature of the solid metallic lithium. Once the lithium metal has melted, all or part of it drains naturally from each cell. Thus, the first method according to A) allows a simple and uncomplicated recovery of the vast majority of solid metallic lithium.

- 30 **[0089]** Additionally, the first method according to A) proposes a specific orientation of each cell, the latter being, at the very least, inclined. Such an orientation of each cell facilitates the flow of molten lithium out of the cell by gravity.

- 35 **[0090]** Furthermore, and above all, the first method according to A) preferentially provides for cutting the connection between the positive electrodes of at least two, more preferentially all, of the cells of the assembly. In other words, the cutting step makes it possible to break the electrical connection between the positive electrodes of the assembly. Thus, after the cutting step, the assembly comprises a plurality of cells

that are no longer electrically connected to each other, which reduces the reactivity of the assembly, and therefore the risk of the assembly catching fire when recovering the lithium.

5 **[0091]** The first edge can be characterized by the fact that it defines the side via which the lithium, once in the liquid state, must flow.

[0092] The first method according to A) can be implemented to process one or more cell assemblies, in particular a plurality of cell assemblies forming a battery pack and connected together in parallel within said battery pack.

10 **[0093]** At least two cell assemblies can be aligned side by side, without overlapping, for example in a direction parallel to the first edge.

[0094] Heating

[0095] According to one non-limiting embodiment, the processing temperature is greater than or equal to 180.5°C.

15 **[0096]** According to one embodiment, the processing temperature is less than or equal to a maximum temperature, for example of 300°C.

[0097] Heating can be carried out using hot plates or a heating cabinet.

[0098] Cutting

[0099] The cutting step can be performed:

- 20 - by cutting connection wires between the positive electrodes along a cutting line located at, and in particular at the limit of, the second edge, on the side of said electrical connection wires; or
- by cutting the cells along a cutting line located at, and in particular at the limit of, the second edge, on the side of said cells.

25 **[0100]** The first alternative allows solid metallic lithium to be retained in, or not removed from, the assembly when the electrical connections are cut, which makes it possible to improve the recovery yield of the lithium.

[0101] In this first alternative, the connection wires must be cut sufficiently close to the second edge so that after the cutting, there is no longer any contact between the different positive electrodes.

30 **[0102]** In the second alternative, in order to reduce the amount of lithium lost, the cut must be in the immediate vicinity of the second edge.

[0103] For example, the cutting can be carried out at a distance “d” from the second edge of less than or equal to 2 mm, or less than or equal to 1% of the size of the cells between the first and the second edges of the battery.

35 **[0104]** The cutting step can be carried out by guillotining.

[0105] In this case, the assembly is inserted into a guillotine of suitable size and power.

[0106] The cutting step can be performed before the start of the heating step or after the start of the heating step. In the latter case, preferentially, the cutting step can be carried out before solid metallic lithium begins to melt.

- 5 **[0107]** The cutting step can be performed before the positioning step, after the positioning step, or during the positioning step.

[0108] Electric charging

- 10 **[0109]** According to a particularly advantageous feature, the first method according to A) may further comprise, before the extraction phase, a step of electrically charging the assembly of one or more cells, said extraction phase being applied to said charged assembly.

- 15 **[0110]** By electrically charging the assembly of one or more cells, and carrying out the extraction phase on the electrically charged cells, it is possible to increase the lithium extraction yield. Indeed, the electrical charging of a cell makes it possible to displace the lithium ions toward the negative electrode, thereby increasing the amount of lithium that can be recovered.

[0111] Each cell can be charged individually, or by electrical charging of the assembly of one or more cells.

[0112] Compression

- 20 **[0113]** According to a particularly advantageous embodiment, the extraction phase may further comprise a step of compressing the assembly of one or more cells.

[0114] Thus, the molten lithium is forced to drain out of each cell, thereby increasing the amount of lithium recovered.

- 25 **[0115]** The compression step can be carried out continuously throughout the extraction phase, or discretely once or multiple times during the extraction phase. In the first case, each cell is subjected to compression, partially or completely, throughout the entire duration of the extraction phase. In the second case, the extraction phase includes moments when the assembly of one or more cells is not subjected to compression.

- 30 **[0116]** Advantageously, the compression step can apply compression to the surface of the assembly of one or more cells by sweeping the surface of the assembly of one or more cells from the second edge toward the first edge. Thus, the molten lithium is progressively brought/guided toward the first edge from which a or the negative electrode(s) protrude, thereby increasing the amount of lithium recovered and
35 reducing the risk of contact between the lithium and the one or more positive electrodes.

[0117] For example, the compression step can be performed by passing the assembly of one or more cells between two rollers, or by means of a compression roller that presses the assembly of one or more cells against a bearing surface.

5 **[0118]** Compression can be applied in successive passes, each pass sweeping the surface of the assembly of one or more cells starting from the second edge toward the first edge.

10 **[0119]** The space between the compression rollers, respectively between the compression roller and the bearing surface, may correspond to the thickness of the assembly of one or more cells minus the thickness of the layers of solid metallic lithium. This makes it possible to apply compression for as long as there is still solid lithium in the assembly of one or more cells.

[0120] The space between the two compression rollers, respectively between the compression roller and the bearing surface, can be reduced with each successive pass, so that compression is always being applied to the assembly of one or more cells.

15 **[0121]** The speed at which the battery passes between the compression rollers, respectively of the compression roller, and more generally the sweep speed, may be between a few mm to a few tens of mm, per second.

[0122] Removal of connectors and overflows

20 **[0123]** Additionally, the first method according to A) may comprise, before the extraction phase, a step of removing at least one electrical connector – also called a “crimp” – from the assembly of one or more cells. This facilitates the processing of the assembly of one or more cells.

25 **[0124]** Additionally, the first method according to A) may comprise, before the extraction phase, a step of removing any material overhanging at least one, and particularly each, edge of the assembly of one or more cells.

[0125] Positioning

[0126] According to a first version, the positioning step can position the assembly of one or more cells in an orientation in which the first edge of the assembly of one or more cells is below the second edge of the assembly of one or more cells.

30 **[0127]** Such an orientation of the assembly of one or more cells, and therefore of each cell of the assembly of one or more cells, makes it possible, on the one hand, to facilitate the flow of the molten lithium out of the cell by gravity and, on the other hand, to avoid contact between the molten lithium and the positive electrodes or the current collector of the positive electrode, such contact possibly causing an electrical
35 short-circuit or an electric arc, such a short-circuit possibly causing a fire.

[0128] According to a preferred embodiment of this first version, the positioning step can position the assembly of one or more cells vertically, with the first edge facing downward.

[0129] Thus, the flow of molten lithium out of each cell, by gravity, is improved.

5 **[0130]** In addition, the risk of contact between the molten lithium and the positive electrode(s) is reduced, or even eliminated.

[0131] Preferentially, in this first version, the step of heating the assembly of one or more cells can be carried out under inert gas. Thus, the method according to the invention reduces accident risks, in particular fire risks. In addition, the formation of
10 pollutants that can be generated by undesired, or even uncontrolled, physicochemical reactions during the lithium extraction is avoided.

[0132] According to a non-limiting embodiment, the inert gas can be, or comprise, any one of the following gases: helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn).

15 **[0133]** According to another embodiment of this first version, the step of heating the assembly of one or more cells can be carried out under vacuum.

[0134] According to another embodiment of this first version, the step of heating the assembly of one or more cells can be carried out in dry air, in particular containing less than 0.002% H₂O by mass.

20 **[0135]** According to a second version, the positioning step can position the assembly of one or more cells in an orientation in which the first edge of the assembly of one or more cells is above the second edge of the assembly of one or more cells. In this case, the extraction phase further comprises, before the heating step, a step of immersing the assembly of one or more cells in a liquid, referred to as processing liquid, that is
25 denser than the liquid lithium and electrically insulating.

[0136] This second version proposes a specific orientation of each cell, the latter being at least inclined, so that the first edge from which the one or more negative electrodes protrude is above the level of the second edge, opposite the first edge, from which the one or more positive electrodes protrude. Such an orientation of each cell makes it
30 possible, on the one hand, to facilitate the flow of molten lithium out of the cell by a density difference and, on the other hand, to avoid contact between the molten lithium and the positive electrodes or the current collectors of the positive electrodes, such contact possibly causing an electrical short-circuit, such a short-circuit possibly causing a fire. In addition, immersing the set of cell(s) in a liquid makes it possible to
35 improve the dissipation of heat energy from the cell, in particular during a short-circuit, and therefore to greatly limit the effect thereof.

[0137] In the present application, “density” refers to the ratio between the density of the liquid under consideration and the density of the water.

[0138] According to a preferred embodiment of this second version, the positioning step can position the assembly of one or more cells vertically, with the second edge
5 facing downward.

[0139] Thus, the flow of molten lithium out of each cell, caused by density difference, is improved.

[0140] In addition, the risk of contact between the molten lithium and the positive electrodes is reduced, or even eliminated.

10 **[0141]** Preferentially, the immersion step can be carried out by immersing the assembly of one or more cells completely in the processing liquid.

[0142] The liquid may be a natural or synthetic oil, comprising the following physicochemical properties:

- hydrophobic and non-reactive with respect to lithium,
- 15 - electrically insulating,
- having a density greater than that of lithium,
- thermally stable beyond the melting temperature of lithium, that is 180.5°C,
- a flash point, as well as a self-ignition point, as high as possible.

20 **[0143]** The invention has as its third object a unit for extracting residual lithium from an assembly of one or more electrical energy storage cells comprising residual solid metallic lithium, characterized in that it comprises:

- a tank for soaking the assembly of one or more cells in an aqueous composition;
- one or more means for separating the solids (and/or solid residues) from the
25 aqueous composition;
- a means for adding acid or one of its precursors to the aqueous composition; and
- one or more solid/liquid separation means for recovering the lithium salt(s).

30 **[0144]** The extraction unit according to the third object allows the method according to the first object of the invention to be implemented.

[0145] The means for adding acid or one of its precursors to the aqueous composition can be a membrane metering pump. This makes it possible to introduce a precise volume of the acid solution or its precursors, previously prepared in a tank, depending on the concentration of lithium present in the aqueous composition.

[0146] The solid/liquid separation means for recovering lithium salts can be as defined in the first object of the invention.

[0147] The residual lithium extraction unit may further comprise means for heating and/or stirring the aqueous composition as defined in the first object of the invention.

5 **[0148]** The residual lithium extraction unit may further comprise means for washing the lithium salts and/or means for washing the assembly of one or more cells to implement the washing steps described above of the method according to the first object of the invention.

10 **[0149]** The residual lithium extraction unit may further comprise one or more means for recovering the aqueous composition for reinjection into the soaking tank (in order to implement a new method in accordance with the first object of the invention). This allows the aqueous composition to be recycled in a closed circuit.

15 **[0150]** In general, the residual lithium extraction unit may comprise means configured to implement any combination of at least one of the features described in the first object of the invention, and which are not repeated here in detail for the sake of conciseness.

20 **[0151]** The invention has as its fourth object an integral installation for extracting lithium from an assembly of one or more electrical energy storage cells, each cell comprising a positive electrode, a negative electrode comprising solid metallic lithium, a solid or quasi-solid electrolyte, and optionally a current collector,

said assembly including a first edge from which the one or more negative electrodes of said one or more cells protrude and a second edge, opposite said first edge, and from which the one or more positive electrodes protrude,

said extraction installation comprising:

25 * a lithium extraction unit leading to an assembly of one or more cells comprising residual solid metallic lithium,

said lithium extraction unit containing:

- a means for positioning said assembly in an orientation in which one of said first and second edges is below the other one of said first and second edges; and

30 - a heating means configured to heat said assembly to a temperature, referred to as processing temperature, greater than or equal to the melting temperature of said solid metallic lithium, and

* a residual lithium extraction unit according to the third object of the invention.

35 **[0152]** Said lithium extraction unit may further comprise a means for cutting the electrical connection between the positive electrodes of at least two, and in particular all, of the cells of said assembly.

[0153] In general, the installation may comprise means configured to implement any combination of at least one of the features described in the second object of the invention, and which are not repeated here in detail for the sake of conciseness.

[0154] For example, the cutting means may comprise a guillotine.

5 **[0155]** In particular, the heating means may comprise an oven (heating chamber) or heating plates.

[0156] Advantageously, the oven can be filled with an inert gas, dry air, or evacuated, or even filled with a processing liquid denser than the liquid lithium.

10 **[0157]** Said lithium extraction unit may further comprise means for compressing said assembly.

[0158] The compression means may comprise at least one roller.

15 **[0159]** In particular, the compression means may comprise a single roller that compresses the assembly of one or more cells against a bearing surface. The bearing surface can be heated to accelerate the temperature rise of the assembly of one or more cells.

[0160] Alternatively, the compression means may comprise two rollers between which the assembly of one or more cells is passed.

[0161] In general, the compression means can be configured to apply continuous compression, throughout the extraction phase.

20 **[0162]** Alternatively, the compression means may be configured to apply compression on one or more separate occasions during the extraction phase. In this case, the extraction phase includes moments when the assembly of one or more cells is not subjected to compression.

25 **[0163]** Advantageously, the compression means can be configured to apply compression, of constant or variable value, gradually or by sweeping over the surface of the assembly of one or more cells, from the second edge to the first edge. Thus, the molten lithium is brought/guided gradually toward the first edge located in the low position, which increases the amount of lithium recovered and reduces the risk of contact between the lithium and the positive electrodes.

30 **[0164]** In the case of the use of one or two compression rollers, compression can be applied to the assembly by successive passes. Each pass applies compression by sweeping over the surface of the assembly, from the second edge to the first edge. At the end of each pass, the compression can be stopped, by separating the rollers or by separating the roller from the bearing surface, to return to the second edge in order to
35 restart a new pass.

[0165] The distance between the rollers, respectively between the compression roller and the bearing surface, can be reduced with each pass, and in particular between two successive passages.

[0166] Compression can be applied to at least two assemblies of one or more cells by the same compression means, namely an assembly of rollers, or a roller interacting with a bearing surface.

Description of figures and examples

[0167] Other benefits and features shall become evident upon examining the detailed description of entirely non-limiting embodiments, and from the appended drawings in which:

- Figure 1 is a schematic representation of a first example embodiment of a method according to the first object of the invention;
- Figure 2 is a schematic representation of a second example embodiment of the method according to the first object of the invention;
- Figure 3 is a schematic representation of an example embodiment of a method according to the second object of the invention.

[0168] It is clearly understood that the embodiments that will be described hereafter are by no means limiting. In particular, it is possible to imagine variants of the invention that comprise only a selection of the features disclosed hereafter, in isolation from the other features disclosed, if this selection of features is sufficient to confer a technical benefit or to differentiate the invention with respect to the prior art. This selection comprises at least one preferably functional feature that lacks structural details, or only has a portion of the structural details if that portion is only sufficient to confer a technical benefit or to differentiate the invention with respect to the prior state of the art.

[0169] In the figures, the same reference has been used for the features that are common to several figures.

[0170] The method according to the first object of the invention, shown in Figure 1, comprises a first step i), of immersing in an aqueous composition, preferably water, an assembly of one or more cells, each cell comprising residual solid metallic lithium, a positive electrode, a current collector associated with the positive electrode, and a solid or quasi-solid electrolyte. This step i) dissolves the residual solid metallic lithium in the aqueous composition. The method may further comprise a step i') of adding at least one anti-foaming agent to the aqueous composition. Step i') is as defined in the invention. Once dissolution is complete, a solid/liquid separation step ii) is carried out to separate the solids and solid residues from the aqueous composition. Solids and solid residues, for example, are removed or discharged from the aqueous composition.

- Step ii) may also comprise a step ii') of washing or rinsing said solids (or solid residues), preferably with water. Washing is preferentially carried out above the aqueous composition, and in particular above the soaking tank. This improves the recovered lithium salt yield of the method. Once the solids and solid residues have been removed
- 5 from the aqueous composition, an acid such as phosphoric acid or a stream of CO₂ (carbonic acid precursor) is added to the aqueous composition in step iii), so as to form one or more lithium salts which are insoluble in the aqueous composition. The next step iv) consists in recovering the lithium salts formed, by solid/liquid separation, preferably by filtration.
- 10 **[0171]** The method according to the first object of the invention, shown in Figure 2, comprises the aforementioned steps i), i'), ii), ii'), iii) and iv) as described above for Figure 1 and further comprises, prior to step i), any of steps a), b), c) or a combination of at least two of steps a), b), c). These steps are optional. According to Figure 2, an assembly of one or more cells, each cell comprising residual solid metallic lithium, a
- 15 positive electrode, a current collector associated with the positive electrode, and a solid or quasi-solid electrolyte, is cut according to a step a), so as to obtain lamellae or pieces of one or more cells and to improve the dissolution of lithium in the aqueous composition during step i). Step a) can be followed by a step b) in which the cut assembly is ground, so as to obtain a ground assembly of one or more cells and further
- 20 improve the dissolution of lithium in the aqueous composition in step i). Step b) can be followed by a step c) of heating the assembly to oxidize residual lithium. This step c) avoids generating too much hydrogen during step i). The method may further comprise step i') of adding at least one anti-foaming agent to the aqueous composition. Step i') is optional and is as defined in the invention.
- 25 **[0172]** The method shown in Figure 2 then comprises step i) as described for Figure 1, then optionally step i'), followed by solid/liquid separation step ii) and washing step ii') as described for Figure 1.
- [0173]** The aqueous composition obtained from steps ii) and ii') can be purified in step d) to remove all compounds which are soluble in the aqueous composition, except
- 30 lithium. This step d) is preferably carried out by solid/liquid separation, and more particularly by hot filtration. In step d), the solid or quasi-solid electrolyte and/or its derivatives become insoluble in the aqueous composition when hot, and can be easily separated from the lithium which is still soluble in the aqueous composition by filtration.
- 35 **[0174]** The method shown in Figure 2 then comprises steps iii) and iv) as described for Figure 1, optionally followed by a step v) for washing out the lithium salts. These can optionally be dried in step vi).
- [0175]** The method according to the second object of the invention, shown in Figure 3, comprises, prior to the method according to the first object of the invention (method

according to B)), shown in Figures 1 and 2, a method for extracting the vast majority of solid metallic lithium from an assembly of one or more cells, each cell comprising a negative electrode comprising solid metallic lithium, a positive electrode, optionally a current collector, and a solid or quasi-solid electrolyte (method according to A)). Such a method according to A) comprises an optional step, during which the electrical connectors, and in particular the current concentrators, also called “crimps”, of the battery are removed.

[0176] During a following, optional step, any overhanging material, and in particular solid metallic lithium, at each side edge of the assembly is removed.

[0177] Then, the method according to B) of the method according to the second object of the invention comprises a phase of extracting the metallic lithium from the cells of the assembly. The extraction phase comprises a step of positioning the assembly in an orientation in which the first edge from which the negative electrodes protrude is at a lower level than the second edge from which the positive electrodes and/or the collectors protrude. In particular, the step positions the assembly in a vertical orientation, that is to say parallel to the gravity vector, with the first edge from which the negative electrodes protrude facing downward. Preferentially, but without any limitation, the assembly is held in this orientation throughout the entire extraction phase.

[0178] The extraction phase further comprises a step of heating the assembly to a processing temperature greater than or equal to the melting temperature of the solid metallic lithium present in the assembly, for example 180.5°C. This temperature will cause the solid metallic lithium to melt and be extracted from each cell by flowing naturally under the effect of gravity. Preferentially, but in no way limiting, the assembly is kept at this temperature throughout the extraction phase. Advantageously, the heating step is carried out in a closed chamber filled with inert gas.

[0179] The extraction phase may further comprise an optional step of compressing the assembly in order to expel the molten lithium out of each cell of the assembly. The compression can be carried out continuously during all, or part, of the extraction phase. Alternatively, the compression step can be repeated on several separate occasions during the extraction phase. Preferentially, the compression step applies compression in a progressive manner, or by sweeping, over the surface of the battery, starting with the second edge from which the positive electrodes protrude and going toward the first edge from which the negative electrodes protrude.

[0180] The method comprises a step of cutting the electrical connection between the positive electrodes/current collectors of at least two, and in particular of all the cells of the assembly. Such a cutting step makes it possible to cut the electrical link between the positive electrodes of the cells of the assembly, thereby reducing the reactivity of the assembly. Thus, the risk of the assembly catching fire during the extraction phase is

reduced, so that the recovery of the solid metallic lithium can be carried out more reliably and with less risk.

[0181] In the example shown, the step of cutting the electrical connections is carried out before the extraction phase. Alternatively, the cutting step can be carried out during the extraction phase, before, during or after the positioning step, or before, during or after the heating step.

[0182] In addition, the invention is not limited to the embodiments described above, but can apply to solid or quasi-solid electrolyte assemblies or batteries comprising no polymer at the cathode. The invention can be applied to any battery having solid metallic lithium and a cathode that is stable up to the melting point temperature of the solid metallic lithium.

[0183] Example 1: preparation of an electric battery comprising residual solid metallic lithium

[0184] A Lithium Metal Polymer (LMP[®]) battery module has been dismantled and a battery cell has been removed for use in this example. Next, a Li melt extraction step was carried out according to the method as described in WO2023/036741 A2. The metallic lithium obtained was weighed. In this example, 91% of the metallic lithium initially present in the cell has been extracted. Residual solid metallic lithium remains trapped in the battery cell.

[0185] Example 2: extraction of residual lithium using a method in accordance with the invention

[0186] An electrical storage cell of the all-solid-state lithium battery type comprising residual lithium (about 10% by mass with respect to the total mass of lithium present in the initial battery) as prepared in Example 1 was immersed in a soaking tank comprising water (as an aqueous composition), so as to cover said battery with water (about 18 L of water). After about 12h of immersion in the aqueous composition (water), dissolution of the metallic lithium in the water is complete [step i)].

[0187] The tank water (soaking water or aqueous composition) was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma spectrometry (ICP-MS) to measure lithium concentration. The results obtained show that all the residual Li has been dissolved and recovered in the aqueous composition.

[0188] Step i) also leads to delamination of the electrolyte, positive electrode and current collector films. These solids are removed from the tank [step ii)] and rinsed with about 2 L of water above the tank [step ii')].

[0189] Then, about 2.25 g of phosphoric acid (H₃PO₄ 85%, Sigma Aldrich) was added with mechanical stirring to about 1 L of the aqueous composition as prepared above

including residual lithium and previously brought to 60°C [step iii)]. After 2 h of reaction, the aqueous composition is filtered to separate the Li salts from the aqueous composition [step iv)]. The lithium salts obtained are then dried at 100°C for 3 h [step vi)]. This produces a white powder.

5 **[0190]** Example 3: extraction of residual lithium using a method in accordance with the invention

[0191] Three electrical storage cells of the all-solid-state lithium battery type comprising residual lithium (about 10% by mass with respect to the total mass of lithium present in the initial battery) were immersed in a soaking tank comprising
10 water (as an aqueous composition), so as to cover said battery with water (about 37 L of water). After about 20 h of immersion in the water, dissolution of the metallic lithium in the water is complete [step i)].

[0192] The aqueous composition was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma spectrometry (ICP-
15 MS) to measure lithium concentration. The results obtained show that all the residual Li has been dissolved and recovered in aqueous composition. The results also show that the amount of lithium dissolved in the aqueous composition is proportional to the number of cells immersed in the aqueous composition.

[0193] Step i) also leads to delamination of the electrolyte, positive electrode and
20 current collector films. The solids are removed from the tank [step ii)] and rinsed with about 3 L of water above the tank [step ii')].

[0194] The resulting aqueous composition is heated to 95°C for 1 h so that the electrolyte or its polymer components become insoluble. The resulting composition is filtered to produce a purified aqueous composition [step d)].

[0195] Then, about 9 g of phosphoric acid (H_3PO_4 85%, Sigma Aldrich) was added with mechanical stirring to about 1 L of the aqueous composition as prepared above including residual lithium and previously brought to 60°C [step iii)]. After 2 h of
25 reaction, the aqueous composition is filtered to separate the Li salts from the aqueous composition [step iv)]. The lithium salts obtained are then dried at 100°C for 3 h [step
30 vi)]. This produces a white powder.

[0196] X-ray diffraction (XRD) analyses carried out on a sample of the white powder obtained show diffraction peaks corresponding to the Li_3PO_4 phase. No other crystallographic phase could be observed. This result indicates the formation of a product composed mainly of Li_3PO_4 .

[0197] The aqueous composition remaining after step iv) has a pH of 7.6. It can
35 therefore be reused in a new method according to the invention as the aqueous composition used in step i).

[0198] The solid residues recovered from step ii') are ground and analyzed by X-ray diffraction (XRD). Analysis results have shown that the solids are composed solely of LiFePO_4 , which is used as the positive electrode active material, and aluminum, which is used as the current collector. This result confirms that the solids separated from the aqueous composition at the end of step ii') are devoid of metallic lithium or its derivatives, such as lithium hydroxide, LiOH .

[0199] Example 4: Extraction of residual lithium using a method in accordance with the invention

[0200] Example 2 was reproduced using a stream of CO_2 in the aqueous composition instead of phosphoric acid. The passage of the CO_2 stream through the aqueous composition leads to the formation of H_2CO_3 carbonic acid and the precipitation of Li_2CO_3 salts. The recovery yield of Li_2CO_3 is improved by heating the solution before injecting CO_2 , due to the lower solubility in hot water of Li_2CO_3 .

[0201] The CO_2 stream is maintained until an aqueous composition with a pH of 7 is obtained.

[0202] Example 5: Extraction of residual lithium using a method in accordance with the invention

[0203] Example 2 was reproduced by performing a cutting step [step a)] prior to step i).

[0204] To do this, the cell was cut lengthwise into 5 strips. The 5 strips are then placed in a tank containing about 18 L of water (as the aqueous composition) [step i)]. After just 2 h, the dissolution of the metallic lithium is complete and the films are totally delaminated. The other steps are identical to those described in Example 2.

[0205] Cutting out the cell reduces the dissolution time of the residual Li.

[0206] Of course, the number of strips is just an example, as dissolution time was improved regardless of the number of strips. It is also possible to cut the one or more cells into other shapes (for example pieces).

[0207] Example 6: Separation of active material from current collector

[0208] The solids obtained in Example 3, containing LiFePO_4 and aluminum, were used: about 700 g of the solids was pre-milled using a Shini SG-1628N (2.2Kw) knife mill equipped with a 160 x 280 mm cutting chamber with 2 fixed blades and 3x4 staggered moving blades. Using a sizing grid, the final particle size is between 5 mm and 10 mm. The resulting powder is then passed through an ECS-40 eddy current separator. Two fractions were obtained, one rich in aluminum and the other containing mostly active matter, also known as Black Mass. The method according to the invention allows complete recycling of lithium, active material, current collector metal and the aqueous composition used in step i).

CLAIMS

- 1.A method for extracting residual lithium from an assembly of one or more electrical energy storage cells comprising residual solid metallic lithium, said method comprising
5 at least the following steps:
 - i) immersing said assembly in an aqueous composition,
 - ii) separating the solids from the aqueous composition, the solids being positive electrode active materials and/or current collectors,
 - iii) adding at least one acid or precursor thereof capable of forming at least one lithium
10 salt that is insoluble in the aqueous composition, and
 - iv) recovering lithium salt.
- 2.The method according to claim 1, characterized in that the aqueous composition comprises at least 90% by weight of water, with respect to the total weight of the aqueous composition.
- 15 3.The method according to claim 1 or 2, characterized in that the acid or one of its precursors is chosen from mineral acids, carboxylic acids, and mixtures thereof.
- 4.The method according to any one of the preceding claims, characterized in that the acid or one of its precursors is added to the aqueous composition at a rate of at least 10 g/L of aqueous composition.
- 20 5.The method according to any one of the preceding claims, characterized in that the aqueous composition at the end of step iii) has a neutral pH.
- 6.The method according to any one of the preceding claims, characterized in that step ii) comprises or is followed by a step ii') of washing said solids.
- 7.The method according to any one of the preceding claims, characterized in that prior
25 to step i), it further comprises a step a) for cutting the assembly of one or more cells.
- 8.The method according to any one of the preceding claims, characterized in that prior to step i), it further comprises a step b) for grinding the assembly of one or more cells.
- 9.The method according to any one of the preceding claims, characterized in that prior to step i), it further comprises a step c) for oxidizing residual lithium to lithium oxide.
- 30 10.The method according to any one of the preceding claims, characterized in that it further comprises a step d) during which the aqueous composition comprising dissolved lithium is purified.
- 11.A method for the integral extraction of lithium from an assembly of one or more electrical energy storage cells comprising solid metallic lithium, said method
35 comprising:

A) a first method for extracting lithium from an assembly of one or more electrical energy storage cells, each cell comprising a negative electrode containing solid metallic lithium, a positive electrode, a solid or quasi-solid electrolyte, and optionally a current collector,

- 5 said assembly of one or more cells including a first edge from which the one or more negative electrodes of said one or more cells protrude and a second edge, opposite said first edge, and from which the one or more positive electrodes protrude, said method comprising an extraction phase comprising the following steps:
- positioning said assembly in an orientation in which one of said first and second
 - 10 edges is below the other one of said first and second edges, and
 - heating said assembly to a temperature, referred to as processing temperature, greater than or equal to the melting temperature of said solid metallic lithium,
- said first extraction method leading to an assembly of one or more electrical energy storage cells comprising residual solid metallic lithium, and

- 15 B) a second method for extracting residual lithium as defined in any one of the preceding claims.

12. The method according to claim 11, characterized in that it further comprises a step of cutting the electrical connection between the positive electrodes of at least two, and in particular all, of the cells of said assembly.

- 20 13. A unit for extracting residual lithium from an assembly of one or more electrical energy storage cells comprising residual solid metallic lithium, characterized in that it comprises:

- a tank for soaking the assembly of one or more cells in an aqueous composition;
- 25 - one or more means for separating the solids from the aqueous composition;
- a means for adding acid or one of its precursors to the aqueous composition; and
- one or more solid/liquid separation means for recovering the lithium salt(s).

- 30 14. An integral installation for extracting lithium from an assembly of one or more electrical energy storage cells, each cell comprising a positive electrode, a negative electrode comprising solid metallic lithium, a solid or quasi-solid electrolyte, and optionally a current collector,

- said assembly including a first edge from which the one or more negative electrodes of said one or more cells protrude and a second edge, opposite said first edge, and from
- 35 which the one or more positive electrodes protrude,

said extraction installation comprising:

* a lithium extraction unit leading to an assembly of one or more cells comprising residual solid metallic lithium,

said lithium extraction unit containing:

- 5 - a means for positioning said assembly in an orientation in which one of said first and second edges is below the other one of said first and second edges; and
- a heating means configured to heat said assembly to a temperature, referred to as processing temperature, greater than or equal to the melting temperature of said solid metallic lithium, and
- 10 * a residual lithium extraction unit as defined in claim 13.