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METHODE DE NEUTRALISATION ET DE RECYCLAGE DE BATTERIES RECHARGEABLES DE POLYMERE DE METAL LITHIUM EPUISEES

A METHOD FOR NEUTRALIZING AND RECYCLING SPENT LITHIUM METAL POLYMER RECHARGEABLE BATTERIES

Abrégé/Abstract:
The invention relates to a method for the neutralization and the recycling of spent rechargeable lithium batteries, particularly lithium metal polymer batteries, comprising at least one negative electrode active material, a separator, an electrolyte, one positive electrode active material, a current collector and a cell casing. After mechanical dismantling of the casing, the method involves three distinct possible processes, i.e., digestion into a solvent, incineration, or molten salt oxidation. The three processes include the steps of mechanically dismantling the batteries to remove the metal casing and the electric hardware as scrap, lowering the temperature of the free electrochemical cells (ECs) below ambient temperature, and shredding the ECs into pieces while in cold state before further processing. The processes also include the further steps of digestion in a solvent, molten salt oxidation or incineration, during which the highly reactive and hazardous spent batteries are first of all reduced to inert materials exhibiting a low chemical reactivity. Afterwards, the processes involve collecting the solid, liquid and gaseous discharges from the reactor, dissolving the solid and liquid discharges with an appropriate solvent and absorbing the gaseous effluents with an alkaline solution, mixing the resultant wash streams, separating precipitates formed from the mixed stream and neutralizing the remaining solution. Finally, the last step consists in recovering efficiently, safely, and in a relatively economical manner the valuable by-products such as vanadium and lithium compounds for reuse in the manufacture of electrochemical cells.
ABSTRACT

The invention relates to a method for the neutralization and the recycling of spent rechargeable lithium batteries, particularly lithium metal polymer batteries, comprising at least one negative electrode active material, a separator, an electrolyte, one positive electrode active material, a current collector and a cell casing. After mechanical dismantling of the casing, the method involves three distinct possible processes, i.e., digestion into a solvent, incineration, or molten salt oxidation. The three processes include the steps of mechanically dismantling the batteries to remove the metal casing and the electric hardware as scrap, lowering the temperature of the free electrochemical cells (ECs) below ambient temperature, and shredding the ECs into pieces while in cold state before further processing. The processes also include the further steps of digestion in a solvent, molten salt oxidation or incineration, during which the highly reactive and hazardous spent batteries are first of all reduced to inert materials exhibiting a low chemical reactivity. Afterwards, the processes involve collecting the solid, liquid and gaseous discharges from the reactor, dissolving the solid and liquid discharges with an appropriate solvent and absorbing the gaseous effluents with an alkaline solution, mixing the resultant wash streams, separating precipitates formed from the mixed stream and neutralizing the remaining solution. Finally, the last step consists in recovering efficiently, safely, and in a relatively economical manner the valuable by-products such as vanadium and lithium compounds for reuse in the manufacture of electrochemical cells.
A METHOD FOR NEUTRALIZING AND RECYCLING SPENT LITHIUM METAL POLYMER RECHARGEABLE BATTERIES

BACKGROUND OF THE INVENTION

Despite the importance of strategic materials used into the fabrication of lithium secondary batteries, only few industrial processes were developed commercially to recycle specifically spent lithium batteries, both primary and secondary. Actually, only three major companies have developed commercially a recycling process for the neutralization and/or recovery of valuable by-products from spent lithium batteries. Today, the leading lithium batteries recycler is the U.S. company Toxco, Inc. based in Anaheim, California. Toxco began processing lithium batteries at its recovery plant located at Trail, British Columbia, Canada. Toxco operates a cryogenic process originally developed by its former president William J. McLaughlin [U.S. Pat. 5,345,033 (1994)] and which is capable to recycle ca. 500 tons/year of spent lithium batteries. A major part of these are high performance batteries used as back-up power sources by the US Army (e.g., torpedoes, missiles). Hence numerous chemicals are recycled together without selective sorting (e.g., Li/SO₂, Li/SOCl₂, Li-Ion, lithium thermal batteries, and lithium reserve batteries). Essentially, the TOXCO process involves reducing the reactivity by lowering the temperature using cryogenic liquids such as nitrogen or argon. The frozen batteries are then immersed under a large volume of aqueous caustic solution made of sodium hydroxide and sodium carbonate. In this bath, the still frozen battery case is crushed. Active cell materials such as lithium react to release hydrogen and heat. Under these harsh conditions, hydrogen ignites burning all flammable organic solvents. At the end of the process cobalt and lithium carbonate, and in a lesser extent, paper and plastics, carbon black, and metal scrap are also recovered as secondary by-
products. Lithium carbonate is purified by electrodialysis and sold by the subsidiary LithChem.

The second company is BDT Inc. (i.e., formerly Battery Destruction Technology) located at Clarence, NY. BDT is a firm specialized in the destruction of hazardous wastes, with a particular knowledge of spent lithium batteries. The current processing capacity is about 350 tons per year of both spent lithium batteries and lithium metallic scrap. The destruction process [U.S. Pat. 4,647,928 (1987)] consists in crushing the spent batteries under an alkaline aqueous solution of sodium hydroxide with a swing type hammer mill. The resulting sludge is clarified by sieving through a coarse screen, solid wastes are removed by filtration and recovered for disposal and landfilling, while the alkaline filtrate is pH adjusted and redirected to the mill.

The third company is Sony Electronics Inc. which has developed a process specifically devoted to recycling their own spent Li-Ion batteries used in electronic devices (i.e., laptop computers, camcorders, digital cameras, and cellular phones). The process which uses a calcination of spent cells is highly efficient owing to the cogeneration by burning electrolytes. It is capable of recovering the cobalt oxide with a sufficiently high quality to reuse the latter directly in the fabrication of new Li-Ion batteries, and the metallic scrap consists of secondary by-product (e.g., copper and stainless steel). This technology is well established and recycling of spent lithium-ion cells is today performed in Japan with a current processing capacity of 120-150 tons per year. An improvement to the existing process is performed with a pilot plant which is located in the US at Dothan, Alabama, with R&D current capacity of 150 kg per year. Finally, a recent process for the recycling of lithium cell materials was devised by the Japanese Company Canon [U.S. Pat. 5,882,811, (1999)], but no other information is available about
an existing commercial plant. Nevertheless, none of these processes were devoted to the specificity of lithium metal solid polymer electrolyte batteries for recovering both lithium and vanadium.

Lithium metal polymer batteries, designated under the common acronym LMPB, are promising rechargeable power sources especially developed by ARGOTECH Productions Inc. for :(1) automotive applications [i.e., hybrid electric vehicle (HEV), and fully electric vehicle (EV)], and (2) the stationary market [i.e., electric power utilities, telecommunications]. The basic electrochemical system of these secondary batteries is made of : (1) an ultra-thin lithium metal foil as anode, (2) a solid polymer electrolyte containing a lithium salt, (3) an insertion lithium vanadium oxide compounds as cathode, and (4) a carbon coated aluminum current collector. Owing to it thin film design, the elementary cell (EC) exhibits both high gravimetric (270 Wh/kg) and volumetric energy (415 Wh/kg) densities. However, owing to their content of strategic cell materials, high energy density, and elevated chemical reactivity, spent lithium metal polymer batteries represent hazardous wastes that could lead to major economical, safety, and environmental issues in the commercialization of large lithium polymer batteries. Therefore, a large commercialization plant must consider the recycling of these spent batteries in order to : (1) neutralize and deactivate these hazardous wastes (e.g., particularly Li metal, and V₂O₅), ensuring a maximum plant health and safety; (2) recycle all the strategic cell materials in order to recover efficiently and in an economical manner the valuable by-products for decreasing production costs and preserving natural resources from depletion, (3) and finally to avoid any release of hazardous materials into the environment in order to fit in both - Zero Emission - program such as that developed by CARB and federal and provincial environmental regulations.
Incineration Process

Freezing

The first step consists in cooling the mass of spent ECs below –20°C. The freezing step is necessarily required in order to diminish the chemical reactivity of hazardous cell components during handling.

Size reduction -

Due to the fact that active cell materials are tightly encapsulated in a polymeric film, the frozen ECs must encounter a comminution process in order to release the active materials and enhance their active surface area. In addition, due to the plastic nature of most of the cell materials, cryogenic shredding is the preferred technique among size reduction processes. Actually, the combination of a cryogenic fluid and a rotary cutting mill is intended (1) to harden the soft cell materials to render them brittle and easy to grind, and (2) to insure safe operating conditions by maintaining an inert atmosphere around cuttings. Cryogenic shredding is performed using a cutting mill with sharp knives made of tool steel or cemented carbides operating under a continuous flow of liquid argon. The cuttings produced are smaller than 5 mm diameter. Oversize cuttings are removed by sieving under argon and are recycled to the cutting mill. The resulting slurry (i.e., undersize cuttings + liquid argon) is continuously poured into an incineration vessel. When it is completely full, the reactor is then tightly closed and connected to a compressed air supply. Then, argon is recovered by evaporation while releasing a mass of shredded spent ECs at the bottom of the reactor.

Incineration -

Batch incineration is carried out in a vessel made of bulk heat resistant alloy (e.g., Hastelloy®-X, Inconel®-617, or Pyromet®-625). The reaction in the reactor is initiated by heating up the spent mass. After reaching 130°C, usually an exothermic and fast reaction takes place for few seconds with a peak temperature around 1200°C. Afterwards, the
temperature is maintained constant at 600°C during 8 hours. Note that
the elevated gross or high heating values (HHV) of spent ECs (i.e.,
ranging from 16 to 20 MJ/kg depending on the type) can be efficiently
used to recover heat by cogeneration. During combustion, the off-gases
produced leaving the reaction vessel are cooled by means of a tubular
shell heat exchanger and are directed through a dust collector (i.e., high
efficiency particulate filter, baghouses, or electrostatic separator) in order
to remove entirely any entrained particulates (i.e., Li₂O, Al₂O₃, V₂O₅).
Then the dust free gas is directed to a wet scrubber containing a spent
lime solution (Ca(OH)₂) for absorbing all the hazardous gaseous
effluents (i.e., CO₂, HF, and SO₂). These gases react to form a sludge of
harmless precipitates made of calcium carbonate (CaCO₃), calcium
fluoride (CaF₂), and calcium sulphate (CaSO₄). These solid compounds
could be easily removed by settling and drying, and used as by-products
or are ready for disposal and landfilling. Finally, the released gas passes
through a catalytic converter. The released-gas leaving the catalytic
converter is very clean.

Acid digestion -

After completion of the incineration steps, both the ashes and the
remaining solid residues are discharged from the bottom of the
incinerator and are introduced with collected dust and particulates into a
stirred digestion tank. Digestion is carried out in a glass lined steel
vessel. The digestion reaction is initiated by adding hot sulphuric acid
30%wt H₂SO₄ at 80°C. The ratio of H₂SO₄ to solid residues is chosen so
that the weight ratio of free H₂SO₄ to V₂O₅ in the solution is X (the so-
called ‘acid number’). The exothermic reaction wherein lithium sulphate
is formed increases the temperature to 110-120°C. Nevertheless, to
maintain a proper operating internal temperature (e.g., thermowell,
heating coil, jacketed walls) or external heating (i.e., plate heat
exchanger) is required. After complete dissolution of soluble by-products
(i.e., Al, Al₂O₃, Li₂O, V₂O₅) and completion of side reactions (i.e., gas evolution, and heat generation), the solution is pumped with a positive displacement Moyno or DELASCO pump and cooled to room temperature. Then, the remaining insoluble solids are removed by hydrocycloning or centrifugation and finally filtration using a filterpress equipment.

**Extraction of Vanadium**

The mother liquor and rinsing solutions that contain all the valuable vanadium and lithium are adjusted if necessary to pH below 1. Afterwards, a small amount of potassium chlorate, KClO₃ is carefully added to the heated solution (80°C) in order to oxidize all vanadium (IV) and (III) cations to pentavalent vanadium (V) giving at low pH a yellow solution made of vanadyl (V) sulphate (VO₂)₂SO₄. Then the liquor is concentrated to a molarity of vanadium(V) above 0.2 mol.dm⁻³. After cooling down the mother liquor to 20°C, aqueous ammonia 28 wt % NH₄OH is added until reaching pH = 2 where the flocculation of the hydrated red-brown precipitate of vanadium pentoxide (V₂O₅.250H₂O) occurs. The gelatinous precipitate is then separated by settling and filtration, carefully washed, dewatered, and dried at 200°C. In order to recover V₂O₅, the calcinate must be fired above the melting point of V₂O₅ (i.e., 660°C). The cooled black molten mass of pure V₂O₅ is then crushed and ground in a ball mill to produce a fine powder which passes a 200 mesh sieve, The oversize particles are recycled to the mill.

**Heavy Metals Removal**

The previous filtrate is mixed with washing solutions and adjusted to pH = 2 by adding conc. H₂SO₄. The traces of heavy metals (i.e., Cu²⁺, Sn²⁺) are removed by common cathodic electrodeposition achieved under galvanostatic conditions (50 mA/cm²) onto a copper cathode and using DSA®-O₂ as anodes for releasing oxygen.

**Aluminum Extraction**
The previous filtrate is mixed with washing solutions and concentrated by evaporation. Then, after cooling down the mother liquor to 20°C, aqueous ammonia 28 wt % NH₄OH is added until reaching pH = 5 where flocculation of the gelatinous aluminum hydroxide (Al(OH)₃) occurs. The precipitate is then separated by settling and filtration. The carefully washed, dewatered, dried precipitate is then calcinated and ready for disposal.

**Lithium Extraction**

The purified lithium sulphate liquor is mixed with washing solutions, concentrated by evaporation up to 650g/l Li₂SO₄, adjusted to pH = 8 by adding lithium hydroxide (LiOH), and warmed up to 100°C. Then ammonium carbonate (NH₄)₂CO₃ is added to precipitate lithium carbonate Li₂CO₃ which is separated by filtration. The precipitate is washed and dried. The remaining liquor containing ammonium sulphate is stored for disposal.

**Digestion Process**

**Freezing**

The first step consists in cooling the mass of spent ECs below -20°C. The freezing step is necessarily required in order to diminish the chemical reactivity of hazardous cell components during handling.

**Size reduction**

Since active cell materials are tightly encapsulated in a polymeric film, the frozen ECs must encounter a comminution process in order to release the active materials and enhanced their active surface area. In addition, due to the plastic nature of most of the cell materials, cryogenic shredding is the preferred technique among size reduction processes. Actually, the combination of a cryogenic fluid and a rotary cutting mill is intended (1) to harden the soft cell materials to render them brittle and easy to grind, and (2) to ensure safe operating conditions by maintaining an inert atmosphere around the cuttings. Cryogenic shredding is
performed using a cutting mill with sharp knives made of cemented carbides operating under a continuous flow of liquid argon. The cuttings produced are smaller than 5 mm diameter. Oversize cuttings are removed by sieving under argon and recycled to the cutting mill. The resulting slurry (i.e., undersize cuttings + liquid argon) is continuously poured into a digestion reaction vessel made of glass lined steel. The reactor is then tightly closed and connected to a compressed air supply. Then, argon is recovered by evaporation while releasing a mass of shredded ECs at the bottom of the reactor.

**Acid digestion**

Batch digestion is used. Digestion is carried out in a glass lined steel vessel equipped with an explosion proof stirrer. The digestion reaction is initiated by adding sulphuric acid 30 wt % H$_2$SO$_4$ at RT. The ratio of H$_2$SO$_4$ to spent ECs is chosen so that the weight ratios of free H$_2$SO$_4$ to Li and V$_2$O$_5$ in the solution are X and Y (the so-called ‘acid numbers’). The exothermic reaction of lithium metal with sulphuric acid increases the temperature of the bath to 110-120°C. Nevertheless, to maintain a proper operating temperature, internal (e.g., thermowell, coil, jacketed walls) or external heating (i.e., plate heat exchanger) is required.

Bubbling argon into the bath collect the hydrogen gas evolved during the digestion, and the gas mixture flow is directed to an acid mist collector followed by a burner equipped with a flame arrester. After complete dissolution of soluble by-products (i.e., Al, Li, and V$_2$O$_5$) and completion of side reactions (i.e., gas evolution, and heat generation), the sludge is pumped with a positive displacement Moyno or Delasco pump and cooled to room temperature. and after completion of side reactions (i.e., gas evolution, and heat generation), the solution is pumped with a positive displacement Moyno pump and cooled to room temperature. Then remaining insoluble solids are removed by hydrocycloning or
centrifugation and finally filtration using a filterpress equipment. The retentate is washed, dried, and landfilled.

**Extraction of Vanadium**

The mother liquor and rinsing solutions that contain all the valuable vanadium and lithium are adjusted if necessary to pH below 1. Afterwards, a small amount of potassium chlorate, KClO₃ is carefully added to the heated solution (80°) in order to oxidize all vanadium (IV) and (III) cations to pentavalent vanadium (V) giving at low pH a yellow solution made of vanadyl (V) sulphate (VO₂)₂SO₄. Then the liquor is concentrated to a molarity of vanadium(V) above 0.2 mol.dm⁻³. After cooling down the mother liquor to 20°C, aqueous ammonia 28 wt % NH₄OH is added until reaching pH = 2 at which flocculation of the hydrated red-brown precipitate of vanadium pentoxide (V₂O₅.250H₂O) occurs. The gelatinous precipitate is then separated by settling and filtration, carefully washed, dewatered, and dried at 200°C. In order to recover V₂O₅ the calcinate must be fired above the melting point of V₂O₅ (i.e., 660°C). The cooled black molten mass of pure V₂O₅ is then crushed and ground in a ball mill to produce a fine powder which passes through a 200 mesh sieve, oversize particles are recycled to the mill.

**Heavy Metals Removal**

The previous filtrate is mixed with washing solutions and adjusted to pH = 2 by adding conc. H₂SO₄. The traces of heavy metals (i.e., Cu²⁺, Sn²⁺) are removed by common cathodic electrodereposition achieved under galvanostatic condition (50 mA/cm²) onto a copper cathode and using DSA®-O₂ as anodes.

**Aluminum Extraction**

The previous filtrate is mixed with washing solutions and concentrated by evaporation. Then after cooling down the mother liquor to 20°C, aqueous ammonia 28 wt % NH₄OH is added until reaching pH = 5 where flocculation of the gelatinous aluminum hydroxide (Al(OH)₃)
occurs. The precipitate is then separated by settling and filtration. The carefully washed, dewatered, dried precipitate is then calcinated and ready for disposal.

**Lithium Extraction**

The purified lithium sulphate liquor is mixed with washing solutions and concentrated by evaporation up to 650g/l Li₂SO₄, adjusted to pH = 8 by adding lithium hydroxide (LiOH), and warmed to 100°C. Then ammonium carbonate (NH₄)₂CO₃ is added to precipitate lithium carbonate Li₂CO₃ which is separated by filtration. The precipitate is washed and dried. The remaining liquor containing ammonium sulphate is stored for disposal.

**Molten Carbonate Oxidation Process**

**Freezing**

The first step consists in cooling the mass of spent ECs below 20°C. The freezing step is necessarily required in order to diminish the chemical reactivity of hazardous cell components during handling.

**Size reduction**

Since active cell materials are tightly encapsulated in a polymeric film, the frozen ECs must encounter a comminution process in order to release the active materials and enhanced their active surface area. In addition, due to the plastic nature of most of the cell materials, cryogenic shredding is the preferred technique among size reduction processes. Actually, the combination of a cryogenic fluid and a rotary cutting mill is intended (1) to harden the soft cell materials to render them brittle and easy to grind, and (2) to ensure safe operating conditions by maintaining an inert atmosphere around the cuttings. Cryogenic shredding is performed using a cutting mill with sharp knives made of cemented carbides operating under a continuous flow of liquid argon. The cuttings produced are smaller than 5 mm diameter. Oversize cuttings are removed by sieving under argon and recycled to the cutting mill. The resulting
slurry (i.e., undersize cuttings + liquid argon) is continuously poured into a hopper. Then, argon is recovered by evaporation releasing a mass of shredded ECs at the bottom of the hopper.

**Molten Salt Oxidation**

Batch molten salt oxidation (MSO) is employed and performed in a reaction vessel made of corrosion and heat resistant alloy (e.g., Hastelloy®-X, Inconel®-617). The reaction is initiated by injecting the spent mass into a molten salt bath comprising a mixture of alkali carbonates (i.e., Na₂CO₃, K₂CO₃) at temperatures between 700-950°C. Usually an exothermic and fast reaction takes place for few seconds with a peak temperature around 1200°C. Afterwards, the temperature is maintained constant at 800°C during 8 hours. Note that the elevated gross or high heating values (HHV) of spent ECs (i.e., ranging from 16 to 20 MJ/kg depending on type) can be efficiently used to recover heat by cogeneration. During oxidation, the acid gases generated such as HF, CO₂, and SO₂, are scrubbed from waste and captured in the salt as fluorides, carbonates, and sulphates. Other off-gases leaving the reaction vessel (e.g., CO, NOₓ) are cooled by means of a tube-and-shell heat exchanger and directed through a dust collector (i.e., high efficiency particulate filter, baghouses, or electrostatic separator) in order to remove entirely any entrained particulates. Then the dusted off gas is directed to a wet scrubber. Finally, the off-gas passes through a catalytic converter. The off-gas leaving the catalytic converter is very clean.

**Acid digestion**

After completion of each molten oxidation steps, the bath is cooled and solidified. The cooled mass is then crushed inside the reactor by means of a jack hammer, and the resulting blocks are further ground in a gyratory crusher followed by ball milling. A powdered carbonate mass is introduced with collected dust and particulates into a stirred digestion tank. Digestion is carried out in a glass lined steel vessel. The
digestion reaction is initiated by adding hot sulphuric acid 30 wt % H$_2$SO$_4$ at 80°C. The ratio of H$_2$SO$_4$ to solid residues is chosen so that the weight ratio of free H$_2$SO$_4$ to V$_2$O$_5$ in the solution is X (the so-called ‘acid number’). The exothermic dissolution reaction of alkali carbonates with sulphuric acid increases the temperature to 110-120°C. Nevertheless, to maintain proper operating temperature, internal (e.g., thermowell, coil, jacketed wall) or external heating (i.e., plate heat exchanger) is required. After complete dissolution of soluble by-products (i.e., Al, Al$_2$O$_3$, Li$_2$O, V$_2$O$_5$) and completion of side reactions (i.e., carbon dioxide evolution, and heat generation), the solution is pumped with a positive displacement Moyno or Delasco pump and cooled to room temperature. Then remaining insoluble solids are removed by hydrocycloning or centrifugation and finally filtration using a filterpress equipment.

**Extraction of Vanadium**

The mother liquor and rinsing solutions that contain all the valuable vanadium and lithium are adjusted if necessary to pH below 1. Afterwards, a small amount of potassium chlorate, KClO$_3$ is carefully added to the heated solution (80°C) in order to oxidize all vanadium (IV) and (III) cations to pentavalent vanadium (V) giving at low pH a yellow solution made of vanadyl(V) sulphate (VO$_2$)$_2$SO$_4$. Then the liquor is concentrated to a molarity of vanadium(V) above 0.2 mol.dm$^{-3}$. After cooling down the mother liquor to 20°C, aqueous ammonia 28 wt % NH$_4$OH is added until reaching pH = 2 where flocculation of the hydrated red-brown precipitate of vanadium pentoxide (V$_2$O$_5$·2.5H$_2$O) occurs. The gelatinous precipitate is then separated by settling and filtration carefully washed, dewatered, and dried at 200°C. In order to recover V$_2$O$_5$ the calcinate must be fired above the melting point of V$_2$O$_5$ (i.e., 660°C). The cooled black molten mass of pure V$_2$O$_5$ is then crushed.
and ground in a ball mill to produce a fine powder which passes through a 200 mesh sieve, oversize particles are recycled to the mill.

**Heavy Metals Removal**

The previous filtrate is mixed with washing solutions and adjusted to pH = 2 by adding conc. H₂SO₄. The traces of heavy metals (i.e., Cu²⁺, Sn²⁺) are removed by common cathodic electrolysis achieved under galvanostatic condition (50 mA/cm²) onto a copper cathode and using DSA®-O₂ as anodes.

**Aluminum Extraction**

The previous filtrate is mixed with washing solutions and concentrated by evaporation. Then after cooling down the mother liquor to 20°C, aqueous ammonia 28 wt % NH₄OH is added until reaching pH = 5 where flocculation of gelatinous aluminum hydroxide (Al(OH)₃) occurs. The precipitate is then separated by settling and filtration. The carefully washed, dewatered, dried precipitate is then calcinated and ready for disposal.

**Lithium Extraction**

The purified lithium sulphate liquor is mixed with washing solutions and concentrated by evaporation up to 650g/l Li₂SO₄ and adjusted to pH = 8 by adding lithium hydroxide (LiOH), and warmed to 100°C. Then ammonium carbonate (NH₄)₂CO₃ is added to precipitate lithium carbonate Li₂CO₃ which is separated by filtration. The precipitate is washed and dried. The remaining liquor containing ammonium sulphate is stored for disposal.
CLAIMS

1. A method for neutralizing and recycling spent lithium metal polymer rechargeable batteries which comprises
   cooling a mass of said rechargeable batteries to a temperature below about - 20° C.
   shredding the mass of cooled rechargeable batteries under an inert atmosphere,
   batch incinerating the shredded material, cooling and scrubbing off gases produced,
   digesting ashes and solid residues obtained in the preceding step, in an acid, to give a mother liquor,
   extracting $V_2O_5$ from said mother liquor, and separating heavy metals and aluminum therefrom and
   precipitating lithium carbonate from remaining solution.

2. A method for neutralizing and recycling spent lithium metal polymer rechargeable batteries which comprises
   cooling a mass of said rechargeable batteries to a temperature below about - 20° C,
   shredding the mass of cooled rechargeable batteries under an inert atmosphere,
   digesting the shredded material in an acid, and separating a mixture of inert gas and hydrogen to give a mother liquor,
   extracting $V_2O_5$ from said mother liquor, and separating heavy metals and aluminum therefrom, and
   precipitating lithium carbonate from remaining solution.

3. A method for neutralizing and recycling spent lithium metal polymer rechargeable batteries which comprises
   cooling a mass of said rechargeable batteries to a temperature below about - 20° C,
shredding the mass of cooled rechargeable batteries under an inert atmosphere,

heating the shredded material at a temperature effective to cause oxidation of said shredded material,

removing gases produced during said oxidation,

digesting the shredded material from of gases produced during said oxidation in an acid to give a mother liquor and insoluble solids,

extracting $V_2O_5$ from said mother liquor and separating heavy metals therefrom and precipitating lithium carbonate from remaining solution.
LPB Recycling Digestion Route

1 - Mechanical Opening (i.e., case opening)
2 - Electrical Disconnection (i.e., busbars, electronic cards)
3 - Freezing (in liquid Ar at -185.5°C)
4 - Crushing (Knife Mill)
5 - Screening (Mesh No. 10)
6 - Explosion Proof Motor Drive
7 - Flame-Arrestor (Noa, Inc.)
8 - Coarse Screening
9 - Wash Rinse

By-products (e.g., devices, chips, copper wires, plastics)
Metal Scrap (e.g., stainless steel, copper, aluminum)

Spent Lithium Polymer Cells (i.e., ECs, Trims)

Diaphragm Pump

Prepared by François Cardarelli (Ph.D.)
Decontaminated Solution

Clear Solution

Precipitation/ Settling pH=2

Insoluble V₂O₅, 250 H₂O

Filtration (Fine)

Precipitate

Washing/ Rinsing

Dewatering

Drying (200°C)

Ammonia (i.e., NH₄OH)

Oxidation V(IV) to V(V) with KClO₃ at 80°C

Cathodic Deposits (i.e., Cu, Pb, Sn)

Evaporative Tower

Conc. Liquor

Ammonium Carbonate (i.e., (NH₄)₂CO₃)

Precipitation / Settling

Insoluble Li₂CO₃

Filtration (Fine)

Precipitate

Washing/ Rinsing

Dewatering

Ammonium Sulphate

Evaporative Tower

Conc. Liquor

Lithium, NH₄⁺, SO₄²⁻
LPB Recycling Incineration Flowsheet

1 - Mechanical Opening
(i.e., case opening)

2 - Electrical Disconnection
(i.e., busbars, electronic cards)

Spent Lithium
Polymer Cells
(i.e., ECs, Trims)

3 - Freezing
(in liquid Ar at -185.5°C)

4 - Crushing
(Knife Mill)

5 - Screening
(Mesh No. 10)

Crushed ECs

Incineration
(at 300°C in dry air)

Ashes and Residues
(i.e., Li₂O, V, V₂O₅, Al, Al₂O₃)

Dust Collector
(Baghouse, Electrostatic)

Flue gases (e.g., H₂O, CO₂,
NO₂, SO₂, HF) and dusts
(i.e., Li₂O, Al₂O₃, V₂O₅)

By-products
(e.g., devices, chips, copper,
wires, plastics)

Metal Scrap
(e.g., stainless steel,
copper, aluminum)

Sulphuric Acid
33.3%wt.
Storage Tank

oversize 2 mm

Diaphragm Pump

Prepared by François Cardarelli (Ph.D.)