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(71) Applicant *(for all designated States except US):* **AVESTOR** [CA/CA]; 1560, rue de Coulomb, Boucherville, Québec J4B 7Z7 (CA).

(72) Inventors; and
(75) Inventors/Applicants *(for US only):* **CARDARELLI,**

François [FR/CA]; 5872, rue Brossard, St-Léonard, Québec H1T 3R7 (CA). **DUBÉ, Jonathan** [CA/CA]; 125, rue Lemoyne est, App. 2, Longueuil, Québec J4H 1V1 (CA).

(74) Agents: **OGILVY RENAULT** et al.; 1981 McGill College Avenue, Suite 1600, Montreal, Québec H3A 2Y3 (CA).

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(54) Title: A METHOD FOR RECYCLING SPENT LITHIUM METAL POLYMER RECHARGEABLE BATTERIES AND RELATED MATERIALS
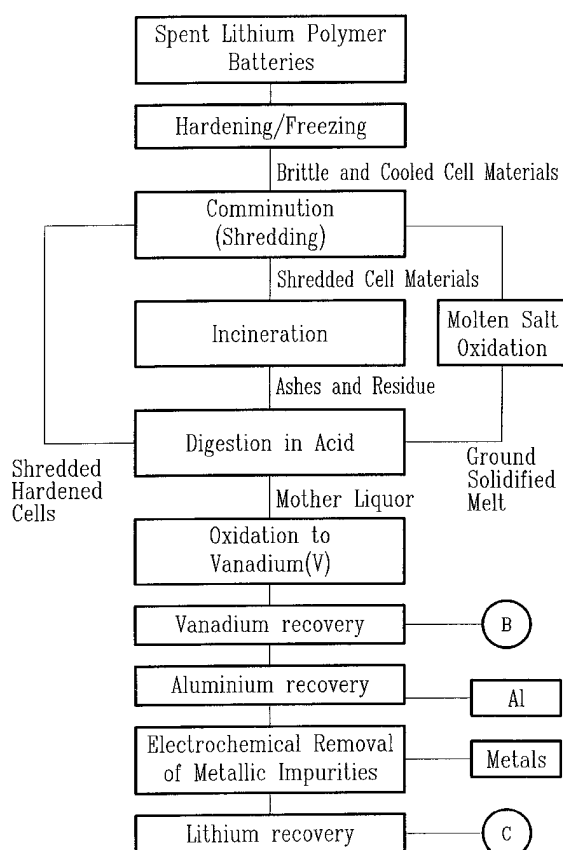
(57) Abstract: The method relates to a pyrometallurgical and hydrometallurgical process for the recovery and recycling of lithium and vanadium compounds from a material comprising spent rechargeable lithium batteries, particularly lithium metal gel and solid polymer electrolyte rechargeable batteries. The method involves providing a mass of the material, hardening it by cooling at a temperature below room temperature, comminuting the mass of cooled and hardened material, digesting with an acid its ashes obtained by incineration, or its solidified salts obtained by molten salt oxidation, or the comminuted mass itself, to give a mother liquor, extracting vanadium compounds from the mother liquor, separating heavy metals and aluminium therefrom, and precipitating lithium carbonate from the remaining solution.

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A METHOD FOR RECYCLING SPENT LITHIUM METAL POLYMER RECHARGEABLE BATTERIES AND RELATED MATERIALS

TECHNICAL FIELD

5   This invention relates to a method for recovering and recycling, by means of a pyrometallurgical and hydrometallurgical process, lithium and vanadium compounds from spent lithium metal solid and gel polymer rechargeable batteries. More particularly, the invention is concerned with the recovery of vanadium and lithium in the form of vanadium pentoxide

10   (V_2O_5) and lithium carbonate (Li_2CO_3) from lithium metal solid and gel polymer electrolyte batteries, scraps therefrom and products used to produce them.

BACKGROUND ART

       Despite the importance of strategic materials used into the

15   fabrication of lithium secondary batteries, only few industrial processes were developed commercially to recycle specifically spent lithium batteries, both primary and secondary. Actually, at present only three major companies have developed commercial recycling processes for the neutralization and/or recovery of valuable by-products from spent lithium

20   batteries. and one is always developing at the pilot scale. Today the leading lithium battery recycler in the U.S. is Toxco, Inc. which is based in Anaheim, California. Toxco processes lithium batteries at its recovery plant located at Trail, British Columbia, Canada. Toxco operates a cryogenic process that is described in U.S. Pat. 5,345,033 and U.S. Pat. 5,888,463

25   and which is capable of recycling about 500 tonnes per 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/SO_2, $Li/SOCl_2$, 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 cases are 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 a subsidiary of Toxco, LithChem International. However the TOXCO process is not specifically appropriate to the recycling of lithium metal solid and gel polymer electrolyte batteries because it focuses on alkaline solutions for dissolution and does not focus on the particular vanadium chemistry.

The second company is BDT Inc. formerly *Battery Destruction Technology* which is located in Clarence, NY. BDT specializes in the destruction of hazardous wastes, particularly spent lithium batteries. The current processing capacity is about 350 tonnes per year of both spent lithium batteries and lithium metallic scrap. The process involved which is described in U.S. Pat. 4,647,928 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. Unfortunately, this process which only intended to neutralize hazardous materials does not allow easy separation and recovery of valuable by-products such as lithium and vanadium compounds.

The third company is Sony Electronics Inc. which, in close collaboration with Sumitomo Metal Mining Company, has developed a process specifically devoted to recovering cobalt oxide from its own spent Li-Ion batteries used in electronic devices, such as laptop computers, camcorders, digital cameras, and cellular phones. The process involves the calcination of spent cells and utilizes the cogeneration resulting from burning electrolytes. It is capable of recovering 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, such as 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 tonnes per year. Improvement to this process is currently performed in a pilot plant that is located in the US at Dothan, Alabama, with a R&D current capacity of 150 kg per year. However, the Sony-Sumitomo process was specifically intended to recover only cobalt oxide from Lithium-Ion batteries and cannot be applied to the lithium metal solid and gel polymer technology. Finally, several recent processes for the recovery of both cathodic materials and lithium from cell materials used in Li-Ion secondary batteries were also developed but were not implemented industrially. Finally the four following novel processes designed by Canon (U.S. Pat. 5,882,811), Kabushiki Kaisha Toshiba (US 6,120,927), Tokyo Shibaura Electric Co. (US 6,261,712),. and Merck Patent GmbH (EP 1056146), are all related to reclamation and recycling of lithium ion batteries. In conclusion, none of the above processes are devoted specifically to the treatment of lithium metal gel and solid polymer electrolyte batteries for recovering both lithium and vanadium therefrom.

Lithium metal polymer batteries, designated under the common acronym LMPB, are promising rechargeable power sources especially developed by the Applicant for automotive applications, such as hybrid

electric vehicles (HEV), and fully electric vehicle (EV), and the stationary market, such as electric power utilities, telecommunications, etc. The basic electrochemical system of these secondary batteries is made of an anode consisting of an ultra-thin lithium metal foil, a solid copolymer electrolyte containing a lithium salt, a cathode comprising insertion lithium vanadium oxide compounds, and a carbon coated aluminium current collector. Owing to its thin film design, the electrochemical cell (EC) exhibits both high gravimetric (270 Wh/kg) and volumetric energy (415 Wh/kg) densities. An ultimate chemical analysis expressed in mass fraction of a typical electrochemical cell is presented in the following Table 1.

Chemical element	Mass fraction
Carbon	28.383 wt %
Oxygen	25.562 wt %
Vanadium	16.612 wt %
Aluminium	11.049 wt %
Lithium	10.222 wt %
Hydrogen	3.879 wt %
Fluorine	2.540 wt %
Sulphur	1.438 wt %
Nitrogen	0.315 wt %

Table 1 – Ultimate chemical composition of an EC

However, in view of 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 provide for the recycling of these spent batteries in order to neutralize and deactivate these hazardous wastes particularly lithium metal, and lithium vanadium oxide due to their chemical reactivity, toxicity and corrosiveness, thereby ensuring a maximum plant health and safety; it must

also 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 acute depletion. Finally such plant should avoid any release of hazardous materials into the

5   environment in order to fit in zero emission programs, developed by federal and government environmental agencies worldwide.

DISCLOSURE OF INVENTION

In accordance with the present invention there is provided a method of recovering and recycling lithium and vanadium compounds from a

10   material comprising spent lithium metal solid polymer rechargeable batteries, and/or scraps therefrom and/or products used to produce said batteries, which comprises comminuting a hardened and cooled mass of said material under an inert atmosphere, treating the comminuted hardened cooled mass to give a mother liquor containing dissolved vanadium salts

15   and heavy metals, extracting vanadium pentoxide (V_2O_5) from the mother liquor separating heavy metals, aluminium and other metallic impurities therefrom, and precipitating lithium carbonate from the remaining solution.

Preferably, the mass of material is comminuted under a flow of liquefied cryogenic gases such as liquid argon, liquid helium and liquid

20   nitrogen.

In accordance with a preferred embodiment, the hardened cooled mass is obtained by hardening the mass of the material by cooling same to a temperature below about 273 K, such as between about 77 K and about 273K, for example 85 K.

25   In accordance with another preferred embodiment, the method comprises batch incinerating the comminuted hardened cooled mass, and treating the comminuted hardened cooled mass to give the mother liquor. Preferably, the comminuted hardened cooled mass is cooled and the gases produced thereby are scrubbed off before treating the cooled mass to give

the mother liquor.

Preferably, the liquor is obtained by digesting ashes and solid residues obtained by batch incinerating the comminuted hardened cooled mass in an acid, such as HF, HCl, HBr, HI, HNO_3, H_3PO_4, H_2SO_4, $HClO_4$,
5   HCOOH, CF_3SO_3H, or mixtures thereof. The preferred acid is H_2SO_4.

According to another embodiment, the mother liquor is obtained by digesting the comminuted hardened cooled mass directly without prior treatment in an acid such as HF, HCl, HBr, HI, HNO_3, H_3PO_4, H_2SO_4, $HClO_4$, HCOOH, CF_3SO_3H, or mixtures thereof, H_2SO_4 being preferred,
10   and separating a mixture of inert gas and hydrogen to give the mother liquor.

In accordance with another embodiment, the method comprises heating the comminuted hardened cooled mass under conditions and at a temperature effective to cause oxidation of the comminuted material and
15   removing gases produced during the oxidation, before treating the cooled mass to give the mother liquor. Oxidation may be carried out by oxidizing and/or burning in a molten salt bath comprising a mixture of molten alkali and alkali-earth metals inorganic salts M_nX_m (with M = Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba and X = F^-, Cl^-, Br^-, I^-, SO_4^{2-}, NO_3^-, CO_3^{2-}, BO_3^{2-}, PO_4^{3-}),
20   the comminuted hardened cooled mass at a temperature effective to cause destruction of the material, for example at a temperature between 500 K and 2000 K, and removing gases produced during the chemical reaction, before treating the cooled mass to give the mother liquor.

In accordance with yet another embodiment, the mother liquor is
25   obtained by digesting the ground solidified salts from which the gases produced during oxidation have been removed, in an acid such as HF, HCl, HBr, HI, HNO_3, H_3PO_4, H_2SO_4, $HClO_4$, HCOOH, CF_3SO_3H, or mixtures thereof, H_2SO_4 being preferred, the mother liquor containing insoluble solids.

BRIEF DESCRIPTION OF DRAWINGS

The invention is illustrated by but is not limited to the annexed drawing which illustrates preferred embodiments of the invention, and in which

5   FIGURES 1A, 1B, and 1C are flow sheets representing various steps of the process according to the invention.

MODES OF CARRYING OUT THE INVENTION

The following description should be read in conjunction with the annexed drawings, which schematically summarize the steps of the various

10   preferred embodiments.

Generally speaking, the invention relates to a method for the recovery and recycling of lithium and vanadium compounds from spent rechargeable lithium batteries, particularly lithium metal gel and solid polymer electrolyte rechargeable batteries, comprising at least one negative

15   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 and providing a mass of cooled and hardened material, the method involves a novel recycling process, consisting of digesting with an acid its ashes obtained by incineration, or its solidified

20   salts obtained by molten salt extraction or the comminuted mass itself to give a mother liquor. The process includes the steps of mechanically dismantling the batteries to remove the metal casing and the electric hardware as scrap, hardening of the soft cell materials by lowering the temperature of the free electrochemical cells (ECs) below ambient

25   temperature., and comminuting the ECs into smaller pieces while in cold state before further processing. The process also includes the further steps of treating the ground cell materials as is or their ashes obtained by incineration, or their solid salts produced after molten salts oxidation (MSO). The ground cell materials, the ashes obtained after incineration, or

solidified salts resulting from molten salt oxidation are dissolved into an acid, during which the highly reactive and hazardous spent lithium batteries are first of all reduced to inert materials exhibiting a lower chemical reactivity. Afterwards, the process involves collecting the solid, liquid and

5   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

10 in a relatively economical manner the valuable by-products such as vanadium and lithium compounds for reuse in the manufacture of electrochemical cells.

The first step consists in hardening the soft materials such as lithium metal and polymer contained in the mass of spent ECs by cooling

15 preferably below 273 K. The freezing step is necessarily required in order to render the soft materials contained into the electrochemical cell such as metallic lithium and gel or solid polymers more brittle and to facilitate the comminution operation unit and also based on the Arrhenius law for the kinetics rate constant to diminish the chemical reactivity of hazardous cell

20 components during handling.

Due to the fact that active cell materials are tightly encapsulated in a polymeric film, the hardened and 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

25 cell materials, cryogenic shredding is the preferred technique among the numerous size reduction processes. For example, the combination of a cryogenic fluid with a rotary cutting mill will harden soft cell materials to render them brittle and easy to grind, and ensure safe operating conditions by maintaining an inert atmosphere around the rotary cutting mill.

Cryogenic shredding is normally performed using a cutting mill with sharp knives made of tool steel or hard cemented carbides preferably operating under a continuous flow of liquid argon. The cuttings produced are usually smaller than 1 millimeter. Oversize cuttings are removed by screening

5   under argon and are recycled to the cutting mill. The resulting slurry comprising undersize cuttings and liquid argon, is continuously poured into an incineration vessel. When it is completely full, the reactor is then closed and connected to a compressed air supply for batch incineration of the shredded mass. Then, argon is recovered by evaporation as is well known to

10   those skilled in the art while releasing a mass of cool shredded spent ECs at the bottom of the reactor.

Batch incineration is preferably carried out in a vessel made of bulk heat resistant alloy (e.g., Hastelloy®-X, Inconel®-617). The reaction in the reactor is initiated by heating up the spent mass. After reaching 130°C,

15   usually an exothermic and fast reaction takes place for few seconds with a peak temperature around 1500 K. Afterwards, the combustion or incineration which is conducted, usually takes place at a temperature above about 1000 K during 8 hours. The pressure is about 900 to about 1500 kPa absolute. For incineration, hot air, pure oxygen, or oxygen enriched

20   containing gas, is passed through the reactor and combustion is maintained at sufficiently high temperature (1000 K), with minimum oxygen content in flowing gas until substantially all the carbonaceous materials in the residues are incinerated leaving primarily free metals or metal oxides. It will be noted that the elevated gross or high heating value (HHV) of spent

25   electrochemical cells, ranging from 16 to 23 MJ/kg (determined according to the standard ASTM D240) depending on the type, can be efficiently used to recover heat by cogeneration. During combustion, the off-gases produced leaving the reaction vessel with excess air or oxygen are cooled by means of a heat exchanger and are directed through a dust collector, such as

baghouses, high efficiency particulate filters, or an electrostatic separator in order to remove entirely any entrained particulates, such as Li_2O, Al_2O_3 and V_2O_5. Then the dust free gas is directed to a wet scrubber containing a spent slacked lime solution (i.e., $Ca(OH)_2$) for absorbing all the hazardous

5   gaseous effluents, such as CO_2, HF, and SO_2. These gases react to form a sludge of harmless precipitates made of calcium carbonate ($CaCO_3$), calcium fluoride (CaF_2), and calcium sulphate di-hydrate ($CaSO_4 \cdot 2H_2O$) chemically identical with the three naturally occurring minerals (i.e., calcite, fluorspar, and gypsum) (See Cardarelli, F. - *Materials Handbook. A*

10   *Concise Desktop Reference.* - Springer Verlag, London, New York (2001), pages 395-478). These solid inorganic compounds can be easily removed by settling and drying, and used as by-products in industrial minerals applications or are ready for safe disposal and landfilling. Finally, the released gases passes through a highly efficient catalytic converter to

15   remove possible residual NO_x. The released-gases leaving the catalytic converter is very clean.

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

20   digestion tank. Digestion is carried out in a glass lined steel vessel or made of any other corrosion resistant materials (e.g., Alloy-20, Alloy 20 Cb, Hastelloy® C-276, zirconium and alloys, niobium or tantalum clad steel). The digestion reaction is initiated by adding hot inorganic or organic acids such as HF, HCl, HBr, HI, HNO_3, H_3PO_4, H_2SO_4, $HClO_4$, HCOOH,

25   CF_3SO_3H, or a mixture of them, but sulphuric acid 30wt % % H_2SO_4 is preferred. The dimensionless *operating acid ratio* (the so-called 'acid number'), i.e., ratio of mass of sulphuric acid to the mass of ashes and solid residues is selected in order to : (i) introduce an amount of acid at least equal but preferably greater than the stoichiometric amount required for

neutralizing all the cell active materials, and (ii) use the amount of acid required to absorb completely all the heat generated preventing any thermal runaways and maintaining the bath below the maximum temperature allowed in the process. The exothermic reaction wherein lithium sulphate is

5   formed increases temporarily the temperature to 110-120°C. Nevertheless, to maintain a proper operating internal temperature during two hours, internal heating, such as thermowell, heating coil, jacketed walls, or external circulating fluid heating is provided with a tubular or plate heat exchanger. After complete dissolution of soluble by-products containing for

10   example Al, Al_2O_3, Li_2O, V_2O_5 and completion of side reactions (i.e., gas evolution, and heat generation), the solution containing also sludge of insoluble material is pumped with a positive displacement pump and cooled to room temperature. Then, the remaining insoluble solids are removed by hydrocycloning or centrifugation and finally filtration using a filterpress

15   equipment. The filtration cake after washing and drying is landfilled.

The mother liquor and rinsing solutions that contain all the valuable vanadium and lithium are adjusted if necessary to pH below 1 with concentrated sulphuric acid. Afterwards, a small amount of an oxidizing chemical such as chlorine, oxygen, ozone, sulfur dioxide, Caro's acids

20   (H_2SO_5 and $H_2S_2O_8$) alkali-metals chlorates $MClO_3$, or permanganates $MMnO_4$ (with M=Li, Na, K), or hydrogen peroxide, is carefully added to the heated solution (80°C), or also an electrochemical oxidation is performed in order to oxidize entirely all vanadium (IV) and (III) cations to pentavalent vanadium (V) giving at low pH a yellow solution made of

25   vanadyl (V) sulphate $(VO_2)_2SO_4$. Oxidizing salts with lithium cation or hydrogen peroxide are preferred reagents because they do not introduce additional foreign elements and impurities in the solution. Actually these foreign cations or anions could render the ultimate recovery of sufficiently pure chemicals economically unfeasible. Then the liquor is concentrated to

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obtain a molarity of vanadium(V) above 200 mol.m^{-3}. After completion, cooling down the mother liquor to 293 K, a cold solution of lithium hydroxide, LiOH, or also aqueous ammonia 28 wt % NH_4OH is added until reaching pH = 2 where flocculation of the hydrated red-brown precipitate of

5   vanadium pentoxide ($V_2O_5.250H_2O$) occurs. The gelatinous precipitate is then separated by settling and filtration, it is carefully washed, dewatered, and dried at 200°C. In order to recover V_2O_5, the calcinate must be fired above the melting point of V_2O_5. The cooled black molten mass of pure V_2O_5 is then crushed and ground in a ball mill to produce a fine powder

10   passing a 200 Tyler mesh sieve. The oversize particles are recycled to the mill.

The previous filtrate is mixed with washing solutions and adjusted to pH = 2 by adding conc. H_2SO_4. The traces of heavy metals coming from solder, wiring (i.e., Cu^{2+}, Pb^{2+}, Sn^{2+}) are removed by common cathodic

15   electrodeposition onto a steel, nickel, copper, or zirconium cathode under galvanostatic conditions with a constant cathodic current density of 200 A.m^{-2} and using an efficient dimensionally stable anode for evolving oxygen in acidic media (i.e., DSA®-O_2) such as Ti/IrO_2, but preferably Nb/IrO_2 or Ta/IrO_2 (See Cardarelli, F. - *Materials Handbook. A Concise*

20   *Desktop Reference.* - Springer Verlag, London, New York (2001), pages 328-331). Other methods can also include a separation using solvent extraction or ion exchange resins techniques.

The purified solution obtained after removal of heavy metals is mixed with washing solutions and concentrated by evaporation. Then, after

25   cooling down the mother liquor to 20°C, a cold solution of lithium hydroxide, LiOH, or an aqueous ammonia 28 wt % NH_4OH is added until reaching pH about 5 where flocculation of the gelatinous aluminium 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 use or disposal.

The purified lithium sulphate liquor obtained after extracting aluminium therefrom is mixed with washing solutions, concentrated by evaporation up to 650 kg.m^{-3} Li$_2$SO$_4$, adjusted to pH about 8 by adding lithium hydroxide (LiOH), and warmed up to 100°C. Then carbon dioxide, CO$_2$ is bubbled, or ammonium carbonate (NH$_4$)$_2$CO$_3$ is added to precipitate lithium carbonate Li$_2$CO$_3$ which is separated by filtration. The precipitate is washed and dried. The remaining liquor containing ammonium sulphate is stored for disposal.

As an alternative embodiment, instead of pouring the slurry obtained by shredding with a rotary cutting mill in an incineration vessel it is continuously poured into a digestion reaction vessel made of glass lined steel or made of any other corrosion resistant materials (e.g., Alloy-20, Alloy 20Cb, Hastelloy® C-276, zirconium and alloys, niobium or tantalum clad steel). The reactor is then closed and argon is recovered by evaporation while releasing a mass of cool shredded ECs at the bottom of the reactor.

The digestion reaction is initiated by adding hot inorganic or organic acids such as HF, HCl, HBr, HI, HNO$_3$, H$_3$PO$_4$, H$_2$SO$_4$, HClO$_4$, HCOOH, CF$_3$SO$_3$H, or a mixture of them, but sulphuric acid 30wt % H$_2$SO$_4$ at 80°C is preferred. The dimensionless operating acid ratio (the so-called 'acid number'), i.e., ratio of mass of sulphuric acid to the mass of spent ECs is selected in order to : (i) introduce an amount of acid at least equal but preferably greater than the stoichiometric amount required for neutralizing all the cell active materials, and (ii) use the amount of acid required to absorb completely all the heat generated preventing any thermal runaways and maintaining the bath below the maximum temperature allowed in the process. The exothermic reaction wherein lithium sulphate is formed increases temporarily the temperature to 110-120°C. Nevertheless, to

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maintain a proper operating internal temperature during one hour, internal heating, such as thermowell, heating coil, jacketed walls, or external circulating fluid heating is provided, such as a tubular or plate heat exchanger are required. After complete dissolution of soluble by-products

5   containing for example Al, Al_2O_3, Li_2O, V_2O_5 and completion of side reactions (i.e., hydrogen gas evolution, and heat generation), the solution also containing sludge of insoluble material is pumped with a positive displacement pump such as a diaphragm, a Moyno® or Delasco pump and cooled to room temperature. Then, the remaining insoluble solids are

10   removed by hydrocycloning or centrifugation and finally filtration using a filterpress equipment. The filtration cake after washing and drying is landfilled.

Extraction of vanadium, removal of heavy metals, and aluminium and lithium extraction are carried out in the same manner as in the first

15   embodiment.

In the third embodiment, instead of batch incinerating the shredded mass, the latter is subject to batch oxidation performed in a molten salt bath.

Batch molten salt oxidation (MSO) is employed and performed in a

20   reaction vessel made of corrosion and heat resistant alloy (e.g., Hastelloy®-X, Inconel®-617, nickel or copper clad steel, titanium and alloys, zirconium and alloys). The reaction is initiated by injecting the spent shredded mass into a molten salt bath comprising a mixture of molten alkali and alkali-earth metals inorganic salts M_nX_m (with M = Li, Na, K, Rb, Cs,

25   Be, Mg, Ca, Sr, Ba and X = F^-, Cl^-, Br^-, I^-, SO_4^{2-}, NO_3^-, CO_3^{2-}, BO_3^{2-}, PO_4^{3-}) at temperatures between 500 K-2000 K, preferably 1000 K. Usually an exothermic and fast reaction takes place for few seconds with a peak temperature around 1500K. Afterwards, the temperature is maintained constant at 1000K during 8 hours. It will be noted that the elevated gross or

high heating values (HHV) of spent ECs ranging from 16 to 23 MJ/kg depending on type can be efficiently used to recover heat by cogeneration. During oxidation, the acid gases generated such as HF, CO_2, and SO_2, are scrubbed from waste and captured in the melt as fluoride, carbonate, and

5   sulphate salts. Other off-gases leaving the reaction vessel, such as CO, NO_x are cooled by means of a heat exchanger and directed through a dust collector, such as baghouses, high efficiency particulate filter, or electrostatic separator, in order to remove entirely any entrained particulates. Then the dusted off-gases are directed to a wet scrubber.

10   Finally, the off-gases pass through a catalytic converter. The off-gases leaving the catalytic converter is very clean.

After completion of each molten oxidation steps, the bath is cooled down and solidified. The solid salt mass is then crushed inside the reactor by means of a jack hammer, and the resulting blocks are further ground in a

15   gyratory crusher followed by ball milling. The powdered salty mass is introduced with collected dust and particulates into a stirred digestion tank. Digestion is carried out in a glass lined steel vessel or a vessel made of any other corrosion resistant materials (e.g., Alloy-20, Alloy 20 Cb, Hastelloy® C-276, titanium and alloys, zirconium and alloys, niobium or tantalum clad

20   steel). The digestion reaction is initiated by adding hot inorganic or organic acids such as HF, HCl, HBr, HI, HNO_3, H_3PO_4, H_2SO_4, $HClO_4$, HCOOH, CF_3SO_3H, or a mixture thereof, but sulphuric acid 30wt % H_2SO_4 at 80°C is preferred. In order, to maintain a proper operating internal temperature during one hour, internal heating, such as thermowell, heating coil, jacketed

25   walls, or external circulating fluid heating is provided with a tubular or plate heat exchanger. After complete dissolution of soluble by-products containing for example Al, Al_2O_3, Li_2O, V_2O_5 and completion of side reactions (i.e., gas evolution, and heat generation), the solution also containing sludge of insoluble material is pumped with a positive

displacement pump such as 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. The filtration cake after washing and drying are landfilled.

5   Extraction of vanadium, removal of heavy metals and extraction of aluminium and lithium are carried out similarly as in the first embodiment.

EXAMPLES

The invention will now be illustrated by the following non-limiting examples.

10   Example 1 (Incineration of ECs and Digestion of Ashes)

The first step consisted in rendering more brittle and easy to comminute a mass of one kilogram of spent electrochemical cells (ECs) having the chemical composition listed in Table 1. The electrochemical cells exhibited various states of charge. Hardening occurred by immersing

15·   the spent ECs directly into liquid argon maintained at 85 K. The dimensionless ratio, denoted r_{AE}, is the mass of liquid argon required per unit mass of ECs and it was calculated by the following equation listed below :

$$r_{AE} = \frac{m_{Ar}}{m_{EC}} = \frac{c_{PEC} \cdot (T_{EC} - T_F)}{c_{PAr} \cdot (T_F - T_{Ar})}$$

20   where m_{Ar} and m_{EC} are the masses expressed in kg of liquid argon and spent ECs respectively, c_{PAr} and c_{PEC} are the specific heat capacities expressed in $J.kg^{-1}.K^{-1}$ of liquid argon and spent ECs respectively, and T_{Ar}, T_{EC}, and T_F are temperatures expressed in kelvin of liquid argon, spent ECs, and the final temperature allowed after immersion respectively. Using liquid argon

25   at 85K and based on the following experimental parameters : (i) an average temperature T_E around 260K of spent ECs which are stored in refrigerated warehouses, (ii) the specific heat capacities of liquid argon c_{PAr} of 1058 $J.kg^{-1}.K^{-1}$ (Perry, R.H., and Green, D.W. - *Perry's Chemical*

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Engineers' Handbook 7th ed. - McGraw-Hill, New York (1997) page 2-217)
and c_{PEC} of spent ECs of 1619 J.kg^{-1}.K^{-1}, and (iii) the final allowed
temperature of the solid-liquid mixture maintained slightly below the
boiling point of argon (87.65K) at 87 K, the practical ratio selected was

5   about 134. That is 134 kg of liquid argon (ca. 95 dm^3) were used for 1 kg of
ECs. In addition, owing to the lower density of spent ECs (1369 kg.m^{-3})
than the density of liquid argon at 85K (1407 kg.m^{-3}), the light spent ECs
were introduced into the liquid argon using either a metallic screen basket
or an expanded or a perforated metal box containing the said cell materials

10   in order to prevent hazardous floatation at the liquid-gas interface. Due to
the issue of ductile-to-brittle transition at low temperature, face centered
cubic (fcc) metals and alloys such as aluminium alloy 6061-T6 and
austenitic stainless steel grade AISI 316L were preferred and selected for
designing components and vessels. The residence time in the Dewar flask

15   was about 30 minutes. Then more brittle, the hardened mass was directed to
a shredder having knives blades made of tungsten carbide (Pulverisette 25,
Fritsch GmbH). During the comminution operation, a continuous flow of
liquid argon at 85 K circulates by gravity inside the shredding chamber
maintaining sufficient hardness of the cell materials, and providing by

20   evaporation an inert medium around the delaminated sheets. The final
specific surface area of shredded cell materials forming delaminated pieces
was measured equal to 1.5 m^2.kg^{-1} compared to the initial value of
0.3 m^2.kg^{-1} with expected benefits for the reaction kinetics. The cuttings
produced were smaller than about one millimeter. Oversize cuttings were

25   removed with a stainless steel 316L wet vibrating screen with aperture of
12 Tyler meshes operated under a flow of liquid argon and directed to the
cutting mill operation. Mass yield during comminution was about 98 wt %.
The resulting cooled slurry (i.e., undersize delaminated cuttings and liquid
argon) was directly collected with a perforated ladle and poured into a

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tubular incinerator. The tubular incinerator vessel had both walls and bottom of 2.54 cm thickness, a total length of 0.9144 m, an outside diameter of 30.48 cm with an actual capacity of about 45 dm^3. The incinerator was made of annealed Inconel®-617. The incinerator was safely

5   designed according to the *ASME Boiler and Pressure Vessels code* in order to withstand the maximum pressure rise in the worst case of thermal runaway related to sudden decomposition reaction of one kg ECs without proper venting. When completely loaded, the reactor and its cover flange were tightly bolted together using a pure annealed gold-platted copper

10   O-ring and connected to an air compressor at 1.5 bars absolute pressure. Then, liquid and gaseous argon were gently removed by displacement while releasing a mass of cool shredded spent ECs inside the reactor. The reaction in the incinerator was initiated by heating up the incinerator retort into an electric heating oven made with a Fibrothal® module with Kanthal® A1

15   heating elements. A flow of 20 (STP)dm^3/min compressed dry air was maintained until completion of the reaction in order to facilitate total combustion of all the carbonaceous materials (e.g., carbon black and copolymer). Two thermocouples B-type recorded both the inside and outer reactor surface temperature. After reaching 130°C, usually an exothermic

20   and fast reaction occurs for few seconds with a peak temperature around 1500 K. Afterwards, the external heating was maintained constant at a temperature of about 1000 K during 8 hours. During combustion, the off-gases produced leaving the reaction vessel were collected and cooled by means of a miniature shell and tube heat exchanger made of stainless steel

25   grade AISI 316L (Exergy Inc.) and were directed through a high efficiency particulate filter in order to remove entirely any entrained particulates (i.e., Li_2O, Al_2O_3, V_2O_5). Then the dust free gas is directed to a wet scrubber containing a spent slacked lime solution ($Ca(OH)_2$) for absorbing all the hazardous gaseous effluents (i.e., CO_2, HF, and SO_2). These gases reacted

to form a sludge of harmless precipitates made of calcium carbonate ($CaCO_3$), calcium fluoride (CaF_2), and calcium sulphate ($CaSO_4$). The solid compounds were removed by settling and dried. Finally, the released gas passed through a small catalytic converter. After completion of the

5   incineration steps, the 711 grams of both ashes and solid residues having the ultimate chemical composition presented in Table 2 were discharged from the incinerator and introduced with collected dust and particulates into the stirred digestion reactor.

Chemical element	Mass fraction
Vanadium pentaoxide (V_2O_5)	40.88 wt %
Aluminium sesquioxide (Al_2O_3)	30.33 wt %
Lithium oxide (Li_2O)	28.79 wt %

Table 2 – Chemical analysis of ashes from incinerated cells

10   The digestion reactor was made of a small jacketed glass-lined steel vessel with a capacity of 37.85 dm^3 (LBO series from Tycon®) and a large bottom discharge. The digestion reaction was initiated by adding a solution of sulphuric acid at ambient temperature, after which it was heated to 80°C. The dimensionless physical quantity called the *operating acid ratio*,

15   denoted R_O, i.e., the mass of acid to the mass of both ashes and solid residues that can be currently used without having thermal runaway issues but sufficient to neutralize all the cell active materials is determined taking the greater value of both the neutralization and the safety acid ratio as listed below.

20                              $$R_O = \max (R_N, R_S)$$

The dimensionless quantity called the *neutralization acid ratio*, denoted R_N, i.e., the mass of acid required to neutralize stoichiometrically all active cell materials to the mass of both ashes and solid residues was calculated using the following theoretical equation:

$$R_N = \frac{m_{acid}}{m_{ashes}} = \frac{MM_{H2SO4}}{x_{acid}} \cdot \left[\frac{x_{Li2O} \cdot}{MM_{Li2O}} + \frac{x_{V2O5}}{MM_{V2O5}} + \frac{3 \cdot x_{Al2O3}}{MM_{Al2O3}} \right]$$

where x_{Li2O}, x_{V2O5}, and x_{Al2O3} are the dimensionless mass fractions of lithium oxide, vanadium pentaoxide, and aluminium oxide present in the ashes and solid residues; where MM_{H2SO4}, MM_{Li2O}, MM_{V2O5}, and MM_{Al2O3}

5   are the molecular molar masses expressed in kg.mol^{-1} of sulphuric acid, lithium oxide, vanadium pentaoxide, and aluminium oxide, and x_{acid} is the sulphuric concentration expressed in mass fractions. This neutralization acid ratio is based on the three following chemical reactions schemes :

10   $Li_2O + H_2SO_4 = Li_2SO_4 + H_2O$ $\Delta h = -10386$ kJ.kg^{-1} of Li_2O

$V_2O_5 + H_2SO_4 = (VO_2)_2\ SO_4 + H_2O$ $\Delta h = -1715$ kJ.kg^{-1} of V_2O_5

$Al_2O_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O$ $\Delta h = -719$ kJ.kg^{-1} Al_2O_3
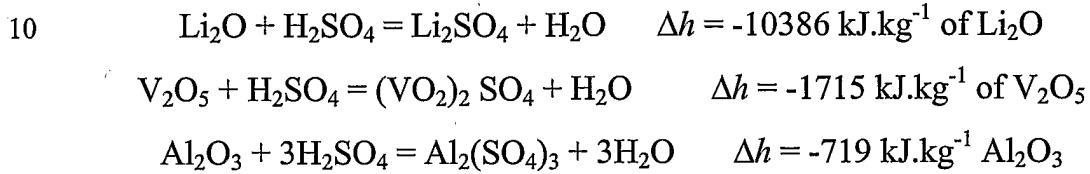
However, for safety reasons especially for preventing thermal
15   runaways, another dimensionless physical quantity must be introduced and calculated, it is the *safety acid ratio*, denoted R_S. It describes the ratio of the mass of acid that can absorb all the heat generated by the exothermic reaction wherein vanadyl, aluminium and lithium sulphates are formed without reaching the maximum allowed temperature to the mass of ashes
20   and solid residues. The *safety acid ratio* can be calculated using the following equation :

$$R_S = \frac{m_{acid}}{m_{ashes}} = \frac{\left[\Delta h_{reaction} - c_{Pashes}(T_{max} - T_{ashes}) \right]}{c_{Pacid}(T_{max} - T_{acid})}$$

with $c_{Pacid} = x_{water} \cdot c_{pwater} + x_{H2SO4} \cdot c_{PH2SO4}$

where m_{acid} and m_{ashes} are the masses expressed in kg of acid and ashes
25   respectively, $\Delta h_{reaction}$, the specific enthalpy of the dissolution reaction in J.kg^{-1}, c_{PH2SO4}, c_{Pacid}, c_{Pwater} and c_{Pashes} are the specific heat capacities expressed in J.kg^{-1}.K^{-1} of concentrated sulphuric acid, the sulphuric acid

aqueous solution, water, and ashes respectively, and T_{acid}, T_{ashes}, and T_{max}, are temperatures expressed in kelvin of the acid, the ashes, and the maximum temperature allowed in the process. For instance, values of neutralization and safety acid ratios are listed for several sulfuric acid concentrations in Table 3 based on the chemical composition of the ashes listed in Table 2.

	Concentrated sulphuric acid (98 wt %. H_2SO_4)	Battery grade sulphuric acid (30 wt %. H_2SO_4)	Diluted sulphuric acid (20 wt %. H_2SO_4)
Neutralization acid ratio (R_N)	2.09	6.82	10.23
Safety acid ratio (R_S)	19.71	8.65	7.99
Operating acid ratio (R_O)	20.00	10.00	15.00

Table 3 – Neutralization, safety and operating acid ratios for ashes with several acid concentrations

Therefore, for safety and economical concerns a sulphuric acid concentration of 30wt %. H_2SO_4 was selected with an *operating acid ratio* of about 10, that is 7.11 kg of acid (ca. 6 dm^3) in our case. After completion of the exothermic dissolution, the operating temperature was maintained at 80°C during 2 hours by heating the jacket. Mixing was obtained with a PTFE-coated impeller (IKA). After complete dissolution of solids (i.e., Al_2O_3, Li_2O, V_2O_5) and completion of side reactions (i.e., gas evolution, and heat generation), the bath acidity was adjusted to pH below 1 by adding concentrated sulphuric acid 98wt %. Afterwards, about 50 grams of lithium chlorate, $LiClO_3$ or concentrated hydrogen peroxide H_2O_2 30%vol. was carefully added to the heated solution (80°C) in order to oxidize all vanadium (IV) and (III) cations to pentavalent vanadium (V) species.

Practically, the addition of the oxidizing chemical continues until the deep
blue solution is totally converted to a yellow solution containing all
vanadium as vanadyl (V) sulphate $(VO_2)_2SO_4$. Then the liquor is
concentrated by evaporation to a molarity of vanadium (V) above

5   200 mol.m^{-3} concentration which was determined by UV-Vis
spectrophotometry. Once digestion and oxidation completed the solution
was bottom pumped into a tank with a positive displacement pump such as
PTFE diaphragm pump (George Fisher) and allowed to cool to ambient
temperature. Then, the few remaining insoluble solids were removed by

10   hydrocycloning or centrifugation and finally filtration using a filterpress
equipment. Afterwards, lithium hydroxide solution or aqueous ammonia
28 wt % NH_4OH was added until reaching pH = 2 where flocculation of the
hydrated red-brown precipitate of vanadium pentoxide $(V_2O_5.250H_2O)$
occurs. The gelatinous precipitate was separated by settling and filtration,

15   carefully washed, dewatered, and dried at 200°C. In order to recover V_2O_5,
the calcinate was fired at 700°C during 2 hours in an Inconel®-617
crucible. The cooled black molten mass of pure V_2O_5 was then crushed and
ground in a pebble mill with yttria stabilized zirconia balls of 10 mm to
produce a fine red powder which passes a 200 Tyler mesh sieve. The final

20   mass was 293 g with a purity of 98.5 wt %. V_2O_5. The oversize particles
were recycled to the pebble mill. The previous filtrate was mixed with
washing solutions and adjusted to pH about 2 by adding concentrated acid
at 98 wt %. H_2SO_4. The traces of heavy metals (i.e., Cu^{2+}, Pb^{2+} Sn^{2+}) were
removed by common cathodic electrodeposition achieved onto a zirconium

25   cathode under galvanostatic conditions with a constant cathodic current
density of 200 A.m^{-2} and using an expanded dimensionally stable anode for
evolving oxygen in acidic media (i.e., DSA®-O_2) such as Ta/IrO_2 (30 g/m^2
IrO_2) (Magnetochemie B.V.). The electrolyzed solution was mixed with
washing solutions and concentrated by evaporation in a kettle. Then, after

cooling down the mother liquor to 20°C, lithium hydroxide solution or aqueous ammonia 28 wt % NH₄OH was added until reaching pH about 5 where flocculation of the gelatinous aluminium hydroxide (Al(OH)₃) occurred. The precipitate was then separated by settling and filtration. The

5   washed, dewatered, dried precipitate was calcinated into a muffle furnace (Carbolite). The 205 grams obtained exhibited a purity of 98 wt %. The purified lithium sulphate liquor was mixed with washing solutions, concentrated by evaporation up to 650 kg/m³ Li₂SO₄ measured by flame spectrophotometry and adjusted to pH about 8 by adding lithium hydroxide

10   (LiOH), and warmed up to 100°C. Then by bubbling carbon dioxide or adding ammonium carbonate (NH₄)₂CO₃, lithium carbonate Li₂CO₃ precipitated and was separated by filtration. The precipitate was washed and dried. The 520 grams of Li₂CO₃ obtained exhibited a purity of 98 wt %. The remaining liquor containing ammonium sulphate was discarded.

15   Example 2 (Direct Digestion of ECs)

The first step consisted in rendering more brittle and easy to comminute a mass of one kilogram of spent electrochemical cells (ECs) having the chemical composition listed in Table 1. The electrochemical cells exhibited various states of charge. The hardening occurred by

20   immersing the spent ECs directly into liquid argon maintained at 85 K. The dimensionless ratio, denoted r_{AE}, is the mass of liquid argon required per unit mass of ECs and it was calculated by the following equation listed below:

$$r_{AE} = \frac{m_{Ar}}{m_{EC}} = \frac{c_{PEC} \cdot (T_{EC} - T_F)}{c_{PAr} \cdot (T_F - T_{Ar})}$$

25   Where m_{Ar} and m_{EC} are the masses expressed in kg of liquid argon and spent ECs respectively, c_{PAr} and c_{PEC} are the specific heat capacities expressed in J.kg⁻¹.K⁻¹ of liquid argon and spent ECs respectively, and T_{Ar}, T_{EC}, and T_F are temperatures expressed in kelvin of liquid argon, spent ECs,

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and the final temperature allowed after immersion respectively. Using liquid argon at 85K and based on the following experimental parameters: (i) an average temperature T_E around 260K of spent ECs which are stored in refrigerated warehouses, (ii) the specific heat capacities of liquid argon c_{PAr}

5   of 1058 J.kg^{-1}.K^{-1} (Perry, R.H., and Green, D.W. - *Perry's Chemical Engineers' Handbook* 7th *ed.* - McGraw-Hill, New York (1997) page 2-217) and c_{PEC} of spent ECs of 1619 J.kg^{-1}.K^{-1}, and (iii) the final allowed temperature of the solid-liquid mixture maintained slightly below the boiling point of argon (87.65K) at 87 K, the practical ratio selected was

10   about 134. That is 134 kg of liquid argon (ca. 95 dm^3) were used for 1 kg of ECs. In addition, owing to the lower density of spent ECs (1369 kg.m^{-3}) than the density of liquid argon at 85K (1407 kg.m^{-3}), the light spent ECs were introduced into the liquid argon using either a metallic screen basket or an expanded or a perforated metal box containing the said cell materials

15   in order to prevent the hazardous flotation at the liquid-gas interface. Due to the issue of ductile-to-brittle transition at low temperature, face centered cubic (fcc) metals and alloys such as aluminium alloy 6061-T6 and austenitic stainless steel grade AISI 316L were preferred and selected for designing components and vessels. The residence time in the Dewar flask

20   was about 30 minutes. Then more brittle, the hardened mass was directed to a shredder having knives blades made of tungsten carbide (Pulverisette 25, Fritsch GmbH). During the comminution operation, a continuous flow of liquid argon at 85 K circulates by gravity inside the shredding chamber maintaining sufficient hardness of the cell materials, and providing by

25   evaporation an inert medium around the delaminated sheets. The final specific surface area of shredded cell materials forming delaminated pieces was measured equal to 1.5 m^2.kg^{-1} compared to the initial value of 0.3 m^2.kg^{-1} with expected benefits for the reaction kinetics. The cuttings produced were smaller than about one millimeter. Oversize cuttings were

removed with a stainless steel 316L wet vibrating screen with aperture of 12 Tyler meshes operated under a flow of liquid argon and directed to the cutting mill operation. Mass yield during comminution was about 98 wt %.

The resulting cooled slurry (i.e., undersize delaminated cuttings and liquid

5   argon) was directly collected with a perforated ladle and poured into the digestion reactor.

The digestion reactor was made of a small jacketed glass-lined steel vessel with a capacity of 37.85 dm^3 (LBO series from Tycon®) with a large bottom discharge. The digestion reaction was initiated by adding a solution

10   of sulphuric acid at ambient temperature then heated to 80°C. In order to prevent the hazardous flotation of lithium metal at the surface of the bath which can cause severe explosion of the hydrogen evolved, the spent ECs was maintained at the bottom of the reactor using an immersed and fine expanded metallic screen made of Hastelloys® C-276. The dimensionless

15   quantity called the *operating acid ratio*, denoted R_O, i.e., the mass of acid to the mass of spent ECs that can be currently used without having thermal runaway issues but sufficient to neutralize all the cell active materials is determined taking the greater value of both the neutralization and the safety acid ratio as listed below.

20                                    $R_O = \max (R_N, R_S)$

The dimensionless quantity called the *neutralization acid ratio*, denoted R_N, i.e., the mass of acid required to neutralize stoichiometrically all active cell materials to the mass of spent ECs was calculated using the following theoretical equation:

25            $$R_N = \frac{m_{acid}}{m_{ECs}} = \frac{MM_{H2SO4}}{x_{acid}} \cdot \left[\frac{x_{Li}}{2 \cdot MM_{Li}} + \frac{x_{V2O5}}{2 \cdot MM_{V2O5}} + \frac{3 \cdot x_{Al}}{2 \cdot MM_{Al}} \right]$$

Where x_{Li}, x_{V2O5}, and x_{Al} are the dimensionless mass fractions of the lithium metal, vanadium pentaoxide, and aluminium metal present in the spent ECs. Where MM_{H2SO4}, MM_{Li}, MM_{V2O5}, and MM_{Al} are the atomic and molecular

molar masses expressed in kg.mol^{-1} of sulphuric acid, lithium metal, vanadium pentaoxide, and aluminium metal, and x_{acid} is the sulphuric concentration expressed in mass fractions. This neutralization acid ratio is based on the three following chemical reactions schemes:

$$2Li + H_2SO_4 = Li_2SO_4 + H_2 \qquad \Delta h = -44835 \text{ kJ.kg}^{-1} \text{ of Li}$$

$$V_2O_5 + H_2SO_4 = (VO_2)_2\, SO_4 + H_2O \qquad \Delta h = -1715 \text{ kJ.kg}^{-1} \text{ of V}_2O_5$$

$$2Al + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2 \qquad \Delta h = -18402 \text{ kJ.kg}^{-1} \text{ Al}$$
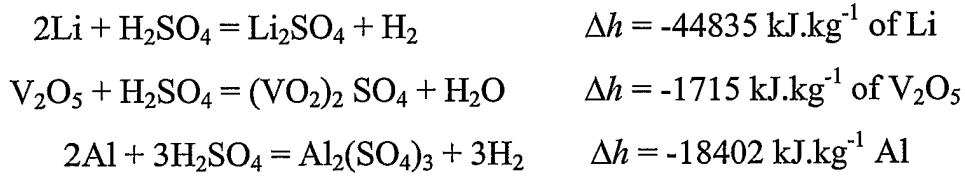
However, for safety reasons especially for preventing thermal runaways, another dimensionless physical quantity must be introduced and calculated, it is the *safety acid ratio*, denoted R_S. It describes the ratio of the mass of acid that can absorb all the heat generated by the exothermic reaction wherein vanadyl, aluminium and lithium sulphate are formed without reaching the maximum allowed temperature to the mass of spent ECs. The *safety acid ratio* can be calculated using the following equation:

$$R_S = \frac{m_{acid}}{m_{EC}} = \frac{\left[\Delta h_{reaction} - c_{PECs}(T_{max} - T_{EC})\right]}{c_{Pacid}(T_{max} - T_{acid})}$$

with $\quad c_{Pacid} = x_{water}.c_{pwater} + x_{H2SO4}.c_{PH2SO4}$

Where m_{acid} and m_{EC} are the masses expressed in kg of acid and spent ECs respectively, $\Delta h_{reaction}$, the specific enthalpy of the dissolution reaction in J.kg^{-1}, c_{PH2SO4}, c_{Pacid}, c_{Pwater} and c_{PEC} are the specific heat capacities expressed in J.kg^{-1}.K^{-1} of concentrated sulphuric acid, the sulphuric acid aqueous solution, water, and spent ECs respectively, and T_{acid}, T_{ECs}, and T_{max}, are temperatures expressed in kelvin of the acid, the spent ECs, and the maximum temperature allowed in the digestion process. For instance, values of neutralization and safety acid ratios are listed for several sulphuric acid concentrations based on the chemical composition of the ashes listed in Table 4.

	Concentrated sulphuric acid (98 wt %. H_2SO_4)	Battery grade sulphuric acid (30 wt %. H_2SO_4)	Diluted sulphuric acid (10 wt %. H_2SO_4)
Neutralization acid ratio (R_N)	1.51	4.95	14.85
Safety acid ratio (R_S)	46.85	30.11	9.50
Operating acid ratio (R_O)	50.00	32.00	15

Table 4 – Neutralization, safety and operating acid ratios for spent ECs with several acid concentrations

Therefore, for safety and economical concerns and due to the size of the reactor vessels sulphuric acid concentration of 30wt %. H_2SO_4 was selected with a corresponding *operating acid ratio* of about 32, that is 32 kg of acid (26 dm^3). After completion of the exothermic dissolution, the operating temperature was maintained at 80°C during 4 hours by heating the jacket. Due to explosion hazards related to hydrogen evolution, mixing was obtained with motor driven impeller by recirculating and heating the acid with a diaphragm pump and a plate heat exchanger made of Hastelloy®-C-276 (Alfa Laval). After complete dissolution of solids (i.e., Al_2O_3, Li_2O, V_2O_5) and completion of side reactions (i.e., hydrogen gas evolution, and heat generation), the bath acidity was adjusted to pH below 1 by adding concentrated sulphuric acid 98 wt %. Afterwards, about 50 grams of lithium chlorate, $LiClO_3$ or concentrated hydrogen peroxide H_2O_2 30 % vol. was carefully added to the heated solution (80°C) in order to oxidize all vanadium(IV) and (III) cations to pentavalent vanadium (V) species. Practically, the addition of the oxidizing chemical continue until the deep blue solution is totally converted to a yellow solution containing all vanadium as vanadyl (V) sulphate $(VO_2)_2SO_4$. Then the liquor is concentrated by evaporation to a molarity of vanadium(V) above

200 mol.m^{-3} concentration which was determined by UV-Vis spectrophotometry. Once digestion and oxidation completed the solution was bottom pumped into a tank with a positive displacement pump such as PTFE diaphragm pump (George Fisher) and let cooled to ambient

5   temperature. Then, the few remaining insoluble solids were removed by hydrocycloning or centrifugation and finally filtration using a filterpress equipment. Afterwards, lithium hydroxide solution or aqueous ammonia 28 wt % NH$_4$OH was added until reaching pH about 2 where flocculation of the hydrated red-brown precipitate of vanadium pentoxide (V$_2$O$_5$.250H$_2$O)

10   occurs. The gelatinous precipitate was separated by settling and filtration, carefully washed, dewatered, and dried at 200°C. In order to recover V$_2$O$_5$, the calcinate was fired at 700°C during 2 hours in an Inconel®-617 crucible. The cooled black molten mass of pure V$_2$O$_5$ was then crushed and ground in a pebble mill with yttria stabilized zirconia balls of 10 mm to

15   produce a fine red powder which passes a 200 Tyler mesh sieve. The final mass was 290 g with a purity of 98.5 wt %. V$_2$O$_5$. The oversize particles were recycled to the pebble mill. The previous filtrate was mixed with washing solutions and adjusted to pH about 2 by adding conc. H$_2$SO$_4$ 98wt %. The traces of heavy metals (i.e., Cu^{2+}, Pb^{2+} Sn^{2+}) were removed by

20   common cathodic electrodeposition achieved onto a zirconium cathode under galvanostatic conditions with a constant cathodic current density of 200 A.m^{-2} and using an expanded dimensionally stable anode for evolving oxygen in acidic media (i.e., DSA®-O$_2$) such as Ta/IrO$_2$ (30 g/m^2 IrO$_2$) (Magnetochemie B.V.). The electrolyzed solution was mixed with washing

25   solutions and concentrated by evaporation in a kettle. Then, after cooling down the mother liquor to 20°C, lithium hydroxide solution or aqueous ammonia 28 wt % NH$_4$OH was added until reaching pH about 5 where flocculation of the gelatinous aluminium hydroxide (Al(OH)$_3$) occurred. The precipitate was then separated by settling and filtration. The washed,

dewatered, dried precipitate was calcinated into a muffle furnace (Carbolite). The 204 grams obtained exhibited a purity of 98 wt %. The purified lithium sulphate liquor was mixed with washing solutions, concentrated by evaporation up to 650 kg/m^3 Li$_2$SO$_4$ measured by flame

5   spectrophotometry and adjusted to pH = 8 by adding lithium hydroxide (LiOH), and warmed up to 100°C. Then bubbling carbon dioxide or adding ammonium carbonate (NH$_4$)$_2$CO$_3$ lithium carbonate Li$_2$CO$_3$ precipitated and was separated by filtration. The precipitate was washed and dried. The 518 grams of Li$_2$CO$_3$ obtained exhibited a purity of 97.5 wt %. The

10   remaining liquor containing ammonium sulphate was discarded.

Example 3 (Molten Salt Oxidation of ECs and Digestion of Salts)

The first step consisted to render more brittle and easy to comminute a mass of one kilogram of spent electrochemical cells (ECs) having the chemical composition listed in Table 1. The electrochemical cells exhibited

15   various states of charge. The hardening occurred by immersing the spent ECs directly into liquid argon maintained at 85 K. The dimensionless ratio, denoted r_{AE}, is the mass of liquid argon required per unit mass of ECs and it was calculated by the following equation listed below:

$$r_{AE} = \frac{m_{Ar}}{m_{EC}} = \frac{c_{PEC} \cdot (T_{EC} - T_F)}{c_{PAr} \cdot (T_F - T_{Ar})}$$

20   Where m_{Ar} and m_{EC} are the masses expressed in kg of liquid argon and spent ECs respectively, c_{PAr} and c_{PEC} are the specific heat capacities expressed in J.kg^{-1}.K^{-1} of liquid argon and spent ECs respectively, and T_{Ar}, T_{EC}, and T_F are temperatures expressed in kelvin of liquid argon, spent ECs, and the final temperature allowed after immersion respectively. Using

25   liquid argon at 85K and based on the following experimental parameters: (i) an average temperature T_E around 260K of spent ECs which are stored in refrigerated warehouses, (ii) the specific heat capacities of liquid argon c_{PAr} of 1058 J.kg^{-1}.K^{-1} (Perry, R.H., and Green, D.W. - *Perry's Chemical*

Engineers' Handbook 7th ed. - McGraw-Hill, New York (1997) page 2-217)

and c_{PEC} of spent ECs of 1619 $J.kg^{-1}.K^{-1}$, and (iii) the final allowed

temperature of the solid-liquid mixture maintained slightly below the

boiling point of argon (87.65K) at 87 K, the practical ratio selected was

5   about 134. That is 134 kg of liquid argon (ca. 95 dm^3) were used for 1 kg of

ECs. In addition, owing to the lower density of spent ECs (1369 $kg.m^{-3}$)

than the density of liquid argon at 85K (1407 $kg.m^{-3}$), the light spent ECs

were introduced into the liquid argon using either a metallic screen basket

or an expanded or a perforated metal box containing the said cell materials

10   in order to prevent the hazardous flotation at the liquid-gas interface. Due to

the issue of ductile-to-brittle transition at low temperature, face centered

cubic (fcc) metals and alloys such as aluminium alloy 6061-T6 and

austenitic stainless steel grade AISI 316L were preferred and selected for

designing components and vessels. The residence time in the Dewar flask

15   was about 30 minutes. Then more brittle, the hardened mass was directed to

a shredder having knives blades made of tungsten carbide (Pulverisette 25,

Fritsch GmbH). During the comminution operation, a continuous flow of

liquid argon at 85 K circulates by gravity inside the shredding chamber

maintaining sufficient hardness of the cell materials, and providing by

20   evaporation an inert medium around the delaminated sheets. The final

specific surface area of shredded cell materials forming delaminated pieces

was measured equal to 1.5 $m^2.kg^{-1}$ compared to the initial value of

0.3 $m^2.kg^{-1}$ with expected benefits for the reaction kinetics. The cuttings

produced were smaller than about one millimeter. Oversize cuttings were

25   removed with a stainless steel 316L wet vibrating screen with aperture of

12 Tyler meshes operated under a flow of liquid argon and directed to the

cutting mill operation. Mass yield during comminution was about 98 wt %.

The resulting cooled slurry (i.e., undersize delaminated cuttings and liquid

argon) was directly collected with a perforated ladle and poured into a tall

reaction vessel made of Inconel® 617 containing already the dry pellets of the pre-melted salts. The reactor is a 0.9144 meter tall vessel with an 304.8 mm outside diameter and wall and bottom thickness of 25.4 mm. The normal salt load is 10 kg of a binary mixture of potassium sulphate (K_2SO_4) and lithium sulphate (Li_2SO_4) having an eutectic composition. When completely loaded, the reactor and its cover flange were tightly bolted together using a pure annealed gold-platted copper O-ring and connected to an air compressor at 1.5 bars absolute pressure. Then, liquid and gaseous argon were gently removed by displacement while releasing a mass of cool shredded spent ECs inside the reactor with pre-melted salt pellets. The molten salt oxidation (MSO) was initiated by heating up the crucible into an electric heating oven made with a Fibrothal® module with Kanthal® A1 heating elements. A flow of 20 (STP)dm^3/min compressed dry air was maintained until the completion of the reaction in order to facilitate the total combustion of all the carbonaceous materials (e.g., carbon black and copolymer). Two thermocouples B-type recorded both the inside and outer reactor surface temperature. After reaching 130°C, usually an exothermic and fast reaction occurs for few seconds with a peak temperature around 1500 K. Afterwards, the external heating was maintained constant to temperature about 1000 K during 6 hours. During combustion, the off-gases produced leaving the reaction vessel were collected and cooled by means of a miniature shell and tube heat exchanger made of stainless steel grade AISI 316L (Exergy Inc.) and were directed through a high efficiency particulate filter in order to remove entirely any entrained particulates (i.e., Li_2O, Al_2O_3, V_2O_5). Then the dust free gas is directed to a wet scrubber containing a spent slacked lime solution ($Ca(OH)_2$) for absorbing all the hazardous gaseous effluents (i.e., CO_2, HF, and SO_2). These gases reacted to form a sludge of harmless precipitates made of calcium carbonate ($CaCO_3$), calcium fluoride (CaF_2), and calcium sulphate ($CaSO_4$). The solid

compounds were removed by settling and dried. Finally, the released gas passed through a small catalytic converter. After completion of the incineration steps, the solidified salt mass was demolded and discharged from the reactor and then crushed with a small jack hammer to small

5   chunks. Solids were introduced with collected dust and particulates into the stirred digestion reactor.

The digestion reactor was made of a small jacketed glass-lined steel vessel with a capacity of 37.85 dm³ (LBO series from Tycon®) with a large bottom discharge. The digestion reaction was initiated by adding a solution

10 of diluted sulphuric acid at ambient temperature then heated to 80°C. For safety and economical concerns a sulphuric acid concentration of 10 wt %. H_2SO_4 was selected with an operating acid ratio of about 2, that is 20 kg of acid. After completion of the dissolution, the operating temperature was maintained at 80°C during 1 hours by heating the jacket. Mixing was

15 obtained with a PTFE-coated impeller (IKA). After complete dissolution of solids and completion of side reactions, the bath acidity was adjusted to pH below 1 by adding concentrated sulphuric acid 98 wt %. Afterwards, about 50 grams of lithium chlorate, $LiClO_3$ or concentrated hydrogen peroxide H_2O_2 30%vol. was carefully added to the heated solution (80°C) in order to

20 oxidize all vanadium (IV) and (III) cations to pentavalent vanadium (V) species. Practically, the addition of the oxidizing chemical continue until the deep blue solution is totally converted to a yellow solution containing all vanadium as vanadyl (V) sulphate $(VO_2)_2SO_4$. Then the liquor is concentrated by evaporation to a molarity of vanadium(V) above

25 200 mol.m⁻³ concentration which was determined by UV-Vis spectrophotometry. Once digestion and oxidation completed the solution was bottom pumped into a tank with a positive displacement pump such as PTFE diaphragm pump (George Fisher) and let cooled to ambient temperature. Then, the few remaining insoluble solids were removed by

hydrocycloning or centrifugation and finally filtration using a filterpress equipment. Afterwards, lithium hydroxide solution or aqueous ammonia 28 wt % NH_4OH was added until reaching pH about 2 where flocculation of the hydrated red-brown precipitate of vanadium pentoxide ($V_2O_5.250H_2O$) occurs. The gelatinous precipitate was separated by settling and filtration, carefully washed, dewatered, and dried at 200°C. In order to recover V_2O_5, the calcinate was fired at 700°C during 2 hours in an Inconel®-617 crucible. The cooled black molten mass of pure V_2O_5 was then crushed and ground in a pebble mill with yttria stabilized zirconia balls of 10 mm to produce a fine red powder which passes a 200 Tyler mesh sieve. The final mass was 293 g with a purity of 98.5 wt % V_2O_5. The oversize particles were recycled to the pebble mill. The previous filtrate was mixed with washing solutions and adjusted to pH about 2 by adding conc. H_2SO_4 98 wt %. The traces of heavy metals (i.e., Cu^{2+}, Pb^{2+} Sn^{2+}) were removed by common cathodic electrodeposition achieved onto a zirconium cathode under galvanostatic conditions with a constant cathodic current density of 200 $A.m^{-2}$ and using an expanded dimensionally stable anode for evolving oxygen in acidic media (i.e., DSA®-O_2) such as Ta/IrO_2 (30 g/m^2 IrO_2) (Magnetochemie B.V.). The electrolyzed solution was mixed with washing solutions and concentrated by evaporation in a kettle. Then, after cooling down the mother liquor to 20°C, lithium hydroxide solution or aqueous ammonia 28 wt % NH_4OH was added until reaching pH about 5 where flocculation of the gelatinous aluminium hydroxide ($Al(OH)_3$) occurred. The precipitate was then separated by settling and filtration. The washed, dewatered, dried precipitate was calcinated into a muffle furnace (Carbolite). The 205 grams obtained exhibited a purity of 98 wt %. The purified lithium sulphate liquor was mixed with washing solutions, concentrated by evaporation up to 650 kg/m^3 Li_2SO_4 measured by flame spectrophotometry and adjusted to pH = 8 by adding lithium hydroxide

(LiOH), and warmed up to 100°C. Then bubbling carbon dioxide or adding ammonium carbonate $(NH_4)_2CO_3$ lithium carbonate Li_2CO_3 precipitated and was separated by filtration. The precipitate was washed and dried. The 520 grams of Li_2CO_3 obtained exhibited a purity of 98 wt %. The remaining liquor containing ammonium sulphate was discarded.It must be understood that the invention is in no way limited to the above embodiments and that many changes may be brought about therein without departing from the scope of the invention as defined by the appended claims.

CLAIMS

1.   A method of recovering and recycling lithium and vanadium compounds from a material comprising spent lithium metal gel and solid polymer electrolyte rechargeable batteries, and/or scraps therefrom and/or

5   products used to produce said batteries, which comprises providing a mass of said material, hardening said mass by cooling at a temperature below room temperature, comminuting said mass of cooled and hardened material, treating said comminuted mass with an acid to give an acidic mother liquor, extracting vanadium compounds from said mother liquor, separating heavy

10   metals and aluminium therefrom and precipitating lithium carbonate from remaining solution.

2.   Method according to claim 1, which comprises comminuting said mass of hardened material under a flow of cryogenic liquefied gases.

3.   Method according to claim 2, wherein said mass of material is

15   hardened by cooling it to a temperature between 0 K and 298 K.

4.   Method according to claim 3, wherein said mass of material is cooled to between 77 K and 273 K.

5.   Method according to claim 4, wherein said mass of material is cooled to 85 K.

20   6.   Method according to claim 1 or 2, which comprises batch incinerating said comminuted hardened cooled mass, and treating said comminuted hardened cooled mass to give said mother liquor.

7.   Method according to claim 4, which comprises cooling said comminuted hardened cooled mass and scrubbing of gases produced

25   thereby before treating same to give said mother liquor.

8.   Method according to claim 6, wherein said liquor is obtained by digesting ashes and solid residues obtained by batch incinerating said comminuted hardened cooled mass in an acid.

9.   Method according to claim 8, wherein said acid is selected from the group consisting of inorganic or organic acids.

10.   Method according to claim 9 wherein said acid is selected from the group consisting of HF, HCl, HBr, HI, HNO_3, H_3PO_4, H_2SO_4, $HClO_4$, HCOOH, CF_3SO_3H, or mixtures thereof.

11.   Method according to claim 10, wherein said acid is sulphuric acid (H_2SO_4).

12.   Method according to claim 1, wherein said comminuted mass is obtained by cryogenic comminution.

13.   Method according to claim 1, wherein said mother liquor is obtained by digesting the comminuted hardened cooled mass in an acid, and separating a mixture of inert gas and hydrogen to give said mother liquor.

14.   Method according to claim 13, wherein said acid is selected from the group consisting of inorganic or organic acids.

15.   Method according to claim 14, wherein said acid is selected from the group consisting of HF, HCl, HBr, HI, HNO_3, H_3PO_4, H_2SO_4, $HClO_4$, HCOOH, CF_3SO_3H, or mixtures thereof.

16.   Method according to claim 15, wherein said acid is sulphuric acid H_2SO_4.

17.   Method according to claim 1, which comprises heating said comminuted hardened cooled mass under conditions and at a temperature effective to cause batch oxidation in a molten salt bath of said comminuted material and removing gases produced during said oxidation, before treating said cooled mass to give said mother liquor.

18.   Method according to claim 17, wherein said oxidation is carried out by oxidizing and/or burning the comminuted hardened cooled mass in a molten salt bath comprising a mixture of molten alkali and alkali-earth metal inorganic salts, the comminuted hardened cooled mass at a temperature effective to cause destruction of the comminuted material.

19.   Method according to claim 18, wherein said inorganic salts are selected from the group consisting of M_nX_m wherein M = Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba and X = F⁻, Cl⁻, Br⁻, I⁻, SO_4^{2-}, NO_3^-, CO_3^{2-}, BO_3^{2-}, PO_4^{3-}.

20.   Method according to claim 17, wherein said temperature is between 500 K and 2000 K.

21.   Method according to claim 18, wherein said temperature is between 700 K and 1500 K.

22.   Method according to claim 20, wherein said temperature is 1000 K.

23.   Method according to claim 17, which comprises digesting the comminuted, hardened cooled mass from which said gases produced during said oxidation have been removed, in an acid, said mother liquor containing insoluble solids.

24.   Method according to claim 23, wherein said acid is selected from the group consisting of HF, HCl, HBr, HI, HNO_3, H_3PO_4, H_2SO_4, $HClO_4$, HCOOH, CF_3SO_3H, or mixtures thereof.

25.   Method according to claim 24, wherein said acid is sulphuric acid. H_2SO_4.

26.   Method according to claim 8, wherein said mother liquor is treated to oxidize substantially entirely all vanadium (III) and (IV) cations to pentavalent vanadium (V).

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          ┌─────────────────────────────┐
          │   Spent Lithium Polymer     │
          │         Batteries           │
          └─────────────────────────────┘
                         │
          ┌─────────────────────────────┐
          │     Hardening/Freezing      │
          └─────────────────────────────┘
                         │
                         │  Brittle and Cooled Cell Materials
          ┌─────────────────────────────┐
          │       Comminution           │
          │       (Shredding)           │
          └─────────────────────────────┘
                         │
                         │  Shredded Cell Materials
          ┌─────────────────────────────┐    ┌──────────────┐
          │        Incineration         │    │ Molten Salt  │
          │                             │    │  Oxidation   │
          └─────────────────────────────┘    └──────────────┘
                         │
                         │  Ashes and Residue
          ┌─────────────────────────────┐
          │       Digestion in Acid     │
          └─────────────────────────────┘
                         │
                         │  Mother Liquor
          ┌─────────────────────────────┐
          │       Oxidation to          │
          │       Vanadium(V)           │
          └─────────────────────────────┘
                         │
          ┌─────────────────────────────┐            ⃝ B
          │     Vanadium recovery       │────────────
          └─────────────────────────────┘
                         │
          ┌─────────────────────────────┐          ┌──────┐
          │     Aluminium recovery      │──────────│  Al  │
          └─────────────────────────────┘          └──────┘
                         │
          ┌─────────────────────────────┐          ┌────────┐
          │  Electrochemical Removal    │──────────│ Metals │
          │   of Metallic Impurities    │          └────────┘
          └─────────────────────────────┘
                         │
          ┌─────────────────────────────┐            ⃝ C
          │      Lithium recovery       │────────────
          └─────────────────────────────┘
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Shredded Hardened Cells

Ground Solidified Melt

FIG. 1A

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Vanadium (V) containing
soln.

Precipitation/Settling
at pH = 2

Gelatinous $V_2O_5 \cdot 250H_2O$

Filtration of Precipitate

Washing

Dewatering

Drying

Dry V_2O_5

Calcination and Melting

Melted Vanadium
Pentoxide

FIG. 1B

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┌─────────────────────────────┐
│  Lithium containing solution │
└─────────────────────────────┘
              │
┌─────────────────────────────┐
│  Heating and Concentration  │
└─────────────────────────────┘
              │
┌─────────────────────────────┐
│    Precipitation/Settling   │
└─────────────────────────────┘
              │
┌─────────────────────────────┐
│   Filtration of Precipitate │
└─────────────────────────────┘
              │
┌─────────────────────────────┐
│       Washing/Rinsing       │
└─────────────────────────────┘
              │
┌─────────────────────────────┐
│         Dewatering          │
└─────────────────────────────┘
              │
┌─────────────────────────────┐
│          Drying             │
└─────────────────────────────┘
              │
┌─────────────────────────────┐
│      Lithium Carbonate      │
└─────────────────────────────┘
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FIG. 1C

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   H01M6/52   H01M10/54

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 888 463 A (ADAMS TERRY S ET AL, ANAHEIM, US) 30 March 1999 (1999-03-30) cited in the application column 1, line 20 - line 34 column 1, line 55 - line 65 column 2, line 24 - line 31 figure 1	1-26
A	US 5 352 270 A (SHACKLE DALE R., MORGAN HILL, US) 4 October 1994 (1994-10-04) column 2, line 34 - line 38 claim 8 figure 1	1-26

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| X | Further documents are listed in the continuation of box C. | | X | Patent family members are listed in annex. |

° Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 January 2002	21/01/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Peis, S

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	PINGWEI Z ET AL: "Hydrometallurgical process for recovery of metal values from spent lithium-ion secondary batteries" HYDROMETALLURGY, ELSEVIER SCIENTIFIC PUBLISHING CY. AMSTERDAM, NL, vol. 47, no. 2-3, 1998, pages 259-271, XP004109817 ISSN: 0304-386X * the whole text *	1-26

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US 5352270	A	04-10-1994	AU	4857093 A	12-04-1994
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