

AN APPARATUS AND A METHOD FOR SEPARATION OF GRAPHITE AND BLACK MASS FROM SPENT LITHIUM-ION BATTERIES

FIELD OF THE INVENTION

5 The present invention relates to the field of recycling of spent lithium-ion batteries. More particularly, the present invention relates to an apparatus and a method for separation of graphite and black mass from spent lithium-ion batteries without any effluent generation.

BACKGROUND OF THE INVENTION

10 Lithium-ion batteries are used in many products such as electronics, toys, wireless headphones, handheld power tools, small and large appliances, electric vehicles and electrical energy storage systems. The increased demand for Li-ion batteries in the marketplace is attributed largely to the high energy density of the battery. Energy density means the amount of energy that a system stores in an amount of space. Lithium-ion
15 batteries can be smaller and lighter than other types of batteries while holding the same amount of energy. This miniaturization has resulted in rapid increase in the smaller, portable and cordless products.

Lithium-ion batteries are made of materials such as cobalt, graphite and lithium, which are considered as critical minerals. Critical minerals are raw materials that are
20 economically and strategically important and have a high risk of their supply being disrupted and for which there are no easy substitutes. When the lithium-ion batteries are disposed off in the trash, these critical resources are also lost outright.

Additionally, if the battery or any electronic device that contains the battery is disposed off in the trash or placed in the municipal recycling bin with the household recyclables
25 such as plastic, paper or glass, the battery gets damaged or crushed in transport or from processing and sorting of equipments, creating a fire hazard. Moreover, if lithium batteries waste is not properly managed, it causes harm to human health and the environment.

US10960403B2 discloses a process, apparatus and system for recovering materials from rechargeable lithium-ion batteries. The process involves the steps of processing lithium

battery materials in a comminuting apparatus comprising, a first comminuting device that is submerged in an immersion liquid, thereby creating reduced-size battery materials and liberating an electrolyte material and a black mass material comprising anode and cathode powders from the lithium battery materials and providing a size-reduced feed stream comprising the reduced size battery materials and the black mass material and the electrolyte materials entrained within the immersion liquid; processing the size-reduced feed stream to obtain a black mass solid stream that comprises the black mass material and a retained portion of the immersion liquid having entrained electrolyte materials. However, the citation discloses a lengthy method for recovery of materials from batteries that involves three stage crushing, leaching and extraction by using chemicals such as dimethyl sulphoxide, acetone, ethyl acetate, dimethyl formamide and N-methyl pyrrolidone.

CN105375077A discloses a process for recycling electrode material from lithium-ion batteries, comprising the steps of harvesting a mixture of anode and cathode electrode materials from waste lithium-ion batteries, and separating the anode electrode material from the cathode electrode material by means of dense liquid separation. Moreover, the liquid based density separation of electrode powder disclosed in the citation is among the aqueous/non-aqueous solution of chloroform, bromopropane, bromobenzene, thallium ethoxide or thallium formate having density of 2-2.5g/cc.

Wang et al., (Electrochimica Acta volume 313, 01 August 2019, pages 423-431; doi.org/10.1016/j.electacta.2019.05.050) discloses reclaiming graphite from spent lithium ion batteries ecologically and economically. The reclaim process involves the H₂ evolution by the reaction between water and residual Li present inside graphite, which separates the electrolytically decomposed products from graphite. However, the steps of manual dismantling, taking out copper foil with graphite from cell and washing with distilled water manually to separate graphite makes the method complicated and time-consuming.

Makuza et al., (Resources, conservation and recycling 174 (2021)105784; doi.org/10.1016/j.resconrec.2021.105784) discloses a dry grinding and carbonated ultrasound-assisted water leaching process for recycling the black mass of spent lithium-ion batteries. The method enhances the selective extraction of lithium and recovery of high-value metals. Although, the citation discloses the separation of cathode and anode materials, however, the method is based on optimum conditions such as roasting at high

temperature of 600°C and using harmful chemicals such as sulphuric acid and carbon-dioxide gas.

Although, the aforementioned prior art discloses about the methods for recycling of valuable materials that are recycled for further use, however, the methods disclosed have some limitations like using harmful chemicals such as acids, release of toxic gases, use of expensive instruments to recover the valuable materials from spent lithium batteries.

Therefore, to overcome the shortcomings of the prior art, there is a need to develop an easy to operate, eco-friendly, time-efficient method and apparatus to separate materials of interest from spent lithium-ion batteries.

OBJECT OF THE INVENTION

The main object of the present invention is to provide an apparatus for separation of graphite and black mass from spent lithium-ion batteries.

Another object of the present invention is to provide a method for separation of graphite and black mass from spent lithium-ion batteries.

Yet another object of the present invention is to provide an apparatus and a method for separation of graphite and black mass from spent lithium-ion batteries that involves simple mechanical processes.

Yet another object of the present invention is to provide an economical and chemical-free method for separation of graphite and black mass from spent lithium-ion batteries.

Still another object of the present invention is to provide a method for separation of graphite and black mass from spent lithium-ion batteries that is time-efficient, clean, green and environment-friendly.

SUMMARY OF THE INVENTION

The present invention relates to an apparatus and a method for separation of graphite and black mass from spent lithium-ion batteries that follows simple physical operations such

as wet sieving and washing with water followed by mechanical processes such as density separation, sonication and magnetic separation without generating any effluent.

5 In an embodiment, the present invention provides an apparatus for separation of graphite and black mass from spent lithium-ion batteries comprising of: a primary unit for separating graphite and electrode material from spent lithium-ion batteries; a secondary unit for separating black mass from said electrode material and a tertiary unit for separating steel case and aluminium foil.

10 Here, said primary unit includes a shredder, a rotary washer and a press filter for separating graphite. The rotary washer is having a slurry tank, a porous rotary drum, a water jet connection at the center and a header pipeline with nozzle and a screw conveyor. The porous rotary drum of rotary washer is connected with the screw conveyor for outward movement of electrode materials and slurry from the slurry tank is feed into filter press by a pump to separate graphite and filtrate.

15 Further, said secondary unit includes a density separator, a sonicator, a rotary washer and a press filter for separating black mass. Additionally, said tertiary unit is having a magnetic separator for separation of steel case and aluminium foil.

20 In another embodiment, the present invention provides a method for separation of graphite and black mass from spent lithium-ion batteries comprising steps of: (a) wet shredding spent lithium ion batteries to obtain a shredded material; (b) washing the shredded material obtained in step (a) with water to obtain an anode slurry and a cathode mass, separately; (c) feeding the anode slurry obtained in step (b) into a filter-press to obtain a graphite cake and a filtrate; (d) separating the cathode mass obtained in step (b) by density separation to obtain copper foil, plastics and an aluminium foil-containing black mass; (e) sonicating the aluminium foil-containing black mass obtained in step (d) with water for 5-10 minutes in an ultrasonic bath to obtain a cathode slurry; (f) feeding the cathode slurry obtained in step (e) by following same process as in steps (b) and (c) to obtain a black mass and a steel casing with aluminium foil and (g) separating the steel casing with aluminium foil obtained in step (f) by magnetic separation.

30 Here, the washing in step (b) is done in a rotary washer. The shredded material is washed by the water with rotation in a range of 10-40 rpm and during washing the anode material moves towards a slurry tank through pores with water. The pressure of water in water jet

connection in step (b) is maintained in a range of 2-3kg/cm² during rotary washing through nozzles from said header pipeline.

Further, the cathode mass obtained in step (b) includes aluminium foil-containing black mass, plastics and copper foil. The ultrasonic bath in step (e) is having capacity in a range of 200-300 watt and operational frequency in a range of 25-35 khz.

The above objects and advantages of the present invention will become apparent from the hereinafter set forth brief description of the drawings and description of the invention appended herewith.

10 BRIEF DESCRIPTION OF THE DRAWINGS

An understanding of the apparatus and the method for separation of graphite and black mass from spent lithium-ion batteries of the present invention may be obtained by reference to the following drawings:

Figure 1 is a schematic representation of method for separation of graphite and black mass from spent lithium-ion batteries according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will now be described hereinafter with reference to the accompanying drawings in which a preferred embodiment of the invention is shown. This invention may, however, be embodied in many different forms and should not be construed as being limited to the embodiment set forth herein. Rather, the embodiment is provided so that this disclosure will be thorough, and will fully convey the scope of the invention to those skilled in the art.

The present invention now will be described hereinafter with reference to the detailed description, in which some, but not all embodiments of the invention are indicated. Indeed, the invention may be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will satisfy applicable legal requirements. Like numbers

refer to like elements throughout. The present invention is described fully herein with non-limiting embodiments and exemplary experimentation.

5 The present invention relates to an apparatus and a method for separation of graphite and black mass from spent lithium-ion batteries that follows simple physical operations such as wet sieving and washing with water followed by mechanical processes such as density separation, sonication and magnetic separation without generating any effluent.

10 In a preferred embodiment, the present invention provides an apparatus for separation of graphite and black mass from spent lithium-ion batteries comprising of: a primary unit (100) for separating graphite and electrode material from spent lithium-ion batteries; a secondary unit (200) for separating black mass from said electrode material and a tertiary unit (300) for separating steel case and aluminium foil.

15 Here, said primary unit (100) is having a shredder (101) to obtain a shredded material from said spent lithium-ion batteries, a rotary washer (102) for separating graphite from said shredded material and a press filter (103) to obtain a graphite cake. The rotary washer (102) is having a slurry tank, a porous rotary drum with pores of size ranging from 2-4 mm for movement of slurry from said porous rotary drum towards said slurry tank, a water jet connection at the center and a header pipeline with nozzle and a screw conveyor. The porous rotary drum of rotary washer (102) is connected with said screw conveyor for outward movement of electrode materials and slurry from said slurry tank is feed into filter press (103) by a pump to separate graphite and filtrate.

20 Further, said secondary unit (200) is having a density separator (201) with a plurality of density chambers for separating plastics, copper foil and aluminium foil with black mass; a sonicator (202) for sonication of said aluminium foil with black mass; a rotary washer (203) for separating black mass from said aluminium foil and a press filter (204) for obtaining black mass. Additionally, said tertiary unit (300) is having a magnetic separator (301) for separation of steel case and aluminium foil.

30 In another preferred embodiment, the present invention provides a method for separation of graphite and black mass from spent lithium-ion batteries comprising steps of: (a) wet shredding spent lithium ion batteries to obtain a shredded material; (b) washing the shredded material obtained in step (a) with water to obtain an anode slurry and a cathode mass, separately; (c) feeding the anode slurry obtained in step (b) into a filter-press (103)

to obtain a graphite cake and a filtrate; (d) separating the cathode mass obtained in step (b) by density separation to obtain copper foil, plastics and an aluminium foil-containing black mass; (e) sonicating the aluminium foil-containing black mass obtained in step (d) with water for 5-10 minutes in an ultrasonic bath to obtain a cathode slurry; (f) feeding the cathode slurry obtained in step (e) by following same process as in steps (b) and (c) to obtain a black mass and a steel casing with aluminium foil and (g) separating the steel casing with aluminium foil obtained in step (f) by magnetic separation.

Here, the washing in step (b) is done in a rotary washer (102) having a porous rotary drum with pore size in a range of 2-4 mm and a water jet connection at the center to separate copper and aluminum metal pieces from the shredded material. The shredded material is washed by the water with rotation in a range of 10-40 rpm and during washing the anode material moves towards a slurry tank through pores with water to obtain said anode slurry. The pressure of water in water jet connection in step (b) is maintained in a range of 2-3kg/cm² during rotary washing through nozzles from said header pipeline.

Further, the cathode mass obtained in step (b) includes aluminium foil-containing black mass, plastics and copper foil. The graphite cake in step (c) is obtained by unloading said filter press (103). The filtrate in step (c) is water and is re-used for washing.

Additionally, the cathode mass in step (d) is separated into copper foil, plastics and aluminum foil-containing black mass by a density separator (201). The copper foil, plastics and aluminum foil-containing black mass are collected into a plurality of density chambers of said density separator (201) due to the difference in densities.

The ultrasonic bath in step (e) is having capacity in a range of 200-300 watt and operational frequency of in a range of 25-35 khz.

The porous rotary drum of the rotary washer is having diameter of 0.8m and length of 2m. Additionally, the screw conveyor is having length of 1.5 m and width of 50 mm.

Referring to **Figure 1**, a schematic representation of method for separation of graphite and black mass from spent lithium-ion batteries is illustrated.

EXAMPLE 1

Separation of graphite and black mass from spent lithium-ion batteries

The method for separation of graphite and black mass from spent lithium-ion batteries was carried out batch wise and around 500 kg of spent lithium-ion batteries were taken for each batch. The input and output details of the five batches are presented in **Tables 1, 2, and 3** below.

Table 1: Separation of graphite from batteries by washing system

Batch No	Input	Out put	
	Fed into shredder	From filter press 1	From rotary drum 1 (> 3 mm)
	Wt of batteries, Kg	Anode material, Kg	Al, Cu, Plastic & cathode material mix, Kg
1	500	102	398.0
2	520	104	416.0
3	510	101	409.0
4	518	101	417.0
5	523	102	421.0

Table 2: Separation of copper foil, plastics from the casing, Al foil with cathode material

Batch No	Input	Output		
	Cu-Al foil with cathode material	From density separator		
	fed to density separator	Cu foil, Kg	Plastics, Kg	Casing+Al-foil+cathode material, Kg
1	398	50	18.7	330.0
2	416	52	19.4	343.2
3	409	51	19.1	336.6
4	417	51.8	19.4	341.9
5	421	52.3	19.6	345.2

Table 3: Separation of cathode material, Al-foil, and steel casing

Batch No	Input	Out put		
	Sonicator	Filter press 2	Magnetic separator	
	Casing+Al-foil+cathode material, Kg	Cathode material	Steel casing	Al-foil
1	330.0	168.0	107.5	54.5
2	343.2	174.7	111.8	56.7
3	336.6	171.4	109.7	55.6
4	341.9	174.0	111.4	56.5
5	345.2	175.7	112.4	57.0

Therefore, the present invention provides an economical, clean, green and time-efficient method and apparatus for separation of graphite and black mass from spent lithium-ion batteries without using any chemicals.

Many modifications and other embodiments of the invention set forth herein will readily occur to one skilled in the art to which the invention pertain having the benefit of the teachings presented in the foregoing descriptions and the associated drawings. Therefore, it is to be understood that the invention is not to be limited to the specific embodiments disclosed and that modifications and other embodiments are intended to be included within the scope of the appended claims. Although specific terms are employed herein, they are used in a generic and descriptive sense only and not for purposes of limitation.

CLAIMS

We claim:

1. An apparatus for separation of graphite and black mass from spent lithium-ion batteries comprising of:
5 a primary unit (100) for separating graphite and electrode material from spent lithium-ion batteries;
a secondary unit (200) for separating black mass from said electrode material;
a tertiary unit (300) for separating steel case and aluminium foil;
characterized in that,
10 said primary unit (100) is having a shredder (101) to obtain a shredded material from said spent lithium-ion batteries, a rotary washer (102) for separating graphite from said shredded material and a press filter (103) to obtain a graphite cake;
said secondary unit (200) is having a density separator (201) with a plurality of density chambers for separating plastics, copper foil and aluminium foil with black
15 mass; a sonicator (202) for sonication of said aluminium foil with black mass; a rotary washer (203) for separating black mass from said aluminium foil and a press filter (204) for obtaining black mass;
and
said tertiary unit (300) is having a magnetic separator (301) for separation of steel
20 case and aluminium foil.
2. The apparatus as claimed in claim 1, wherein the rotary washer (102) is having a slurry tank, a porous rotary drum with pores of size ranging from 2-4 mm for movement of slurry from said porous rotary drum towards said slurry tank, a water
25 jet connection at the center and a header pipeline with nozzle and a screw conveyor.
3. The apparatus as claimed in claim 2, wherein the porous rotary drum of rotary washer (102) is connected with said screw conveyor for outward movement of
30 electrode materials and slurry from said slurry tank is feed into filter press (103) by a pump to separate graphite and filtrate.

4. A method for separation of graphite and black mass from spent lithium-ion batteries comprising steps of:

- (a) wet shredding spent lithium ion batteries to obtain a shredded material;
- (b) washing the shredded material obtained in step (a) with water to obtain an anode slurry and a cathode mass, separately;
- (c) feeding the anode slurry obtained in step (b) into a filter-press (103) to obtain a graphite cake and a filtrate;
- (d) separating the cathode mass obtained in step (b) by density separation to obtain copper foil, plastics and an aluminium foil-containing black mass;
- (e) sonicating the aluminium foil-containing black mass obtained in step (d) with water for 5-10 minutes in an ultrasonic bath to obtain a cathode slurry;
- (f) feeding the cathode slurry obtained in step (e) by following same process as in steps (b) and (c) to obtain a black mass and a steel casing with aluminium foil; and
- (g) separating the steel casing with aluminium foil obtained in step (f) by magnetic separation;

characterized in that,

the washing in step (b) is done in a rotary washer (102) having porous rotary drum with pore size in a range of 2-4 mm and a water jet connection at the center to separate copper and aluminum metal pieces from the shredded material;

the shredded material in step (b) is washed by the water with rotation in a range of 10-40 rpm and during washing the anode material moves towards a slurry tank through pores with water to obtain said anode slurry;

the cathode mass obtained in step (b) includes aluminium foil-containing black mass, plastics and copper foil;

the filtrate in step (c) is water and is re-used for washing; and

the cathode mass in step (d) is separated into copper foil, plastics and aluminum foil-containing black mass by using a density separator (201).

5. The method as claimed in claim 4, wherein pressure of water in water jet connection in step (b) is maintained in a range of 2-3kg/cm² during rotary washing through nozzles from said header pipeline.
- 5 6. The method as claimed in claim 4, wherein said graphite cake in step (c) is obtained by unloading said filter press (103).
7. The method as claimed in claim 4, wherein copper foil, plastics, and aluminum foil-containing black mass in step (d) are collected into plurality of density
10 chambers of said density separator (201).
8. The method as claimed in claim 4, wherein the ultrasonic bath in step (e) is having capacity in a range of 200-300 watt and operational frequency in a range of 25-35 khz.