

RECOVERY OF COMPONENTS FROM CARBON-RICH MATERIALS

The present invention relates to a process to recover components, including graphite from carbon-rich or graphite-containing materials, for example, from products such as batteries and petroleum refining by-products. The process is also able to recover all other components including metals, non-metals, electrolytes and binders. When applied to black mass from shredded solid-state batteries, the process comprises (a) recovery of binders and electrolytes (b) recovery of graphite and (c) recovery of all metals including Lithium. The process does so in a safe manner, and in a closed loop, introducing no sulphates or additional metal ions and allowing for complete recovery of constituents in a closed loop process.

Batteries are an essential component of vehicles such as trucks, ships and cars; household energy storage units; industrial energy units and commercial buildings energy units. As their application increase and the number of batteries in the world rises, so will the expired, defaulted and damaged batteries. There is therefore a desire for methods for recovering materials from these batteries.

<https://www.recycling-magazine.com/2021/09/10/black-mass-one-of-the-hottest-issues-in-battery-recycling/> discusses the term “black mass” as referring to shredded material from solid state batteries.

<https://cea.hal.science/cea-03321722/document> discusses electrochemical approaches for the recovery of metals from electronic.

<https://www.hazenresearch.com/capabilities/hydrometallurgy/precipitation> looks at hydrometallurgical methods for recovering metals through precipitation.

It is an aim of the present invention to provide a safe method for recovering all constituents from a battery and other carbon-containing products, to tackle problems associated with the prior art, or to provide a commercially viable alternative thereto.

According to a first aspect there is provided a method for the recovery of graphite from graphite-containing materials, the method comprising:

- (a) providing a powdered or granulated graphite-containing material;
- (b) mixing a first solution with the powdered or granulated graphite-containing material to form a first mixture and agitating the first mixture,

(c) filtering the first mixture to obtain a first permeate and a first residue,
(d) mixing the first residue with a second solution to dissolve metal therefrom to form a second mixture,
(e) filtering the second mixture to form a second permeate and a second residue,
5 wherein the second residue is a graphite powder;
(f) recovering metals from the second permeate to form a metal-depleted second permeate,
wherein the first solution comprises:
(i) water;
10 (ii) a first organic compound; and
(iii) a second organic compound

Each aspect or embodiment as defined herein may be combined with any other aspect(s) or embodiment(s) unless clearly indicated to the contrary. In particular, any features indicated
15 as being preferred or advantageous may be combined with any other feature indicated as being preferred or advantageous.

The invention involves a number of steps which may be performed sequentially, concurrently or simultaneously. The process may be continuous or batch.

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The present inventors have provided a safe process for the recovery of materials from shredded solid-state battery material, also known as "black mass" and all graphite containing derivatives. The method allows for recovery of a range of materials including metals, non-metals, binders, electrolytes and graphite. Recovery of these materials means that they can
25 be reused to make fresh products and address concerns. Moreover, the process described herein may expanded to all graphite containing or metal containing products such as solar panels, petroleum derivatives, filters and polymer membranes. These products include coke or carbonaceous products of charring and calcining organic materials.

30 Preferably the powdered or granulated graphite-containing material comprises or consist of one or more of:

- (I) shredded solid-state battery material;
- (II) shredded solar panel material; and
- (III) petroleum derivative material.

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Preferably the powdered or granulated graphite-containing material comprises or consist of shredded solid-state battery material. Preferably the shredded solid state battery material is

obtained from shredding de-cased solid state batteries. As a consequence, the first permeate comprises electrolytes and/or binders. Batteries generally consist of a casing surrounding and protecting the inner constituents which are cathode, anode and electrolytes. Materials used in the core include graphite, electrolytes such as LiPF_6 , binders such as methyl carbonate, metals including lithium, copper, nickel, cobalt, aluminium, manganese, and iron. Some of these materials such as LiPF_6 can potentially be dangerous causing explosion or emission of dangerous fumes of hydrofluoric acid. Popular hydrometallurgical process are complex, expensive and introduce sulphates to the mix.

10 This invention is suitable for the treatment of all batteries, particularly solid state batteries such as NMC, LFP, Li-ion, NiMH and alkaline batteries. Batteries at all stages of life including end of life, failed or default batteries can be processed to recover all of their ingredients including binders, electrolytes, graphite, lithium, and all other metals. The process can be applied to specific battery type such as NMC, or a mixture of battery types
15 recovering whatever is in the starting mix. Ideally, the process is applied to “black mass” which is the shredded battery material without the casing. The invented process can also be applied to products similar to batteries which have graphite and / or metal ions such as in petroleum derivatives, semiconductor, superconductor and electronic devices. This invention recovers all components in a safe manner with immeasurably small emissions if any. The
20 invention does not introduce sulphates or other metal ions to the mix.

The first treatment step involves forming a first mixture by the addition of a solution comprising: (i) water; (ii) a first organic compound; and (iii) a second organic compound, preferably an organic solvent. In this step the water provides the majority of the solution. The
25 bulk of the water helps to provide agitation when mixed and dislodges dirt, while solvating any released reactive polar components.

Preferably the first organic compound is one or more selected from the group consisting of benzene, carbon tetrachloride, phenols, toluene, ketones, amines, xylenes, , alcohols,
30 polyamides or esters.

Preferably the second organic compound is a solvent, and preferably is or comprises a long chain ($\text{C}_{16}+$) organic compound, such as an oil.

35 Preferably step (b) is performed at a temperature of from 0°C to 200°C , preferably from 0 to 10°C or from 100 to 200°C . The temperature selected will depend on the material being treated. .

Step (b) is preferably performed for a time of from 30 minutes to 48 hours, preferably 1 to 24 hours.

5 The process then involves a step of c) filtering the first mixture to obtain a first permeate and a first residue. The first permeate is a liquid which, when the method is performed on black mass from a battery, contains electrolyte and binder materials. These can be recovered from the permeate by known techniques and recycled. Even physical separation techniques can be used to achieve a good yield of these materials, with the remainder being recyclable into
10 the process.

The first retentate is a graphite rich solid which is then redispersed into a second solution. The step also desirably involves agitation.

15 Preferably the second solution comprises an acid or alkali, depending on the material. Using such materials helps to dissolve metals from the black mass to provide dissolved ions in solution. These can then be recovered using known techniques in the art. Preferably in step (f) the metals are recovered from the second permeate by electrolysis or precipitation.

20 Preferably filtration in steps (c) and (e) are performed using a mesh filter, preferably less than 5 micron. These mesh filter are suitable for trapping the graphite powder that is typically present in black mass, especially in battery applications. Suitable mesh filters of this type are readily available.

25 Preferably the method is a closed loop method, such that: (A) the first permeate is reused as at least a portion of the first solution, optionally after a separation step to remove dissolved materials from therefrom; and/or (B) the metal-depleted second permeate is reused as at least a portion of the second solution. Preferably any gases released during the process steps are redissolved in water and reused in the process.

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Preferably the method consists of the recited steps disclosed herein.

The inventors have further discovered that the invention can be put into effect without requiring a step of shredding a battery to be treated. Accordingly, preferably the powdered or
35 granulated graphite-containing material is obtained in an initial step of treating an un-shredded, decased battery, comprising of foils, electrolyte, binders and electrode materials, by immersion in a non-aqueous solvent, optionally with agitation. By "decased" it is meant

that the outer casing and/or wrapping of the battery has been removed or at least opened to expose the battery contents.

In this embodiment, the assembly is immersed in a liquid (the non-aqueous solvent) which disengages the electrode material from the foil in part or whole, thereby dropping the powder under gravity with or without agitation by mechanical or ultrasound means. The electrode materials are thereby recovered intact without measurable or significant chemical degradation, and the process of “shredding” can be eliminated. This is a significant reduction in the process complexity.

The non-aqueous solvent preferably comprises of one or a combination of the following polar and non-polar liquids – benzene and its derivatives, toluene, xylene, halogenated hydrocarbons, esters, alcohols, ether, cyclic ethers, acetates and ketones.

A preferred embodiment of the invention will now be described further in which there is a series of steps which process batteries into useful constituents:

1) A process to recover electrolytes and binder from solid state batteries consisting of -

(a) Adding a chemical in solution where the added chemical is selected from a group such as organic dispersants, for example such as benzene, polyamides, alcohols or esters .

(b) Adding a chemical wherein this chemical is one or more selected from a range of organic compounds such phenols, organic acid, organic bases or combinations, carbocyclic and/ or BTEX chemicals such as ketones, amines, xylene and toluene – either alone or a combination thereof.

(c) Further adding an organic solvent optionally comprising such as carbon tetrachloride or acetone to aid with steps (a) and (b).

(d) Stirring the black mass in sequence or together with steps (a) and (b) until the binder, electrolyte are separated from black mass.

(e) Filtering the black mass mix to recover the binder and electrolytes.

These steps produce a cleaned and “safer” black mass or petroleum derivative.

2) The filtrate (also called permeate) from step 1 is ready to be further processed to extract graphite and metals by –

(a) Washing, with or without agitation, the filtrate of Step 1) with a chemical cleaning solution comprising for example of acid or alkali until the metal ions are dissolved.

(b) Filtering, washing and drying the residue to recover the cleaned graphite.

(c) Using the filtrate from step 2 (b) to recover the metals by known methods such as electrolysis or precipitation.

3) All effluents, whether liquids or gases, are recycled back into the process. The gases are dissolved in water and the mix used back into the process. The liquids are recycled, with or without further treatment. Hence the process can be a closed loop process.

Figures

The invention will now be described further in relation to the following non-limiting figures, in which:

Figure 1 shows a flowchart of an example of the process steps in an embodiment of the invention.

As shown in Figure 1, a powdered black mass material is provided in Step A. This is analysed to check its composition by a range of techniques, such as XRD, SEM, ICP, NMR and GCMS to determine the most suitable solutions to be employed.

In Step B the black mass powder is mixed with a first solution. This comprises an excess of water. This provides the mass for the agitation of the black mass and acts as a diluent to help stabilise released metal compounds (such as LiPF_6) released from the mass.

In step C the first mixture formed in step B is filtered. This recovers a safer, cleaner black mass (D) and a permeate (E). The permeate (E) can be processed to remove liquid contaminants and then reused as the first solution. The liquid contaminants will contain components such as binders and electrolytes when the black mass is from a battery.

In step (E) the safer, cleaner black mass (D) is washed with an acid solution which serves to dissolve the metal from the mass and forms a second mixture. The metal is typically metals such as Mn, Li, Co and Ni from battery and may be rare earth metals for petroleum coke materials. In step (G) the second mixture is then filtered, such as with a mesh filter to form a graphite material (H) and a second permeate (I). The second permeate (I) contains the dissolved metal ions which can be separated out by standard techniques such as electrolysis. Once the dissolved metal ions are recovered the remaining acid solution can be recycled into step (E).

Examples

The invention will now be described further in relation to the following non-limiting examples.

Example 1:

5 1 kg of black mass from shredded battery material, which is a granulated powder, is poured into a tank containing 50 L of cold water, 2 L benzene and 100 mL vegetable oil. The mixture is then stirred for 24 h and filtered. The filtrate contains the electrolytes and binders, which are thereby safely removed for storage and further use. The recovered solid powder is a safer version of black mass, and is now washed with a solution of dilute sulfuric acid to
10 extract metal ions. 50 L of 1M sulfuric acid can be mixed with 50 L of water and stirred with the powder for 24 h and filtered. The recovered metal ions are extracted as metals using standard electrolysis processes

Example 2:

15 Example 1 was repeated, but the benzene can be replaced with another phenol, alcohol or ketone, toluene or xylene, the rest of the process being same.

Example 3:

20 Example 1 was repeated, but the vegetable oil was replaced with another surfactant such as stearates, the rest of the process being same.

Example 4:

25 Example 1 was repeated with the raw material now being an un-shredded battery minus the outer metal case. The un-shredded battery is immersed in an organic solvent liquid which will delaminate, unhinge and/ or disperse the electrode material away from the foils by acting on the adhesive and binder mechanisms of the powder to the foils and to the powder itself either in part or fully. The foils can then be recovered and the liquid recycled. The recovered
30 powder can proceed to the next step of the process.

Example 5:

Example 1 was repeated, but the sulfuric acid can be replaced with other acids such as oleic acid, nitric acid, hydrochloric acid or palmitic acid – or mixtures of these the rest of the
35 process being the same.

Example 6:

Example 1 was repeated, the electrolysis process can be replaced by standard precipitation with dilute NaOH solution, ammonia solution, carboxylate solution or mixtures thereof, the rest of the process being the same. The precipitate can then be calcined at temperatures of about 300°C to 900°C to obtain oxides.

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Example 7:

Example 1 was repeated, the temperature of the water in the first step can be kept near 0°C, Rest of the process is same.

10 *Example 8:*

Example 1 was repeated, but steam or superheated steam was used up to 200°C in the first step. Rest of the process is same.

15 In all examples a high-grade graphite product was obtained. This had undergone no change in its physical structure (as can occur in hydrometallurgical processes with highly corrosive acids) and the graphite was suitable for reuse in making fresh batteries. Metals were recovered from the process in a high yield and, because of the closed-loop recycling of the solutions no metals were otherwise lost.

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Claims:

1. A method for the recovery of graphite from graphite-containing materials, the method
5 comprising:
- (a) providing a powdered or granulated graphite-containing material;
 - (b) mixing a first solution with the powdered or granulated graphite-containing material to form a first mixture and agitating the first mixture,
 - (c) filtering the first mixture to obtain a first permeate and a first residue,
 - 10 (d) mixing the first residue with a second solution to dissolve metal therefrom to form a second mixture,
 - (e) filtering the second mixture to form a second permeate and a second residue, wherein the second residue is a graphite powder;
 - (f) recovering metals from the second permeate to form a metal-depleted second
15 permeate,
- wherein the first solution comprises:
- (i) water;
 - (ii) a first organic compound; and
 - (iii) a second organic compound.
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2. The method according to any preceding claim, wherein the powdered or granulated graphite-containing material comprises or consist of one or more of:
- (I) shredded solid-state battery material;
 - (II) shredded solar panel material; and
 - 25 (III) petroleum derivative material.
3. The method according to claim 1 or claim 2, wherein the powdered or granulated graphite-containing material is obtained in a step of treating an un-shredded, decased battery, comprising of foils, electrolyte, binders and electrode materials, by immersion in a
30 non-aqueous solvent, optionally with agitation.
4. The method according to any preceding claim, wherein the powdered or granulated graphite-containing material comprises or consist of shredded solid-state battery material and wherein the first permeate comprises electrolytes and/or binders.
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5. The method according to any preceding claim, wherein the shredded solid state battery material is obtained from shredding de-cased solid-state batteries.

6. The method according to any preceding claim, wherein the first organic compound is selected from the group consisting of benzene, carbon tetrachloride, phenols, alcohols, toluene, ketones, amines, polyamides or esters.
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7. The method according to any preceding claim, wherein step (b) is performed at a temperature of from 0°C to 200°C.
8. The method according to any preceding claim, wherein the second organic
- 10 compound is or comprises a long chain (C16+) organic compound, preferably an oil.
9. The method according to any preceding claim, wherein the second solution comprises an acid or alkali, preferably an acid.
- 15 10. The method according to any preceding claim, wherein the second solution has a pH of less than 5, preferably 1-5.
11. The method according to any preceding claim, wherein in step (f) the metals are recovered from the second permeate by electrolysis or precipitation.
- 20 12. The method according to any preceding claim, wherein filtration in steps (c) and (e) are performed using a mesh filter.
13. The method according to any preceding claim, wherein the method is a closed loop
- 25 method, such that:
- (A) the first permeate is reused as at least a portion of the first solution, optionally after a separation step to remove dissolved materials from therefrom; and/or
- (B) the metal-depleted second permeate is reused as at least a portion of the second
- 30 solution.
14. The method according any preceding claim, wherein the method consists of the recited steps.