

“A METHOD FOR PROCESSING SPENT LITHIUM IRON PHOSPHATE BATTERIES”

FIELD OF THE INVENTION

5 The present invention relates to the field of waste recycling processes. More particularly, the present invention relates to a method for processing spent lithium iron phosphate batteries that involve simple physical and chemical processes to recover valuable metals for reuse or reutilisation.

10 BACKGROUND OF THE INVENTION

Lithium-ion batteries (LIBs) are widely utilized in portable gadgets and electric vehicles due to good performance, high discharge voltage and energy density. With the emergence of electric vehicles, utilizing lithium-ion batteries as energy storage devices, the demand for lithium-ion batteries throughout the entire industry is tremendously increasing.

15 Meanwhile, there is also an increase in waste generated from discarded lithium-ion batteries and other batteries that are posing a challenge to the existing recycling processes. However, because of the high energy density, high safety and low price of lithium-ion batteries, recycling waste lithium-ion batteries is difficult. Because of the toxic chemical compounds in these waste batteries, direct disposal causes major environmental

20 difficulties. The mismanagement of battery waste, if not handled properly, poses negative influence on the environment and resources. Although lithium iron phosphate (LiFePO_4) material is relatively environmental friendly, the corresponding spent LIBs cause potential environmental problems by the electrolyte or improper disposal.

Conventionally, waste lithium iron phosphate (LFP) batteries are recycled using two

25 methods, which are pyrometallurgy (i.e., direct regeneration) and hydrometallurgy (i.e., individual metal leaching). However, emission of toxic gases (such as sulphur dioxide, hydrogen sulfide, carbon dioxide) at high temperatures in these methods was subsequently discovered to be harmful to the environment. Furthermore, the hydrometallurgical recovery of full metal ions (i.e., Li, Fe and P) in solution raises the process cost due to the

30 excessive usage of minerals.

CN109179359A discloses a method of extracting lithium and ferric phosphate from lithium iron phosphate (LiFePO_4) waste material, comprising the steps of immersing lithium iron phosphate powder with sodium hydroxide (NaOH) to obtain an aluminum removal material; performing an aerobic calcination reaction on the aluminum removal material to obtain a calcined material; cooling the calcined material and adding acid to obtain pickle liquor and iron phosphate; performing solid-liquid separation on the pickle liquor to obtain an iron phosphate solid and an acidic lithium liquid; washing the iron phosphate and drying to obtain battery-grade iron phosphate and regulating pH value of the acidic lithium liquid to alkaline level and filtering to obtain a purified lithium liquid.

10 This citation requires an oxygen environment and a high temperature range upto 1050°C to carry out roasting process.

CN112410556B discloses a method for recovering waste lithium iron phosphate powder. The recovery method comprises the steps of adding water and carrying out stirring to obtain lithium iron phosphate waste slurry; adding an acid solution and an oxidant into the lithium iron phosphate waste slurry to obtain acidic lithium iron phosphate waste slurry; adjusting pH to obtain a first lithium-containing solution and first filter residues; adding a second alkaline regulator into the first lithium-containing solution and adjusting pH to obtain a second lithium-containing solution and second filter residues; adding carbonate into the second lithium containing solution to obtain lithium carbonate precipitates; collecting the first filter residues and the second filter residues, washing and then adding a hydrochloric acid solution to obtain an iron-containing solution and third filter residues and adjusting pH to obtain iron phosphate colloid and calcining the iron phosphate colloid to obtain iron phosphate powder. Although, the citation provides the high recovery rate for lithium and recycling of iron phosphate, however, the method is complex, lengthy and tedious. In the process of calcining the iron phosphate colloid, ammonium chloride gas is discharged, ammonium chloride can decompose ammonia and hydrogen chloride at high temperature, therefore, tail gas generated in the process of calcining the iron phosphate colloid cannot be directly discharged to the environment as the environment can be polluted, through collecting the tail gas, therefore, the tail gas is prevented from being directly discharged to the environment. The discharging process for the generated tail gas adds additional cost that makes the method expensive.

WO201836568A1 discloses a method for extracting lithium carbonate from lithium iron phosphate battery waste material, where the lithium iron phosphate material is subjected to oxidative acid hydrolysis, alkali is added to remove iron, and after lithium carbonate is precipitated, the filtrate is a lithium carbonate product. However, the citation discloses a lengthy and in-efficient process.

CN109626350B discloses a method for preparing battery-grade iron phosphate from waste lithium iron phosphate battery positive plates, where the waste lithium iron phosphate positive plate disassembled from the battery at low temperature, crushing and screening to obtain an aluminum sheet and a positive material mainly containing lithium iron phosphate and treating the positive material with an organic solvent after continuously ball-milling to remove organic matters and then the lithium iron phosphate is dissolved by the phosphoric acid and the ferric iron source is subsequently added, so that the utilization rate of the phosphoric acid is improved, more battery-grade iron phosphate is obtained. However, this citation discloses the method of disassembling the battery by heating for long time followed by ball milling and treatment with chemicals to separate positive and negative electrode material before carrying out the process of leaching that makes the method complex.

WU et al., in 2022 (Trans. Nonferrous Met. Soc. China 32(2022) 2071–2079) discloses the selective recovery of lithium from spent lithium iron phosphate batteries using oxidation pressure sulfuric acid leaching system, where oxidation pressure leaching was proposed to selectively dissolve Li from waste LiFePO_4 batteries in a stoichiometric sulfuric acid solution. Using O_2 as an oxidant and stoichiometric sulfuric acid as leaching agent, above 97% of Li was leached into the solution. The lithium is recovered as lithium phosphate. However, this citation discloses the use of pressure leaching, which has been limited to be applied in the hydrometallurgical extraction of non-ferrous metals only and the metals other than lithium remained as impurity in the leaching residue.

Yang et al., in 2018 (Green Chemistry, 2018, 20, 3121-3133; doi: 10.1039/C7GC03376A), discloses a sustainable process for selective recovery of lithium from waste lithium iron phosphate (LFP) batteries, where the lithium leaching was comprehensively investigated. The effects of various parameters on selective recovery of lithium was carried out by using an acidic solution in the presence of hydrogen peroxide under optimized conditions. Although, the citation provides a method to recover lithium

as lithium carbonate, however, the steps of washing precipitated Li_2CO_3 with boiling ultrapure water and drying in a vacuum oven for longer time period of 12 hours makes the process time consuming and complex.

However, the abovementioned prior arts disclosing about waste lithium iron phosphate (LFP) recovery methods have several shortcomings such as complex and complicated process for dismantling of batteries, roasting at a very high temperature range, requirement of additional set up or treatment plant for releasing used gases or effluents to the environment.

Therefore, there is a need to develop a green and viable method for processing spent lithium batteries that is simple, easy to use, economical and eco-friendly, in order to overcome the drawbacks in the purview of cited prior arts.

OBJECT OF THE INVENTION

The main object of the present invention is to provide a method for processing spent lithium iron phosphate batteries.

Another object of the present invention is to provide a method for recovering valuable metals from spent lithium iron phosphate batteries.

Yet another object of the present invention is to provide a method for processing lithium iron phosphate batteries by following simple physical and chemical processes.

Yet another object of the present invention is to provide an environment friendly and commercially feasible method for processing spent lithium iron phosphate batteries.

Still another object of the present invention is to provide a method for processing spent lithium iron phosphate batteries to recover metal having purity in a range of 98-99% and recovery percentage rate is greater than 95%.

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SUMMARY OF THE INVENTION

The present invention provides an environment friendly method for processing spent lithium iron phosphate (LFP) batteries for recovery of iron in the form of iron phosphate by following simple physical and chemical processes that are industrially feasible.

In an embodiment, the present invention provides a method for processing spent lithium iron phosphate (LFP) batteries comprising the steps of: (a) obtaining cells and other components from dismantled and discharged spent lithium iron phosphate (LFP) batteries; (b) shredding the cells obtained in step (a) to obtain a shredded material; (c) roasting the shredded material of step (b) at a pre-defined temperature for a pre-defined time to remove organic matrix and obtaining a roasted material; (d) treating the roasted material of step (c) by a physical process to obtain a slurry and a metal part separately; (e) filtering the slurry of step (d) to obtain a cake and filtrate and reusing the filtrate in next batch; (f) agitating the cake obtained in step (e) with a suitable reagent and water for 3-5 times for a pre-determined time to obtain a leached slurry; (g) filtering the leached slurry of step (f) to obtain a leach liquor and a residue; (h) precipitating selectively iron from the leach liquor of step (g) at a pre-defined pH with a suitable precipitating condition to obtain a precipitated cake and a lithium containing filtrate separately; (i) taking the lithium containing filtrate of step (h) for lithium recovery and washing the precipitated cake obtained in step (h) with water to remove free sodium salt and obtaining a washed cake and (j) drying the washed cake of step (i) at a pre-determined temperature for 2-3 hours to recover iron phosphate.

Here, the other components in step (a) includes printed circuit board, plastic, steel and rubber and the shredding in step (b) is carried out with a twin shaft shredder having an output size in a range of 6-14mm.

The present invention relates to a method that involves simple physical and chemical processes for recovering valuable metals from spent lithium iron phosphate batteries. The process is economically as well as commercially feasible on a large scale recycling of spent LFP batteries. The method for processing spent lithium iron phosphate batteries of the present invention recovers iron in the form of iron phosphate having purity in a range of 98-99%.

The method for processing spent LFP batteries of the present invention recovers iron in the form of iron phosphate having percentage recovery rate in a range of 95-98%.

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

5 BRIEF DESCRIPTION OF THE DRAWINGS

An understanding of the method for processing spent lithium iron phosphate batteries of the present invention may be obtained by reference to the following drawings:

Figure 1 is a schematic representation of a process flow sheet for processing spent lithium iron phosphate batteries according to an embodiment of the present invention.

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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
15 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.
20 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.

25 The present invention relates to an environment friendly method for processing spent lithium iron phosphate (LFP) batteries for recovery of iron in the form of iron phosphate by following simple physical and chemical processes that are industrially feasible.

In a preferred embodiment, the present invention provides a method for processing spent lithium iron phosphate (LFP) batteries comprising the steps of: (a) obtaining cells and

other components from dismantled and discharged spent lithium iron phosphate (LFP) batteries; (b) shredding the cells obtained in step (a) to obtain a shredded material; (c) roasting the shredded material of step (b) at a pre-defined temperature for a pre-defined time to remove organic matrix and obtaining a roasted material; (d) treating the roasted material of step (c) by a physical process to obtain a slurry and a metal part separately; (e) filtering the slurry of step (d) to obtain a cake and filtrate and reusing the filtrate in next batch; (f) agitating the cake obtained in step (e) with a suitable reagent and water for 3-5 times for a pre-determined time to obtain a leached slurry; (g) filtering the leached slurry of step (f) to obtain a leach liquor and a residue; (h) precipitating selectively iron from the leach liquor of step (g) at a pre-defined pH with a suitable precipitating condition to obtain a precipitated cake and a lithium containing filtrate separately; (i) taking the lithium containing filtrate of step (h) for lithium recovery and washing the precipitated cake obtained in step (h) with water to remove free sodium salt and obtaining a washed cake and (j) drying the washed cake of step (i) at a pre-determined temperature for 2-3 hours to recover iron phosphate.

Here, the other components in step (a) include printed circuit board, plastic, steel and rubber and the shredding in step (b) is carried out with a twin shaft shredder having an output size in a range of 6-14mm and the organic matrix in step (c) includes binders and electrolytes.

Further, the pre-defined temperature and pre-defined time of step (c) is in a range of 400-600°C and 2-3 hours, respectively.

The method for processing spent LFP batteries of the present invention provides the physical process in step (d) that includes washing of the roasted material with water followed by wet sieving to obtain said slurry and the metal part separately. The metal part obtained in step (d) includes mix foils having size in a range of 1-3mm.

Additionally, the suitable reagent in step (f) is sulphuric acid in an amount ranging from 0.4 -0.6 times weight of the cake obtained in step (e) and the predetermined time to obtain the leached slurry of step (f) is 2-4 hours. The suitable precipitating condition of step (h) includes agitating the leach liquor of step (h) with 30% w/v soda ash solution and 0.5-2% v/v hydrogen peroxide for 2-3 hours followed by filtration and the pre-defined pH in step

(h) is in a range of 1.0-3.0. The lithium containing filtrate obtained in step (h) is having lithium concentration in a range of 2.8-2.9g/L.

The method for processing spent lithium iron phosphate batteries of the present invention recovers iron in form of iron phosphate having purity in a range of 98-99%.

- 5 The method for processing spent LFP batteries of the present invention recovers iron in form of iron phosphate having percentage recovery rate in a range of 95-98%.

Referring to **Figure 1**, a process flow sheet for processing spent lithium iron phosphate batteries is illustrated. The process flow sheet represents the step by step simple physical and chemical processes such as discharging of spent LFP batteries, dismantling, shredding,
10 roasting, wet sieving, filtration, leaching, precipitation washing with water that are employed in the method for processing spent LFP of the present invention.

EXAMPLE 1

Method for processing spent lithium iron phosphate batteries

15 **Batch 1**

In batch 1, 7.1 kg of spent lithium iron phosphate (LFP) batteries were discharged and dismantled manually to get 4.83 kg of cells and 2.27 kg of other components (PCB, plastic, steel and rubber). The cells (4.83 kg) were shredded and then roasted at 500°C for 2 hours. The roasted material (3.84 kg) obtained was washed with water followed by sieving to get
20 2.8 kg cake of black mass (dry weight-1.96 kg) and 1.88 kg of steel-casing and foil. **Table 1** represents the detailed material balance of the mechanical operation to get black mass.

Table 1: Material balance of the mechanical operation to get black mass

Step No	Process steps	Input details			Output details		
		Material	Batch 1	Batch 2	Material	Batch 1	Batch 2
			quantity, kg	quantity, kg		quantity, kg	quantity, kg
1	Discharging	Spent LIBs (LFP batteries)	7.1	7.105	Discharged batteries	7.1	7.11
2	Dismantling	Discharged batteries	7.1	7.11	Cells	4.83	4.84
					Other components(Al, PCB, plastic, steel, rubber)	2.27	2.27
3	Shredding	Cells	4.83	4.84	Shredded material	4.83	4.84
4	Roasting	Shredded material	4.83	4.84	Roasted material	3.84	3.89
5	Washing/wet sieving	Roasted material	3.84	3.89	Roasting loss	0.99	0.94
					Black mass (dry wt)	1.96	1.99
					steel-casing & foils	1.88	1.91

From the obtained black mass, 1 kg of material was agitated with 0.57 kg of sulphuric acid and 5 L of water for 4 hours. After 4 hours, the slurry was then filtered to get the leach liquor (5 L) and the residue (0.49 kg – dry wt.). The analysis of black mass, leach liquor and residue of batch 1 is given in **Table 2**.

Table 2: Analysis of black mass, leach liquor and residue of batch 1

Material description	Unit	Analysis of Elements			
		Fe	Li	P	Al
Black mass	%	20	2	12	0.2
Leach liquor	g/L	38.5	4.2	22	0.3
Residue	%	1.5	0.37	2	0.1

To the leach liquor (5 L), 2.49 L of soda ash solution 25% (w/v) and 35mL of hydrogen peroxide were added under agitation for 2 hours. The slurry was filtered and the filtrate was taken for lithium recovery while the cake was further washed with water (1:5). The washed cake was dried at 110°C for 3 hours to get ferric phosphate (0.65 kg). The analysis of filtrate and wash liquor obtained after post-treatment of leach liquor of batch 1 is given in **Table 3**.

Table 3: Analysis of elements after post-treatment of leach liquor of batch 1

Material description	Unit	Analysis of Elements				
		Fe	Li	P	Al	
Fltrate	g/L	0.05	2.8	0.0	0.3	56.1
Wash liquor	g/L	0.0	0.0	0.0	0.0	17.9

Batch 2

In batch 2, 7.105 kg of spent LFP batteries were discharged and dismantled manually to get 4.835 kg of cells and 2.27 kg of other components (PCB, plastic, steel and rubber). The cells (4.835 kg) were shredded and then roasted at 500°C for 2 hours. The roasted material (3.89 kg) obtained was washed with water followed by sieving to get 2.92 kg cake of black mass (dry weight-1.99 kg) and 1.91 kg of steel-casing and foil. **Table 1** represents the detailed material balance of the mechanical operation to get black mass.

From the obtained black mass, 1 kg of material was agitated with 0.576 kg of sulphuric acid and 5 L of water for 4 hours. After 4 hours, the slurry was then filtered to get the leach liquor (5 L) and the residue (0.49 kg, dry wt.). The analysis of black mass, leach liquor and residue of batch 2 is given in **Table 4**.

Table 4: Analysis of black mass, leach liquor and residue of batch 2

Material description	Unit	Analysis of Elements			
		Fe	Li	P	Al
Black mass	%	20.2	2.2	12.6	0.2
Leach liquor	g/L	38.9	4.2	23.0	0.2
Residue	%	1.5	0.20	2.0	0.1

To the leach liquor (5 L), 2.49 L of soda ash solution 25% (w/v) and 35 mL of hydrogen peroxide were added under agitation for 2 hours. The slurry was filtered and the filtrate was taken for lithium recovery while the cake was further washed with water (1:5). The washed cake was dried at 110°C for 3 hours to get iron phosphate/ferric phosphate (0.66 kg). The analysis of filtrate and wash liquor obtained of batch 2 is given in **Table 5**.

Table 5: Analysis of elements after post-treatment of leach liquor of batch 2

Material description	Unit	Analysis of Elements				Na
		Fe	Li	P	Al	
Filtrate	g/L	0.06	2.9	0.0	0.2	54.4
Wash liquor	g/L	0.0	0.0	0.0	0.0	17.3

The impurity profile of the products obtained in batches 1 and 2 was determined by Microwave Plasma Atomic emission spectra (MP-AES) and purity was analyzed by titration. The analysis of iron phosphate obtained in batches 1 and 2 is given in **Table 6**.

Table 6. Chemical analysis of iron phosphate

Elements, %	Batch No	
	I	II
Cu	0.076	0.076
Ni	0.0001	0.0001
Co	0.0001	0.0001
Li	0.1	0.073
Mn	0.0001	0.0001
Al	0.61	0.52
Ca	0.029	0.015
Mg	0.019	0.012
Na	1.01	1.01
Assay	98.16	98.29

Therefore, the present invention provides an economical, environment-friendly, simple and industrially feasible method for processing spent lithium iron phosphate batteries to recover iron in the form of iron phosphate having percentage recovery rate in a range of 95-98% and purity in a range of 98-99%.

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. A method for processing spent lithium iron phosphate (LFP) batteries, characterized in that, the method comprising the steps of:
 - 5 a) obtaining cells and other components from dismantled and discharged spent lithium iron phosphate (LFP) batteries;
 - b) shredding the cells obtained in step (a) to obtain a shredded material;
 - c) roasting the shredded material of step (b) at a pre-defined temperature for a pre-defined time to remove organic matrix and obtaining a roasted
10 material;
 - d) treating the roasted material of step (c) by a physical process to obtain a slurry and a metal part separately;
 - e) filtering the slurry of step (d) to obtain a cake and filtrate and reusing the filtrate in next batch;
 - 15 f) agitating the cake obtained in step (e) with a suitable reagent and water for 3-5 times for a pre-determined time to obtain a leached slurry;
 - g) filtering the leached slurry of step (f) to obtain a leach liquor and a residue;
 - h) precipitating selectively iron from the leach liquor of step (h) at a pre-defined pH with a suitable precipitating condition to obtain a precipitated cake and
20 a lithium containing filtrate separately;
 - i) taking the lithium containing filtrate of step (h) for lithium recovery and washing the precipitated cake obtained in step (h) with water to remove free sodium salt and obtaining a washed cake; and
 - 25 j) drying the washed cake of step (i) at a pre-determined temperature for 2-3 hours to recover iron phosphate.
2. The method for processing spent LFP batteries as claimed in claim 1, wherein the other components in step (a) include printed circuit board, plastic, steel and rubber.
- 30 3. The method for processing spent LFP batteries as claimed in claim 1, wherein the shredding in step (b) is carried out with a twin shaft shredder having an output size in a range of 6-14mm.

4. The method for processing spent LFP batteries as claimed in claim 1, wherein the pre-defined temperature and pre-defined time of step (c) is in a range of 400-600°C and 2-3 hours, respectively and the organic matrix obtained in step (c) includes binders and electrolytes.
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5. The method for processing spent LFP batteries as claimed in claim 1, wherein the physical process in step (d) includes washing of the roasted material with water followed by wet sieving to obtain said slurry and the metal part separately.
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6. The method for processing spent LFP batteries as claimed in claim 1, wherein the metal part obtained in step (d) includes mix foils having size in a range of 1-3mm.
7. The method for processing spent LFP batteries as claimed in claim 1, wherein the suitable reagent in step (f) is sulphuric acid in an amount ranging from 0.4-0.6 times weight of the cake obtained in step (e) and the predetermined time to obtain the leached slurry of step (f) is 2-4 hours.
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8. The method for processing spent LFP batteries as claimed in claim 1, wherein the suitable precipitating condition of step (h) includes agitating the leach liquor of step (h) with 30% w/v soda ash solution and 0.5-2% v/v hydrogen peroxide for 2-3 hours followed by filtration and the pre-defined pH in step (h) is in a range of 1.0-3.0.
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9. The method for processing spent LFP batteries as claimed in claim 1, wherein the lithium containing filtrate obtained in step (h) is having lithium concentration in a range of 2.8-2.9g/L.
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10. The method for processing spent LFP batteries as claimed in claim 1 wherein the pre-determined temperature in step (j) is in a range of 110°C and the recovered iron phosphate in step (j) is having purity in a range of 98-99%.
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11. The method for processing spent LFP batteries as claimed in claim 1, wherein said method recovers iron in form of iron phosphate having percentage recovery in a range of 95-98%.

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