

PROCESS FOR RECYCLING LITHIUM IRON PHOSPHATE BATTERIES

FIELD OF INVENTION

The present invention generally relates to a method for recycling spent lithium-ion batteries.

5 More particularly, it relates to a method for recycling spent lithium iron phosphate batteries.

BACKGROUND

Lithium-ion batteries contain valuable materials which would go to waste when the batteries are spent and discarded. With the rising use of lithium-ion batteries, the recovery of valuable materials from spent lithium-ion batteries have become an important industry. In particular, lithium iron phosphate ("LFP") batteries are becoming a common type of lithium-ion batteries. The consumption of LFP batteries is increasing sharply in electric vehicles and power grids in preference to other types of lithium-ion batteries because they tend to be cheaper, safer and last longer. Therefore, the LFP presence in lithium-ion batteries' waste streams cannot be simply ignored, even though most processes focus solely on the recovery of nickel, cobalt and manganese.

Post-consumption of lithium-ion batteries, especially LFP batteries could alleviate the life cycle impact of electric vehicles by almost 50% [1]. The global warming potential associated with the production of every kg of LFP active material calculated using life cycle analysis hovers around 19 to 55 MJ. Therefore, recycling all lithium-ion batteries, not just the ones rich in nickel, cobalt and manganese will be a great opportunity for boosting the local economies as long circular economy principles are in place.

25 Conventionally, spent LFP batteries are first dismantled to separate out their cathodes. The cathodes are then crushed or shredded for recycling. The rest of the spent LFP batteries, for example, the anodes, are discarded as waste. Separating different parts of the batteries is very labour intensive and time consuming. Therefore, conventional recycling methods are not able to adequately handle the recycling of battery parts of LFP batteries, specifically from black mass which is obtained by shredding spent batteries and comprises both cathodes and anodes without first undergoing further pre-processing prior to recycling.

Present efforts of recycling LFP batteries tend to focus on the recovery of lithium to the detriment of other less expensive but nonetheless usable materials like iron and iron phosphate. CN107240731B, describes methods of obtaining lithium from LFP batteries in the form of lithium carbonate through chemical processes, without referring to obtaining iron or

iron phosphate. Consequently, significant quantities of such materials are allowed to be discarded as waste instead of being recovered.

LFP black mass contains many types of impurities that could adversely affect the purity of valuable materials recovered from recycling. This black mass needs to undergo further processing including chemical separation to remove impurities such as fluoride, aluminium, and copper. Conventional processes for recycling black mass obtained from other types of batteries typically remove aluminium by changing pH levels which is similar process for LFP results in iron being removed together with the aluminium. Conventional processes typically remove copper by cementation or by precipitation through addition of sodium hydroxide but utilizing this process for LFP black mass results in other elements such as iron phosphate being removed with the copper. These methods of removing such impurities do not allow for any isolated recovery of such elements as they are removed together with other elements.

Aluminium plays a pivotal role as a cathodic current collector in lithium-ion batteries and LFP batteries are no exception. Failure to separate aluminium current conductor from the active material could decrease the capacity of regenerated cathodes by almost 40 percent if aluminium's molar ratio to the active material exceeds 3 percent. Additionally, in known LFP processes, removal of impurities is a necessary step to isolate and recover valuable materials (e.g., lithium) for reuse, but results in other usable materials being merely discarded as waste [2, 3].

Further, conventional LFP battery recycling processes do not properly address removal of fluorine. Tasaki, Ken, et al. [4] illustrates this by describing the dangers of the presence of hydrogen fluoride as a result of lithium hexafluorophosphate, which is present in most lithium-ion batteries, in electrolyte solutions reacting with small amounts of water or alcohols, without offering any solutions. Fluorine compounds are corrosive and could damage recycling equipment, have a negative impact on the purity of elements that may be subsequently extracted, and have a damaging effect on battery performance.

Thus, there exists a need for an LFP battery recycling process which reduces the loss of valuable materials and a need to better handle the removal of impurities.

The invention seeks to answer these needs. Further, other desirable features and characteristics will become apparent from the rest of the description read in conjunction with the accompanying drawings.

SUMMARY OF INVENTION

In one aspect of the invention, there is provided a method of recycling black mass obtained from lithium iron phosphate batteries, comprising an alkaline leaching step, comprising adding an alkaline solution with a pH of 13-14 to the black mass to obtain a first leachate and a first solid residue, an acid leaching step, comprising adding a 4M-6M acid solution to the first solid residue for a first duration to obtain a second leachate, passing the second leachate through a first ion-exchange column wherein fluoride ions from the second leachate are retained in the first resin column to obtain a first eluate, passing the first eluate through a second ion-exchange column wherein copper ions from the first eluate are retained in the second resin column to obtain a second eluate, an iron precipitation step, comprising raising the pH of the second eluate to 2.5-5 and adding a quantity of phosphoric acid to the second eluate, to obtain a first solution and an iron (III) phosphate precipitate, combining the first leachate and the first solution to obtain a second solution and adjusting the pH of the second solution to about 6.5 to obtain a residual precipitate and a lithium solution, wherein the quantity of phosphoric acid is sufficient to achieve an equivalent stoichiometric ratio of ferric iron and phosphate anions in the second eluate.

Optionally, the acid solution is selected from a group consisting of sulphuric acid and hydrochloric acid. Optionally, the acid leaching step further comprises diluting the acid solution by about $\frac{1}{2}$ and adding a first oxidising agent to the acid solution for a second duration to obtain the second leachate. Optionally, the first and second duration are each about 30-60 minutes and run consecutively. Optionally, the iron precipitation step further comprises adding a second oxidising agent to the second eluate.

Optionally the first and/or second oxidising agent are selected from a group consisting of hydrogen peroxide, ozone, oxygen, chlorine and potassium permanganate. Optionally, the first and/or second oxidising agent added is hydrogen peroxide and about 500ml per kg of the black mass. Optionally, the iron (III) phosphate precipitate has a purity of >99.5%. Optionally, the residual precipitate comprises mainly aluminium hydroxide, copper (II) hydroxide, calcium fluoride and iron (III) hydroxide.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a block diagram depicting a lithium iron phosphate recycling process according to a primary embodiment of the present invention.

Fig. 2 depicts an XRD analysis graph of the precipitate obtained from a first solution.

DETAILED DESCRIPTION

In the following detailed description, reference is made to the accompanying drawings which form a part hereof. The processes and systems described in the detailed description and drawings are for illustrative purposes and are not meant to be limiting. Other embodiments
5 can be utilised, and other changes can be made, without departing from the scope of the disclosure presented herein. In the present disclosure, depiction of a given element or consideration or use of a particular element number in a particular Fig. or a reference thereto in corresponding descriptive material can encompass the same, an equivalent, or an analogous element or element number identified in another Fig. or descriptive material
10 associated therewith.

Black mass is prepared by crushing/shredding at least the cathodic and anodic LFP battery materials all together. The black mass may collectively include all the key elements of spent LFP batteries, including both anodic and cathodic materials.

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Referring to Fig. 1, a block diagram **100** depicting a lithium iron phosphate recycling process according to a primary embodiment of the present invention is depicted. The black mass obtained earlier is subjected to an alkaline leaching step. An alkaline solution of pH 13-14 is added to the black mass to obtain a first leachate and a first solid residue to leach aluminium
20 present in the black mass into the first leachate **101**. In a non-limiting example, the alkaline solution is a 10% sodium hydroxide solution. While a strong alkali i.e., one that fully ionises in water, is preferred, it would be readily apparent to a skilled person that any alkali can be used so long as the resultant pH is 13-14 and the alkali does not introduce unwanted contaminants such as aluminium hydroxide. Examples of suitable alkali include sodium hydroxide, lithium
25 hydroxide, and potassium hydroxide.

The amount of alkaline solution used should be proportionate to the quantity of black mass used and of a volume that is at least sufficient to allow full immersion of the black mass in the alkaline solution. By way of example, 18-25l of sodium hydroxide solution for every 1kg of
30 black mass may be used. Preferably, 20l of sodium hydroxide solution for every 1kg of black mass is used. Preferably, a reaction temperature of 60-80°C is attained. Preferably the reaction time is 30-60 minutes. Preferably, mechanical agitation is provided throughout the reaction time to ensure high levels of aluminium enter solution and homogeneity of the first leachate.

35 The first solid residue is subjected to an acid leaching step. 4M-6M of an acid solution is added to the first solid residue for a first duration to obtain a second leachate **102**. Preferably, and at the end of the first duration, the acid solution is diluted by about ½ and an oxidising agent is

added to the acid solution for a second duration to obtain the second leachate. Preferably the oxidising agent is selected from a group consisting of hydrogen peroxide, ozone, oxygen, chlorine and potassium permanganate. More preferably the oxidising agent is hydrogen peroxide. As a very low pH is desired, the acid solution is preferably a strong acid i.e., one that fully dissociates into its ions in an aqueous solution. In a non-limiting example, the acid solution is a sulphuric acid solution. It would be readily apparent to a skilled person that any acid solution can be used so long as the acid solution does not introduce unwanted contaminants. The amount of acid solution used should be proportionate to the quantity of the black mass used and of a volume that is at least sufficient to allow full immersion of the first residue in the acid solution. Approximately 95% of the iron and copper and 70% of lithium are expected to enter the second leachate.

The first and second duration are preferably each about 30-60 minutes and run consecutively. Preferably, a reaction temperature of 60-80°C is maintained throughout the first and second duration. Preferably, mechanical agitation is provided throughout the first and second duration.

By way of example, 8-10l of sulphuric acid is added to the first solid residue for every 1kg of starting quantity of black mass used for a first duration. At the end of the first duration, 8-10l of deionised water is added to dilute the acid solution by about 1/2 with a first oxidising agent being concurrently added for a second duration, the first and second duration being each about 30-60 minutes. The first oxidising agent is preferably selected from a group consisting of hydrogen peroxide, ozone, oxygen, chlorine and potassium permanganate. The first oxidising agent is more preferably hydrogen peroxide and added in quantity of 400-600ml per kg of black mass but most preferably 500ml per kg of black mass.

At the end of the second duration, the second leachate may optionally be put through a press filter to separate graphite residue from the second leachate. The filter membrane may be made of polypropylene, cellulose acetate, polyvinylidene fluoride. The filter membrane should preferably have pore size of 2-15 micron. A skilled person will readily appreciate that other filter membrane materials may be employed so long as it does not degrade when subject to the temperature and pH of the second leachate and is of the appropriate pore size. In this manner, the second leachate passes through the membrane whilst the graphite residue is retained by the filter.

While a significant quantity of approximately 28% of the fluoride ions are expected to enter the first leachate during the alkaline leaching stage, sufficiently undesirable amounts which may damage recycling equipment, have a negative impact on the purity of subsequent extracted

elements, and have a negative effect on subsequent battery performance will remain as fluoride ions in the second leachate and will need to be removed. To this end, the second leachate is passed through a first ion exchange column where fluoride ions from the second leachate are retained in the first ion exchange column to obtain a first eluate **103**.

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In a preferred embodiment of the invention, the first ion exchange column is a fixed bed column comprising a fluoride selective ion exchange resin, the resin being a chelating resin loaded with aluminium ions and comprises a polymer structure of gel polystyrene crosslinked with divinylbenzene and sulfonic acid functional group. It will be readily understood by a skilled person that any ion exchange column that is highly selective for fluoride ions in acidic conditions may be employed in this manner.

The second leachate is cooled to a temperature of approximately 30-40 °C before being passed through the first ion exchange column with a retention time of about 10-40 minutes depending on the specific properties of the chelating resin. As the second leachate is passed through the first ion exchange column, fluoride ions present in the second leachate come into contact with the functional group of the chelating resin resulting in an exchange of chloride for fluoride, with the fluoride being retained in the first ion exchange column while the first eluate is passed out of the first ion exchange column with only trace amounts of fluoride ions present in the first eluate. The first ion exchange column can be regenerated by running an aluminium solution, for example an aluminium chloride solution of $\leq 35\text{g/l}$ concentration. In this manner, fluoride ions retained in the first ion exchange column and be subsequently eluted out and recovered for subsequent reuse.

The first eluate is then passed through a second ion exchange column where copper ions present in the first eluate are retained in the first resin column to obtain a first eluate **104**. In a preferred embodiment of the invention, the second ion exchange column is a fixed bed column comprising a cationic exchange resin. The cationic exchange resin preferably comprises a copolymer of styrene-divinylbenzene, gel matrix, and bis-picolylamine functional group. The functional group of the cationic exchange resin may optionally be polyethyleneimine, aminomethylphosphonic acid, iminodiacetic acid, carboxylic acid, or any other suitable functional group with a high affinity for copper ions. The gel matrix may optionally be epoxy, modified epoxy, polyester, or other suitable matrix systems. An example of a suitable cationic exchange resin is Dupont AMBERSEP™ M4195. It will be readily understood by a skilled person that any ion exchange column that is highly selective for copper in acidic conditions may be employed in this manner.

The first eluate is passed through the second ion exchange column with a retention time of approximately 10-40 min, depending on the resin characteristics. Stoichiometric and efficient removal is possible due to higher Cu^{2+} affinity than X^+ for cation exchange sites, i.e., the copper- X separation constant is greater than 1 ($\alpha_{\text{Cu/X}} > 1$) (where X is a random cationic resin). The copper ions are thus selectively retained in the second ion exchange column while a second eluate is passed out. The copper ions may be recovered and reused. The cationic exchange resin used for copper extraction can be regenerated and reused for subsequent cycles of copper extraction. Resin regeneration is done by using a 4M-6M sulfuric acid (HCl or nitric acid can be used instead). Acidic solution passes through the resin column from top to bottom or vice versa to remove the copper ions from the resin.

The second eluate is subjected to further processing where an iron (III) phosphate precipitate is obtained from the second eluate. The pH of the first eluate is also raised to about 2.5-5 to allow iron (III) phosphate to precipitate to obtain a first solution **105**. The pH may be raised by adding an alkali such as sodium hydroxide till the desired pH of about 2.5-5 is obtained. It will be readily understood by a skilled person that any alkali can be added so long as it does not introduce contaminants. A quantity of phosphoric acid is subsequently added to the first solution until equivalent stoichiometric ratios of ferric iron and phosphate anions in the solution are achieved. The amount of ferric ions in the first solution and accordingly, the amount of phosphoric acid to add since the ratio will be skewed toward ferric ions can be derived from the expected quantity of ferric iron present in the starting quantity of black mass used. The iron (III) phosphate can then be separated from the first solution by physical means such as a press filter. In a preferred embodiment a second oxidising agent is also added to the second eluate to facilitate the oxidation of ferrous ions present in the first solution to ferric ions. The second oxidising agent is preferably selected from a group consisting of hydrogen peroxide, ozone, oxygen, chlorine and potassium permanganate. The second oxidising agent is more preferably hydrogen peroxide and added in quantity of 400-600ml per kg of black mass but most preferably 500ml per kg of black mass.

Referring to Fig. 2, the peak in the graph shows a high concentration of iron (III) phosphate without other obvious peak in the graph indicating high purity of the iron (III) phosphate. Subsequent analysis by inductively coupled plasma - optical emission spectrometry (results not shown) revealed a purity of at least 99.5% purity of the iron (III) phosphate product obtained from the precipitate.

The first solution which now contains mainly sodium and lithium cations is subsequently combined with the first leachate obtained during the alkaline leaching step as described earlier to obtain a second solution. The pH of the second solution is then adjusted to about 6.5 by adding an alkaline or acidic solution as required to obtain a residual. Since the pH of the first leachate is alkaline while the pH of the first solution is acidic, the resultant second may have a pH that is higher or lower than about 6.5. By way of example, the pH can be lowered to about 6.5 by adding sulphuric acid or can be raised by adding sodium hydroxide, potassium hydroxide or lithium hydroxide. Alternatively, the pH of the second solution may also be raised by adding deionised water. It will be readily understood by the skilled addressee that any acid or alkali can be used to adjust the pH of the second solution so long as it does not introduce contaminants for example aluminium hydroxide.

Optionally, lime also known as calcium hydroxide can also be added to the second solution to remove any fluoride ions present by way of precipitation as calcium fluoride that may be present in the first leachate. The amount of calcium hydroxide added to the second solution should be proportionate to the amount of fluoride present and is preferably about 1% w/v. The pH adjustment will allow the precipitation of a residual precipitate to be obtained along with a lithium solution **106**. Preferably the residual precipitate comprises mainly aluminium hydroxide, copper (II) hydroxide, calcium fluoride and iron (III) hydroxide. Preferably the precipitation occurs over a duration of about 1 hour. Preferably a temperature of about 50-60°C is maintained throughout the precipitation. Preferably the second solution is subject to mechanical agitation during precipitation. The residual precipitate can then be physically separated by way of a press filter to obtain a lithium solution that is largely free of contaminants and can be subjected to further processing to recover the lithium present.

Table 1 depicts the concentrations (g/l) of the elements of interest present in the respective solutions obtained throughout the process.

	Concentration of different elements in solution (g/l)				
	First leachate	Second leachate	First eluate	Second eluate	First solution
Fe	0	11.6	11.6	11.6	0
Al	1.2	0	0	0	0
F	0.7	0.3	0	0	0
Cu	0	0.11	0.11	0	0
P	5	1.5	1.5	1.5	0

Table 1

References

- [1] Larouche, F., Tedjar, F., Amouzegar, K., Houlachi, G., Bouchard, P., Demopoulos, G.P., Zaghib, K., 2020. Progress and Status of Hydrometallurgical and Direct Recycling of Li-Ion Batteries and Beyond. *Materials* 13, 801. <https://doi.org/10.3390/ma13030801>
- [2] Federica Forte, Massimiliana Pietrantonio, Stefano Pucciarmati, Massimo Puzone & Danilo Fontana (2020): Lithium iron phosphate batteries recycling: An assessment of current status, *Critical Reviews in Environmental Science and Technology*, DOI: 10.1080/10643389.2020.1776053.
- [3] Tingting Yan, Shengwen Zhong, Miaomiao Zhou, Xiaoming Guo, Jingwei Hu, Fangfang Wang, Fantao Zeng, and Sicheng Zuo: High-efficiency method for recycling lithium from spent LiFePO_4 cathode. *Nanotechnology Reviews* 2020; 9: 1586–1593.
- [4] Decomposition of LiPF_6 and Stability of PF 5 in Li-Ion Battery Electrolytes: Density Functional Theory and Molecular Dynamics Studies." *Journal of the Electrochemical Society* 150.12 (2003): A1628. DOI: 10.1149/1.1622406

CLAIMS

1. A method of recycling black mass obtained from lithium iron phosphate batteries, comprising:

an alkaline leaching step, comprising adding an alkaline solution with a pH of 13-14 to the black mass to obtain a first leachate and a first solid residue;

an acid leaching step, comprising adding a 4M-6M acid solution to the first solid residue for a first duration to obtain a second leachate;

passing the second leachate through a first ion-exchange column wherein fluoride ions from the second leachate are retained in the first resin column to obtain a first eluate;

passing the first eluate through a second ion-exchange column wherein copper ions from the first eluate are retained in the second resin column to obtain a second eluate;

an iron precipitation step, comprising raising the pH of the second eluate to 2.5-5 and adding a quantity of phosphoric acid to the second eluate, to obtain a first solution and an iron (III) phosphate precipitate;

combining the first leachate and the first solution to obtain a second solution; and

adjusting the pH of the second solution to about 6.5 to obtain a residual precipitate and a lithium solution;

wherein, the quantity of phosphoric acid is sufficient to achieve an equivalent stoichiometric ratio of ferric iron and phosphate anions in the second eluate.

2. The method according to claim 1, wherein the acid solution is selected from a group consisting of sulphuric acid and hydrochloric acid.

3. The method according to claim 1, wherein the acid leaching step further comprises diluting the acid solution by about $\frac{1}{2}$ and adding a first oxidising agent to the acid solution for a second duration to obtain the second leachate.

4. The method according to claim 1, wherein the iron precipitation step further comprises adding a second oxidising agent to the second eluate.

5. The method according to claim 3, wherein the first and second duration are each about 30-60 minutes and run consecutively.
6. The method according to claims 3 or 4, wherein the first and/or second oxidising agent are selected from a group consisting of hydrogen peroxide, ozone, oxygen, chlorine and potassium permanganate.
7. The method according to claim 6, wherein the first and/or second oxidising agent added is hydrogen peroxide and about 500ml per kg of the black mass.
8. The method according to claim 1, wherein the iron (III) phosphate precipitate has a purity of >99.5%.
9. The method according to claim 1, wherein the residual precipitate comprises mainly aluminium hydroxide, copper (II) hydroxide, calcium fluoride and iron (III) hydroxide.