METHOD FOR PREPARING LITHIUM MANGANESE IRON PHOSPHATE CATHODE MATERIAL BY RECYCLING SPENT LITHIUM IRON PHOSPHATE

TECHNICAL FIELD

The present invention relates to the technical field of battery material recycling and reuse, particularly to a method for preparing a lithium manganese iron phosphate ($LiMn_{1-x}Fe_xPO_4$, LMFP) cathode material by recycling spent lithium iron phosphate ($LiFePO_4$, LFP).

BACKGROUND

With the rapid growth of global demand for renewable energy and electric vehicles, lithium-ion batteries have been widely used as an efficient and environmentally friendly energy storage device. LFP cathode materials have become one of the mainstream choices in the field of power batteries due to the high safety, long cycle life, and low cost. However, with the increase in battery usage, a large number of spent LFP batteries are also produced, which not only causes a waste of resources, but also may cause environmental pollution. Therefore, how to efficiently recycle and reuse these spent battery materials has become an important issue in the current lithium-ion battery industry chain.

At present, in the prior art, there have been some studies on recycling spent LFP batteries to prepare cathode materials. For example, the Chinese patent document with publication number CN117977038A provides a method for recycling spent LFP batteries to generate LMFP cathode materials. In this method, organic acid leaching and solid-state sintering are used to obtain LMFP cathode materials. Although the existing technology has made some progress in the recovery of spent LFP and the preparation of LMFP cathode materials, there are still many shortcomings. Existing processes generally have problems such as high energy consumption and complex process flow, which limits the large-scale industrial application. In addition, the recycling and reuse of spent batteries may lead to the degradation of material properties. Therefore, a more efficient, environmentally friendly and economical method for preparing LMFP cathode materials by recycling spent LFP is required to achieve the high-value utilization of spent LFP and meet the performance requirements of LMFP cathode materials to solve the problems existing in the prior art.

SUMMARY

An objective of the present invention is to provide a method for preparing an LMFP cathode material by recycling spent LFP to solve the problems raised in the above background.

To achieve the above objective, the present invention provides the following technical solutions.

The present invention provides a method for preparing an LMFP cathode material by recycling spent LFP, including the steps of:

S1: pretreating spent LFP electrode pieces, followed by calcining in an inert atmosphere, and obtaining spent LFP black powder;

S2: mixing the spent LFP powder with a lithium source, a manganese source and a phosphorus source in a solution, and preparing an intermediate product via a hydrothermal/solvothermal method; and

S3: mixing the intermediate product with a carbon source, followed by ball-milling, calcining the obtained material in an inert atmosphere, and obtaining a regenerated LMFP material after the completion of sintering and natural cooling.

In a further solution of the present invention, in S1, the pretreatment method for the spent LFP electrode pieces includes the steps of soaking the spent LFP electrode pieces in an organic solvent for 6-24 hours, taking the electrode pieces out, followed by air-drying; and the organic solvent used includes at least one of dimethyl carbonate, ethylene carbonate, ethyl methyl carbonate, diethyl carbonate, and propylene carbonate.

In a further solution of the present invention, the calcination conditions for the spent LFP electrode pieces in S1 are that a heating rate is 2-10°C$\cdot$min^{-1}, the temperature is raised to 400-600°C, and the temperature is maintained for 1-5 hours.

In a further solution of the present invention, in S2, the lithium source includes at least one of lithium hydroxide, lithium carbonate, lithium acetate, lithium nitrate, and lithium oxalate, with lithium hydroxide being preferred; the manganese source includes at least one of manganese sulfate, manganese carbonate, manganese chloride, manganese acetate, manganese phosphate, and manganese hydroxide, with manganese sulfate being preferred; and the phosphorus source includes at least one of phosphoric acid, ammonium dihydrogen phosphate, and diammonium hydrogen phosphate, with phosphoric acid being preferred.

In a further solution of the present invention, a molar ratio of the spent LFP black powder and the manganese source in S2 is (1-9):(9-1); and a molar ratio of the manganese source, phosphorus source and lithium source is 1:1:x, and $1 \leq x \leq 3$.

In a further solution of the present invention, the solvent in S2 is a mixed solvent of an organic solvent and water, and the organic solvent includes at least one of ethylene glycol, polyethylene glycol, isopropanol, n-butanol, and glycerol, with ethylene glycol being preferred.

In a further solution of the present invention, in S2, the mixing reaction conditions are as follows: the mixture is placed in an oven, heated to 100-200°C at a rate of 2-5°C/min, held at that temperature for 10-24 hours, and cooled along with the oven.

In a further solution of the present invention, the intermediate product obtained in S2 is a biphasic mixture of LFP and LMFP.

In a further solution of the present invention, the carbon source in S3 includes at least one of sucrose, glucose, maltose, starch, citric acid, phenolic resin, polyethylene glycol, polyethylene oxide, and polyvinylpyrrolidone.

In a further solution of the present invention, the calcination conditions in S3 are that a heating rate is 2-10°C$\cdot$min^{-1}, the temperature is raised to 500-750°C, and the temperature is maintained for 1-10 hours.

Compared with the prior art, the present invention has the following beneficial effects. In the present invention, spent LFP is recycled and converted into high-value LMFP cathode materials. The reuse of spent resources is realized, the dependence on primary mineral resources is reduced, the production cost is reduced, and the requirements of circular economy are met. Traditional treatment methods of spent lithium batteries often have environmental pollution risks, but in the present invention, by adopting the hydrothermal/solvothermal method and the heat treatment process, the discharge of harmful substances is avoided, the negative impact on the environment is reduced, and remarkable environmental protection benefits are achieved. In the present invention, the reaction conditions are mild, the industrial implementation is easy, the structure and performance of the product can be effectively controlled, and the production efficiency is improved.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a process flow diagram of the present invention.

FIG. 2 is a scanning electron microscopy (SEM) image of spent LFP in Example 1.

FIG. 3 is an SEM image of an intermediate product of Example 1.

FIG. 4 is an SEM image of a regenerated LMFP in Example 1.

FIG. 5 is an X-ray diffraction pattern of spent LFP, the intermediate product, and the regenerated LMFP in Example 1.

FIG. 6 is a rate capability plot of spent LFP and the regenerated LMFP in Example 1.

FIG. 7 is a Raman spectrum of the regenerated LMFP in Example 1.

FIG. 8 is an X-ray photoelectron spectroscopy spectrum (Fe 2p) of the regenerated LMFP in Example 1.

FIG. 9 is an X-ray photoelectron spectroscopy spectrum (Mn 2p) of the regenerated LMFP in Example 1.

DETAILED DESCRIPTION

Technical solutions in the examples of the present invention will be described clearly and completely in the following with reference to the accompanying drawings in the examples of the present invention. Obviously, all the described examples are only some, rather than all examples of the present invention. Based on the examples in the present invention, all other examples obtained by those ordinary skilled in the art without creative efforts belong to the scope of protection of the present invention.

Example 1, reference is made to FIGS. 1-9.

An example of the present invention provides a method for preparing an LMFP cathode material by recycling spent LFP, including the following steps.

(1) 5 g of spent LFP electrode sheets were added to 30 mL of dimethyl carbonate solvent with a purity of 99% and soaked for 12 hours. Subsequently, the electrode pieces were air-dried. The air-dried spent LFP electrode pieces were heated to 500°C at a rate of 5°C$\cdot$min^{-1} under an argon atmosphere and held at that temperature for 3 hours, and spent LFP black powder was obtained.

(2) 0.03 mol of lithium hydroxide was weighed and added to 30 mL of ethylene glycol with a purity of 98%, and a lithium hydroxide solution was formed.

(3) 0.01 mol of manganese sulfate and 0.01 mol of phosphoric acid were added to 5 mL of deionized water, after complete dissolution, 25 mL of ethylene glycol with a purity of 98% was added and mixed uniformly, and 0.01 mol of spent LFP powder was added to obtain a mixed solution 1A.

(4) The lithium hydroxide solution in step (2) was added dropwise to the mixed solution 1A in step (3), and after uniform mixing, a mixed solution 1B was obtained.

(5) The mixed solution 1B in step (4) was transferred to the polytetrafluoroethylene liner of a reaction kettle. The hydrothermal reaction kettle was tightened and placed in an oven. The

temperature was raised from room temperature to 180°C at a rate of 2°C/min and held for 10 hours, followed by furnace cooling. The product was washed and dried to obtain an intermediate product.

(6) 1 g of the intermediate product in step (5) and 0.2 g of sucrose were added to 5 mL of anhydrous ethanol with a purity of 99.7%. The mixture was ball-milled at a rotation speed of 450 rpm for 2 hours, and placed in a blast drying oven at 80°C for overnight drying. A mixed material of the intermediate product and sucrose was obtained.

(7) The mixed material in step (6) was heated to 700°C at a rate of 5°C$\cdot$min^{-1} under an argon atmosphere and held at that temperature for 4 hours, and regenerated LMFP material was obtained.

Example 2

An example of the present invention provides a method for preparing an LMFP cathode material by recycling spent LFP, including the following steps.

(1) 5 g of spent LFP electrode sheets were added to 50 mL of dimethyl carbonate solvent with a purity of 99% and soaked for 24 hours. Subsequently, the electrode pieces were air-dried. The air-dried spent LFP electrode pieces were heated to 500°C at a rate of 10°C$\cdot$min^{-1} under an argon atmosphere and held at that temperature for 1 hour, and spent LFP black powder was obtained.

(2) 0.03 mol of lithium hydroxide was weighed and added to 30 mL of ethylene glycol with a purity of 98%, and a lithium hydroxide solution was formed.

(3) 0.023 mol of manganese sulfate and 0.023 mol of phosphoric acid were added to 5 mL of deionized water, after complete dissolution, 25 mL of ethylene glycol with a purity of 98% was added and mixed uniformly, and 0.01 mol of spent LFP powder was added to obtain a mixed solution 2A.

(4) The lithium hydroxide solution in step (2) was added dropwise to the mixed solution 2A in step (3), and after uniform mixing, a mixed solution 2B was obtained.

(5) The mixed solution 2B in step (4) was transferred to the polytetrafluoroethylene liner of a reaction kettle. The hydrothermal reaction kettle was tightened and placed in an oven. The temperature was raised from room temperature to 180°C at a rate of 5°C/min and held for 20 hours, followed by furnace cooling. The product was washed and dried to obtain an intermediate product.

(6) 1 g of the intermediate product in step (5) and 0.1 g of sucrose were added to 5 mL of anhydrous ethanol with a purity of 99.7%. The mixture was ball-milled at a rotation speed of 500 rpm for 2 hours, and placed in a blast drying oven at 80°C for overnight drying. A mixed material of the intermediate product and sucrose was obtained.

(7) The mixed material in step (6) was heated to 650°C at a rate of 5°C·min^{-1} under an argon atmosphere and held at that temperature for 4 hours, and regenerated LMFP material was obtained.

Example 3

An example of the present invention provides a method for preparing an LMFP cathode material by recycling spent LFP, including the following steps.

(1) 5 g of spent LFP electrode sheets were added to 40 mL of dimethyl carbonate solvent with a purity of 99% and soaked for 20 hours. Subsequently, the electrode pieces were air-dried. The air-dried spent LFP electrode pieces were heated to 500°C at a rate of 5°C·min^{-1} under an argon atmosphere and held at that temperature for 1 hour, and spent LFP black powder was obtained.

(2) 0.06 mol of lithium hydroxide was weighed and added to 60 mL of ethylene glycol with a purity of 98%, and a lithium hydroxide solution was formed.

(3) 0.03 mol of manganese sulfate and 0.03 mol of phosphoric acid were added to 10 mL of deionized water, after complete dissolution, 50 mL of ethylene glycol with a purity of 98% was added and mixed uniformly, and 0.02 mol of spent LFP powder was added to obtain a mixed solution 3A.

(4) The lithium hydroxide solution in step (2) was added dropwise to the mixed solution 3A in step (3), and after uniform mixing, a mixed solution 3B was obtained.

(5) The mixed solution 3B in step (4) was transferred to the polytetrafluoroethylene liner of a reaction kettle. The hydrothermal reaction kettle was tightened and placed in an oven. The temperature was raised from room temperature to 180°C at a rate of 2°C/min and held for 10 hours, followed by furnace cooling. The product was washed and dried to obtain an intermediate product.

(6) 2 g of the intermediate product in step (5) and 0.4 g of sucrose were added to 10 mL of anhydrous ethanol with a purity of 99.7% at a mass ratio of 5:1. The mixture was ball-milled at a rotation speed of 450 rpm for 2 hours, and placed in a blast drying oven at 80°C for overnight

drying. A mixed material of the intermediate product and sucrose was obtained.

(7) The mixed material in step (6) was heated to 600°C at a rate of $5°C\cdot min^{-1}$ under an argon atmosphere and held at that temperature for 4 hours, and regenerated LMFP material was obtained.

It is obvious to those skilled in the art that the present invention is not limited to the details of the above illustrative examples, and the present invention may be realized in other specific forms without departing from the spirit or essential characteristics thereof. Therefore, the examples are to be considered in all respects as illustrative and not restrictive, the scope of the present invention is limited by the appended claims rather than the above description, and all changes that come within the meaning and range of equivalents of the claims are intended to be embraced by the present invention. Any reference signs in the claim are not to be construed as limiting the claim concerned.

In addition, it is to be understood that while the present specification has been described in terms of embodiments, not every embodiment includes a single technical solution, and that such narrative style of the specification is only for clarity. Those skilled in the art are to take the specification as a whole, and the technical solutions in each example can also be combined appropriately to form other embodiments that can be understood by those skilled in the art.