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(54) Title: METHOD FOR MAKING LITHIUM IRON PHOSPHATE

Providing a lithium ion source solution comprising lithium ions, a ferrous ion source solution comprising ferrous ions, and a phosphate-radical source solution comprising phosphate-radicals, wherein the lithium ion source solution, the ferrous ion source solution, and the phosphate-radical source solution are respectively formed by dissolving a lithium chemical compound, a ferrous chemical compound, and a phosphate-radical chemical compound in an organic solvent

Mixing the lithium ion source solution, the ferrous ion source solution, and the phosphate-radical source solution at a predetermined temperature in a range from about 90 °C to about 180 °C to form a mixed solution

Heating the mixed solution at the predetermined temperature to co-precipitate the lithium ions, the ferrous ions, and the phosphate-radicals into the lithium iron phosphate

(57) Abstract: A method for making lithium iron phosphate is provided. In the method, a lithium ion source solution including lithium ions, a ferrous ion source solution including ferrous ions, and a phosphate-radical source solution including phosphate-radicals are provided. The lithium ion source solution, the ferrous ion source solution, and the phosphate-radical source solution are respectively formed by dissolving a lithium chemical compound, a ferrous chemical compound, and a phosphate-radical chemical compound in an organic solvent. The lithium ion source solution, the ferrous ion source solution, and the phosphate-radical source solution are mixed at a predetermined temperature in a range from about 90 °C to about 180 °C to form a mixed solution. The mixed solution is heated under the predetermined temperature to make the lithium ions, the ferrous ions, and the phosphate-radicals co-precipitate as the lithium iron phosphate.

FIG. 1



GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,

SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
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METHOD FOR MAKING LITHIUM IRON PHOSPHATE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims all benefits from China Patent Application No. 201310267759.1, filed on June 28, 2013, in the China Intellectual Property Office, the
5 contents of which are hereby incorporated by reference.

BACKGROUND

1. Technical Field

[0002] The present disclosure relates to a method for making lithium iron phosphate.

2. Description of Related Art

10 [0003] Olivine lithium iron phosphate (LiFePO_4) has been intensively investigated as a promising cathode material for rechargeable lithium ion batteries in electric vehicles and large-scale energy storage, because of its suitable operating voltage, good cycling performance and high theoretical capacity, good safety performance, low-cost raw material, and non-toxicity. An impediment to a wide use of LiFePO_4 is its poor
15 conductivities of both electron and Li^+ ions. Nanocrystallization and carbon coating for LiFePO_4 have been proved to be effective to overcome those obstacles.

[0004] LiFePO_4 can be fabricated by methods of solid reaction, coprecipitation, and

hydrothermal synthesis. The solid reaction method needs a high temperature atmosphere (usually above 600 °C) and the synthesized LiFePO_4 are always impure. In addition, morphology of the synthesized LiFePO_4 is hard to tune. The coprecipitation and hydrothermal synthesis methods can effectively tune the morphology of LiFePO_4 .

- 5 However, the coprecipitation method still needs a high temperature heating or a microwave heating process for poor degrees of crystallinity and impurity phases of product obtained by the coprecipitation. The hydrothermal synthesis usually needs a high pressure autoclave, which increases process complexities and safety risks.

[0005] Therefore, what is needed, is to provide a simple and mild method for making
10 LiFePO_4 . In addition, the synthesized LiFePO_4 can have a good electrochemical performance.

BRIEF DESCRIPTION OF THE DRAWING

[0006] Many aspects of the present disclosure can be better understood with reference to the following drawings. The components in the drawings are not
15 necessarily to scale, the emphasis instead being placed upon clearly illustrating the principles of the present embodiments.

[0007] FIG. 1 is a flowchart of a method for making lithium iron phosphate.

[0008] FIG. 2 shows X-ray diffraction (XRD) patterns of the lithium iron phosphate

made by Examples 1-4.

[0009] FIG. 3 shows low-magnification scanning electron microscope (low-magnification SEM) images of the lithium iron phosphate made by the Examples 1-4.

5 **[0010]** FIG. 4 shows high-magnification SEM images, transmission electron microscope (TEM) images, and selected area electron diffraction (SAED, inside of SEM images) images of the lithium iron phosphate made by the Examples 1-4.

[0011] FIG. 5 shows charge-discharge profiles of carbon coated lithium iron phosphate made by the Examples 1-4.

10

DETAILED DESCRIPTION

[0012] The disclosure is illustrated by way of example and not by way of limitation in the figures of the accompanying drawings in which like references indicate similar elements. It should be noted that references to “another,” “an,” or “one” embodiment in this disclosure are not necessarily to the same embodiment, and such references mean at
15 least one.

[0013] Referring to FIG. 1, one embodiment of a method for making lithium iron phosphate includes the following steps:

S1, providing a lithium ion source solution including lithium ions, a ferrous ion

source solution including ferrous ions, and a phosphate-radical source solution including phosphate-radicals, wherein the lithium ion source solution, the ferrous ion source solution, and the phosphate-radical source solution are respectively formed by dissolving a lithium chemical compound, a ferrous chemical compound, and a phosphate-radical
5 chemical compound in an organic solvent;

S2, mixing the lithium ion source solution, the ferrous ion source solution, and the phosphate-radical source solution at a predetermined temperature in a range from about 90 °C to about 180 °C to form a mixed solution, and

S3, heating the mixed solution at the predetermined temperature to co-precipitate the
10 lithium ions, the ferrous ions, and the phosphate-radicals into the lithium iron phosphate.

[0014] In step S1, the lithium ion source solution provides the lithium ions, the ferrous ion source solution provides the ferrous ions, and the phosphate-radical source solution provides the phosphate-radicals. The lithium chemical compound, the ferrous chemical compound (i.e., the Fe element is divalent), and the phosphate-radical chemical
15 compound can be respectively dissolved in the organic solvent to form three separate liquid solutions. The lithium chemical compound can be selected from, but is not limited to, lithium hydroxide (LiOH), lithium chloride (LiCl), lithium sulfate (Li₂SO₄), lithium nitrate (LiNO₃), lithium dihydrogen phosphate (LiH₂PO₄), lithium acetate (CH₃COOLi), and any combination thereof. The ferrous chemical compound can be

selected from, but is not limited to, ferrous sulfate (FeSO_4), ferrous acetate ($\text{Fe}(\text{CH}_3\text{COO})_2$), ferrous chloride (FeCl_2), and any combination thereof. The phosphate-radical chemical compound can be selected from, but is not limited to, phosphoric acid (H_3PO_4), lithium dihydrogen phosphate (LiH_2PO_4), triammonium phosphate ($(\text{NH}_4)_3\text{PO}_4$), monoammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), diammonium phosphate ($(\text{NH}_4)_2\text{HPO}_4$), and any combination thereof.

[0015] The organic solvent can be a diol, and/or polyol solvent, which can be selected from, but is not limited to, ethylene glycol, glycerol, diethylene glycol, triethylene glycol, tetraethylene glycol, 1,2,4-butanetriol ($\text{C}_4\text{H}_{10}\text{O}_3$), erythritol ($\text{C}_4\text{H}_{10}\text{O}_4$), polyethylene glycol, and any combination thereof. The organic solvent can be selected according to the selections of the lithium chemical compound, the ferrous chemical compound, and the phosphate-radical chemical compound. The organic solvent has a relatively high viscosity, and thus helps the lithium iron phosphate to be crystallized as a specific crystalline structure. In one embodiment, the organic solvent is the ethylene glycol. In another embodiment, the organic solvent is the polyethylene glycol. The polyethylene glycol helps to form pure phase olivine lithium iron phosphate with a large surface size and a small thickness which less than 100 nanometers. The length and width sizes can be larger than or equal to 1 micrometer.

[0016] In one embodiment, the mixed solution does not contain any water. In

another embodiment, the mixed solution contains a small amount of water. In some embodiments, the selected lithium chemical compound is a lithium hydrate, such as $\text{LiOH} \cdot \text{H}_2\text{O}$ or $\text{C}_2\text{H}_3\text{LiO}_2 \cdot 2\text{H}_2\text{O}$, and/or the selected ferrous chemical compound is an iron hydrate, such as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. When dissolving the lithium chemical compound and/or the ferrous chemical compound in the organic solvent, the crystal water in the lithium hydrate and/or the iron hydrate is introduced into the mixture. However, a volume ratio of water to organic solvent is less than or equal to 1:10, to avoid affecting the crystallization of the lithium iron phosphate. In one embodiment, the volume ratio is smaller than 1:50.

10 **[0017]** In the mixed solution, a molar ratio of Li:Fe:P is about (2~3):1:(0.8~1.5). That is, in the mixed solution, Fe element is in 1 part, Li element is in 2-3 parts, and P element is in 0.8-1.5 parts. In one embodiment, the molar ratio of Li:Fe:P is about 3:1:1.

[0018] A concentration of the ferrous ion source solution can be in a range from about 0.2 mol/L to about 0.4 mol/L. A concentration of the phosphate-radical source solution can be in a range from about 0.2 mol/L to about 0.4 mol/L. A concentration of the lithium ion source solution can be in a range from about 0.6 mol/L to about 2 mol/L. In one embodiment, the concentration of the lithium ions in the lithium ion source solution is higher than 1.8 mol/L and less than 2 mol/L, which can increase production

efficiency of the lithium iron phosphate. In one embodiment, the concentrations of the ferrous ion source solution and the phosphate-radical source solution individually are about 0.2 mol/L and the concentration of the lithium ion source solution is about 0.6 mol/L.

- 5 **[0019]** In one embodiment, the lithium ion source solution, the ferrous ion source solution, and the phosphate-radical source solution can be mixed by the following steps (named as a PFL method):

S21, mixing the phosphate-radical source solution and the ferrous ion solution to form a first solution; and

- 10 S22, adding the first solution to the lithium ion source solution to form the mixed solution.

- [0020]** The first solution can be preheated to the predetermined temperature before added to the lithium ion source solution. The predetermined temperature can be in a range from about 90 °C to about 180 °C. In one embodiment, the predetermined
- 15 temperature is in a range from about 140 °C to about 180 °C. Alternatively, the lithium ion source solution can be preheated to the predetermined temperature before the first solution is added thereto. The preheated step can facilitate to co-precipitate into a pure-phase and well-crystallized lithium iron phosphate.

- [0021]** The first solution can be added to the lithium ion source solution at a small

flow rate thereof to obtain a well-crystallized lithium iron phosphate. The flow rate of the first solution can be equal to or greater than 3 milliliters per minute (ml/min). In one embodiment, the flow rate is in a range from about 3 ml/min to about 30 ml/min, and a time period for the mixing of the first solution and lithium ion source solution is about 5 minutes to about 10 minutes. In one embodiment, the first solution is added to the lithium ion source solution drop by drop.

[0022] In another embodiment, the lithium ion source solution, the ferrous ion source solution, and the phosphate-radical source solution can be mixed by the following steps (named as an LPF method):

10 S21', mixing the phosphate-radical source solution and the lithium ion source solution to form a suspension, and

S22', adding the suspension to the ferrous ion source solution to form the mixed solution.

[0023] In step S21', a stirring step can be processed during the mixing of phosphate-radical source solution and lithium ion source solution. A stirring velocity can be in a range from about 60 rounds per minute (r/m) to about 600 r/m. A chemical reaction is occurred during the mixing between the phosphate-radical source solution and lithium ion source solution, and the suspension is formed.

[0024] In step S22', the suspension can be added to the ferrous ion source solution

within about 5 minutes to about 10 minutes. The suspension can be added into the ferrous ion source solution at a low flow rate. For example, the flow rate of the suspension can be equal to or greater than 2 ml/min. In one embodiment, the flow rate of the suspension is in a range from about 3 ml/min to about 40 ml/min.

5 [0025] Similarly, at least one of the suspension and the ferrous ion source solution can be preheated to the determined temperature before mixing with each other to facilitate to co-precipitate into a pure-phase and well crystallized lithium iron phosphate.

[0026] In step S3, the coprecipitation reaction can be conducted under an oxygen containing environment or an oxygen free environment. Therefore, the coprecipitation
10 reaction can be conducted in an open reactor or a sealed reactor. The oxygen free environment can be created by using a protective gas, such as, but not limited to, inert gas, nitrogen gas, and hydrogen gas. In one embodiment, the coprecipitation reaction is conducted under the oxygen containing environment. The lithium iron phosphate formed under the oxygen containing environment are well-crystallized. In addition, the
15 coprecipitation reaction can be processed in an open environment. Therefore, the coprecipitation reaction can be conducted under an ordinary pressure (e.g., one atmosphere) without increasing the reaction pressure.

[0027] In step S3, the heating process lasts until the coprecipitation reaction completes. In one embodiment, the phosphate-radical source solution, the lithium ion

source solution, and the ferrous ion source solution can be preheated to the predetermined temperature before mixing with each other and keeping the predetermined temperature until the co-precipitation reaction completes.

[0028] The predetermined temperature can be higher than or equal to 90 °C and lower than a boiling point of the organic solvent. In one embodiment, the predetermined temperature is in a range from about 140 °C to about 180 °C. In one embodiment, the predetermined temperature is in a range from about 160 °C to about 180 °C. The higher the predetermined temperature in the temperature range, the faster the well-crystallized lithium iron phosphate can be formed. The heating temperature for the mixed solution can be gradually raised from about 90 °C to about 180 °C and kept at about 180 °C until the coprecipitation reaction completes, then naturally decreases to a room temperature.

[0029] After the coprecipitation reaction completes, a coprecipitate is formed. The coprecipitate is the lithium iron phosphate. The coprecipitate can be washed, filtered, centrifuged by deionized water several times, and dried.

[0030] The lithium iron phosphate formed by the above method is nano-sized and plate-shaped. A thickness of the plate-shaped lithium iron phosphate can be in a range from about 20 nanometers to about 50 nanometers, a length can be in a range from about 150 nanometers to about 350 nanometers, and a width can be in a range from about 60

nanometers to about 150 nanometers.

[0031] Furthermore, the lithium iron phosphate can be coated by carbon. The carbon-coating process can include the following steps:

T1, preparing a liquid solution of a carbon source chemical compound;

5 T2, adding the lithium iron phosphate into the liquid solution of the carbon source chemical compound to form a solid-liquid mixture; and

T3, heating the solid-liquid mixture.

[0032] The carbon source chemical compound can be a reductive organic chemical compound. The reductive organic chemical compound can be pyrolyzed in an oxygen
10 free condition to form simple carbon (e.g., amorphous carbon). The pyrolysis step does not generate any other solid phase substance. The carbon source chemical compound can be selected from, but not limited to, saccharose, dextrose, SPAN 80, epoxide resin, phenolic resin, furan resin, polyacrylic acid, polyacrylonitrile, polyethylene glycol, polyvinyl alcohol, or any combination thereof. In one embodiment, the carbon source
15 chemical compound is saccharose. The carbon source chemical compound is dissolved in a solvent such as organic solvent and/or deionized water to form the liquid solution having a concentration in a range from about 0.005 grams per milliliter (g/ml) to about 0.05 g/ml. The concentration of the carbon source chemical compound is such that the lithium iron phosphate becomes uniformly coated with carbon after heating. After

adding the lithium iron phosphate into the liquid solution of the carbon-source chemical compound, the solution is dried and heated at about 400°C to about 700°C. In one embodiment, the solid-liquid mixture can be heated at about 650°C. A heating time of the solid-liquid mixture can be in a range from about 2 hours to about 10 hours.

5 Example 1 (PFL method)

[0033] In Example 1, the lithium chemical compound is $\text{LiOH}\cdot\text{H}_2\text{O}$, the ferrous chemical compound is $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, the phosphate chemical compound is H_3PO_4 , and the organic solvent is ethylene glycol (EG). The molar ratio of Li:Fe:P is about 3:1:1. The coprecipitation reaction is performed in a lidded vessel, with silicone oil bath for heating and N_2 gas for the protective gas filled in the lidded vessel. The reaction is conducted at a normal pressure. About 0.03 mol H_3PO_4 and $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ were dissolved in 100 ml EG with vigorous magnetic stirring to form the first solution. The first solution is then slowly added into 200 ml $\text{LiOH}\cdot\text{H}_2\text{O}$ -EG solution under stirring to form the mixed solution. The mixed solution is heated up to about 180 °C and kept for about 60 minutes for coprecipitation reaction. After the coprecipitation reaction is complete, the lidded vessel is cooled naturally to room temperature. The as-prepared coprecipitate is collected after centrifugation, washing and drying at 60 °C. The obtained precipitate is labeled as sample P1.

[0034] The sample P1 are coated with carbon prepared by mixing the sample P1 with

12wt% cane sugar first to form the mixture, and then calcinating the mixture at about 650 °C for about 2 hours under N₂ atmosphere. The obtained sample is label as P1/C.

Example 2 (PFL method)

[0035] The method in Example 2 is substantially the same as the method in Example 1, except that the coprecipitation reaction is processed in air. The obtained samples are labeled as P2 and P2/C respectively.

Example 3 (LPF method)

[0036] In Example 3, the lithium chemical compound is LiOH·H₂O, the ferrous chemical compound is FeSO₄·7H₂O, the phosphate chemical compound is H₃PO₄, and the organic solvent is ethylene glycol (EG). The molar ratio of Li:Fe:P is about 3:1:1. The coprecipitation reaction is performed in a lidded vessel, with silicone oil bath for heating and N₂ gas for the protective gas filled in the lidded vessel. The reaction is conducted at a normal pressure. H₃PO₄ and about 200 ml LiOH-EG solution are mixed first to form the suspension. The suspension is then added into about 100ml FeSO₄-EG solution with vigorous magnetic stirring for about 15 minutes to form the mixed solution. The mixed solution is heated up to about 180 °C and kept for about 60 minutes for coprecipitation reaction. After the coprecipitation reaction is complete, the lidded vessel is cooled naturally to a room temperature. The as-prepared coprecipitate is collected after centrifugation, washing and drying at 60 °C. The obtained precipitate is labeled as

sample L1.

[0037] The sample L1 are coated with carbon prepared by mixing the sample L1 with 12wt% cane sugar first to form the mixture, and then calcinating the mixture at about 650 °C for about 2 hours under N₂ atmosphere. The obtained sample is label as L1/C.

Example 4 (LPF method)

[0038] The method in Example 4 is substantially the same as the method in Example 3, except that the coprecipitation reaction is processed in air. The obtained samples are labeled as L2 and L2/C respectively.

10 [0039] Referring to FIG. 2, all the XRD patterns of the samples P1, P2, P3, and P4 coincide with a standard XRD pattern of olivine-LiFePO₄ of Pnma space group. Time labeled in the FIG. 2, such as -10 min, 0 min, 20 min, shows the time period of the coprecipitation reaction. It can be observed that pure-phase and well-crystallized LiFePO₄ can be obtained within about 20 min at about 180 °C with both PFL and LPF

15 methods. However, intermediates caused by the two methods are different. For samples P1 and P2, the co-precipitation changes from amorphous phosphates to crystalline LiFePO₄, as indicated by the XRD patterns labeled with -10 min, 0 min, and 10 min. Time below 0 min means that the reactants are mixing and the heating temperature is raising. Time above 0 min means the heating temperature reaches to

about 180 °C and is kept at this temperature. Time “-10 min” corresponds to the heating temperature of about 140 °C. When the heating temperature reaches about 180°C (0 min), the typical diffraction lines of olivine LiFePO_4 emerge from the amorphous background. In the following 20 minutes, the intensities of the diffraction lines increased gradually, while the typical amorphous baseline goes flat quickly. The coprecipitation collected after 20 min at 180°C is pure phase LiFePO_4 . Moreover, olivine- LiFePO_4 can be detected at 10 min for sample P1, while at 0 min for sample P2, indicative of faster formation and growth of olivine- LiFePO_4 in air. In addition, there is little change in the intensities of all diffraction lines when the coprecipitations are collected after 20 min. In other words, it takes only 20 min to obtain pure-phase and well-crystallized LiFePO_4 in coprecipitation for both samples of P1 and P2.

[0040] The intermediates for sample L1 and L2 differ from samples P1 and P2, as their XRD patterns confirms that the coprecipitation changes from poor-crystallized Li_3PO_4 to crystalline LiFePO_4 (from -10 min to 10 min). In the following 10 min, the mixture turns out pure-phase LiFePO_4 of low-crystallinity, as the intensity of diffraction line in XRD pattern are much lower than those in P1 and P2. The intensities of diffraction lines tend to be constant after heating under 180°C for 20 min. The intensities of all diffraction lines labeled with “20 min” are as strong as those labeled with “60 min”. The result indicates that samples formed by the PFL method have a relatively

high crystallinity than those samples formed by the LPF method. In addition, samples formed by the two methods have different crystal orientations.

[0041] Referring to FIG. 3, sizes and morphologies and of the samples P1, P2, L1, and L2, are tested by low-magnification SEM images show that all the samples are neat
5 LiFePO₄ nanoplates. Samples P1, P2, and L1 are well-dispersed. Average long shafts of samples P1 and P2 are about 300 nanometers and average long shafts of samples L1 and L2 are less than 200 nanometers.

[0042] Referring to FIG. 4, the morphology and crystal orientation of the samples P1, P2, L1, and L2 are tested by high-magnification SEM (80000×), TEM, and SAED. All
10 of the samples are fragmentary nanoplates. Most nanoplates in the samples P1 and P2 are about 300 nanometers long and 200 nanometers wide in the preferable exposure facet. Most nanoplates in the samples L1 and L2 are about 200 nanometers long and 100 nanometers wide. An averages thickness of the samples P1 and P2 are around 50 nanometers and those of the samples L1 and L2 are around 30 nanometers.

15 [0043] The SAED patterns demonstrate that LiFePO₄ synthesized with the LPF and PFL methods are all single crystal while have totally different crystalline orientations. Referring to FIG. 4A and FIG. 4E, the preferable exposure facet is {020} for the samples P1 and P2. However, it is {200} facet for the samples L1 and L2, according to the zone axis of [200] in FIG. 4D and FIG. 4H. The result indicates that nanoplates in the

samples P1 and P2 are substantially perpendicular to lithium ion transport corridors (which parallel to the b axis). In other words, a thickness direction of the nanoplates in the samples P1 and P2 is substantially parallel to the b axis which is beneficial for creating a short path for insertion and extraction of lithium. The long axis of the
5 nanoplates is along [001] of all four samples. The short axis is along [100] for the samples P1 and P2 in contrast to along [010] for the samples L1 and L2.

[0044] Referring to FIG. 5, charge-discharge profiles for the samples P1/C, P2/C, L1/C, and L2/C are compared. The sample P2/C exhibits the highest initial charge/discharge capacities of about 161 mAh g⁻¹ and 160 mAh g⁻¹, respectively.
10 Considering the carbon coating content is about 3.8 wt% in the sample P2/C, the specific capacity delivered by the sample P2 is very close to the theoretical value of 170 mAh g⁻¹. An initial columbic efficiency of the sample P2/C is about 99.4% and a voltage difference between the charge and discharge curves is very small, indicating a high purity of the olivine LiFePO₄ structure and perfect carbon coating. Though the other three samples
15 P1/C, L1/C and L2/C deliver initial discharge capacities of about 152 mAh g⁻¹, 138 mAh g⁻¹ and 135 mAh g⁻¹, respectively, which are lower than the sample P2/C, their initial columbic efficiency are all higher than 99.0%.

Example 5 (LPF method)

[0045] The method in Example 5 is substantially the same as the method in Example

3, except that the organic solvent is the polyethylene glycol. The synthesized products are high pure olivine LiFePO_4 nanoplates with about 1 micrometers long, 800 nanometers wide, and 70 nanometers thick. In addition, the preferable exposure facet of the synthesized product in Example 5 is {020}.

5 [0046] Depending on the embodiment, certain steps of methods described may be removed, others may be added, and the sequence of steps may be altered. It is also to be understood that the description and the claims drawn to a method may include some indication in reference to certain steps. However, the indication used is only to be viewed for identification purposes and not as a suggestion as to an order for the steps.

10 [0047] Finally, it is to be understood that the above-described embodiments are intended to illustrate rather than limit the present disclosure. Variations may be made to the embodiments without departing from the spirit of the present disclosure as claimed. Elements associated with any of the above embodiments are envisioned to be associated with any other embodiments. The above-described embodiments illustrate the scope of
15 the present disclosure but do not restrict the scope of the present disclosure.

CLAIMS

What is claimed is:

1. A method for making lithium iron phosphate comprising:
 - 5 providing a lithium ion source solution comprising lithium ions, a ferrous ion source solution comprising ferrous ions, and a phosphate-radical source solution comprising phosphate-radicals; wherein the lithium ion source solution, the ferrous ion source solution, and the phosphate-radical source solution are respectively formed by dissolving a lithium chemical compound, a ferrous chemical compound, and a phosphate-radical
10 chemical compound in an organic solvent;
mixing the lithium ion source solution, the ferrous ion source solution, and the phosphate-radical source solution at a predetermined temperature in a range from about 90 °C to about 180 °C to form a mixed solution, and
heating the mixed solution at the predetermined temperature to co-precipitate the
15 lithium ions, the ferrous ions, and the phosphate-radicals into the lithium iron phosphate.
 2. The method of claim 1, wherein the organic solvent is selected from the group consisting of ethylene glycol, glycerol, diethylene glycol, triethylene glycol, tetraethylene glycol, 1,2,4-butanetriol, erythritol, polyethylene glycol, and any combination thereof.

3. The method of claim 1, wherein the mixing comprises:

mixing the phosphate-radical source solution and the ferrous ion source solution to form a first solution; and

5 adding the first solution to the lithium ion source solution to form the mixed solution.

4. The method of claim 3, wherein the mixed solution are formed and heated under an oxygen containing environment.

5. The method of claim 3, wherein the mixed solution are heated at an ordinary pressure.

6. The method of claim 3, wherein the predetermined temperature is in a range from
10 about 140 degrees to about 180 degrees.

7. The method of claim 3, wherein at least one of the lithium ion source solution and the first solution are preheated to the predetermined temperature before mixing with each other.

8. The method of claim 3, wherein the first solution is dripped to the lithium ion source
15 solution at a flow rate from about 3 ml/min to about 40 ml/min and the first solution and the lithium ion source solution mixed within about 5 minutes to about 10 minutes.

9. The method of claim 3, wherein a concentration of the lithium ion source solution is equal to or greater than 1.8 mol/L and less than 2 mol/L.

10. The method of claim 1, wherein the lithium chemical compound is selected from the

group consisting of lithium hydroxide, lithium chloride, lithium sulfate, lithium nitrate, lithium dihydrogen phosphate, lithium acetate, and combinations thereof.

11. The method of claim 1, wherein the ferrous chemical compound is selected from the group consisting of ferrous sulfate, ferrous acetate, ferrous chloride, and combinations thereof.

12. The method of claim 1, wherein the phosphate-radical chemical compound is selected from the group consisting of phosphoric acid, lithium dihydrogen phosphate, triammonium phosphate, monoammonium phosphate, diammonium phosphate, and combinations thereof.

13. The method of claim 1, wherein the mixing comprises:

mixing the phosphate-radical source solution and the lithium ion source solution to form a suspension, and

adding the suspension to the ferrous ion source solution to form the mixed solution.

14. The method of claim 13, wherein at least one of the suspension and the ferrous ion source solution are preheated to the predetermined temperature before mixing with each other.

15. The method of claim 13, wherein the organic solvent is polyethylene glycol.

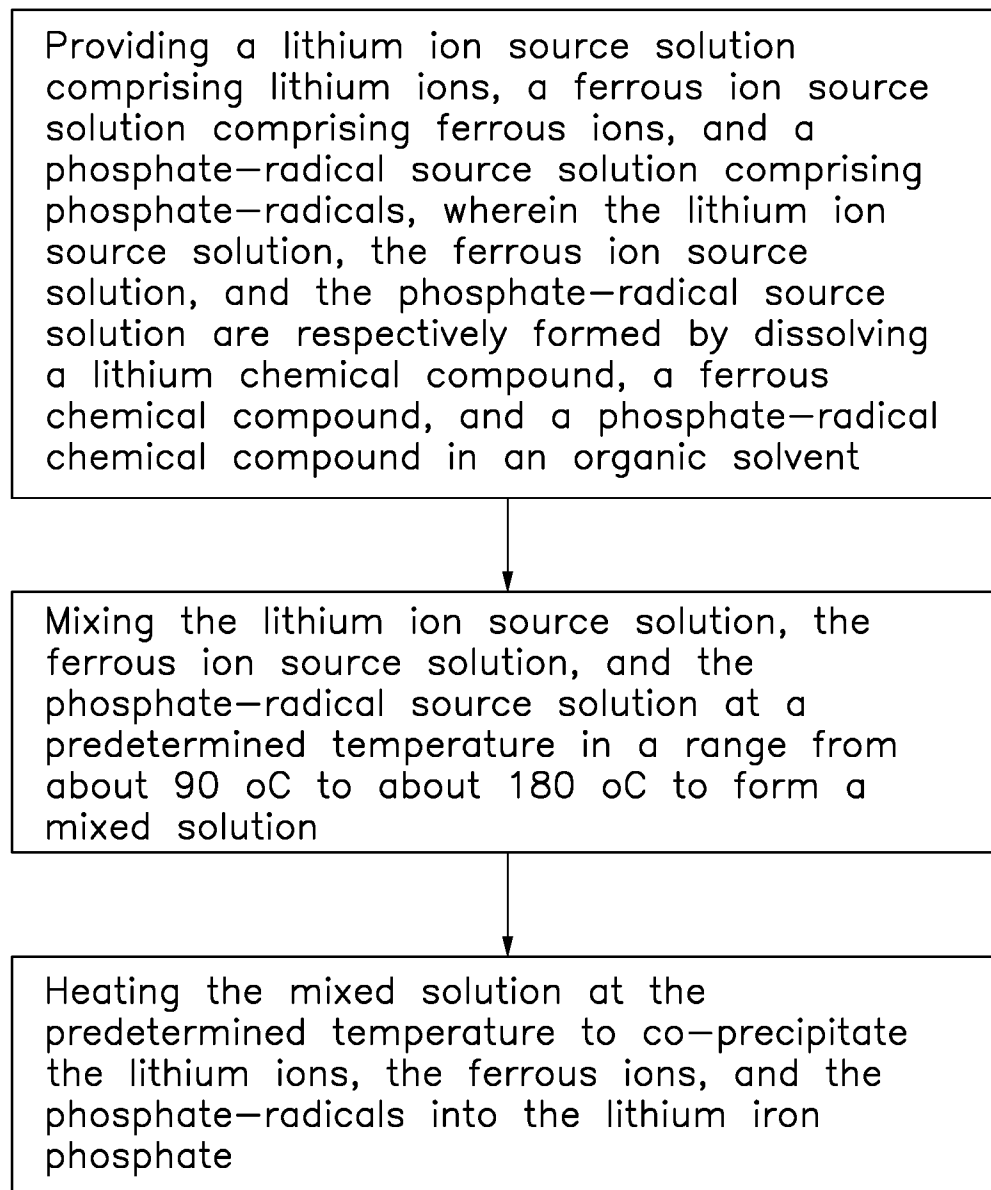


FIG. 1

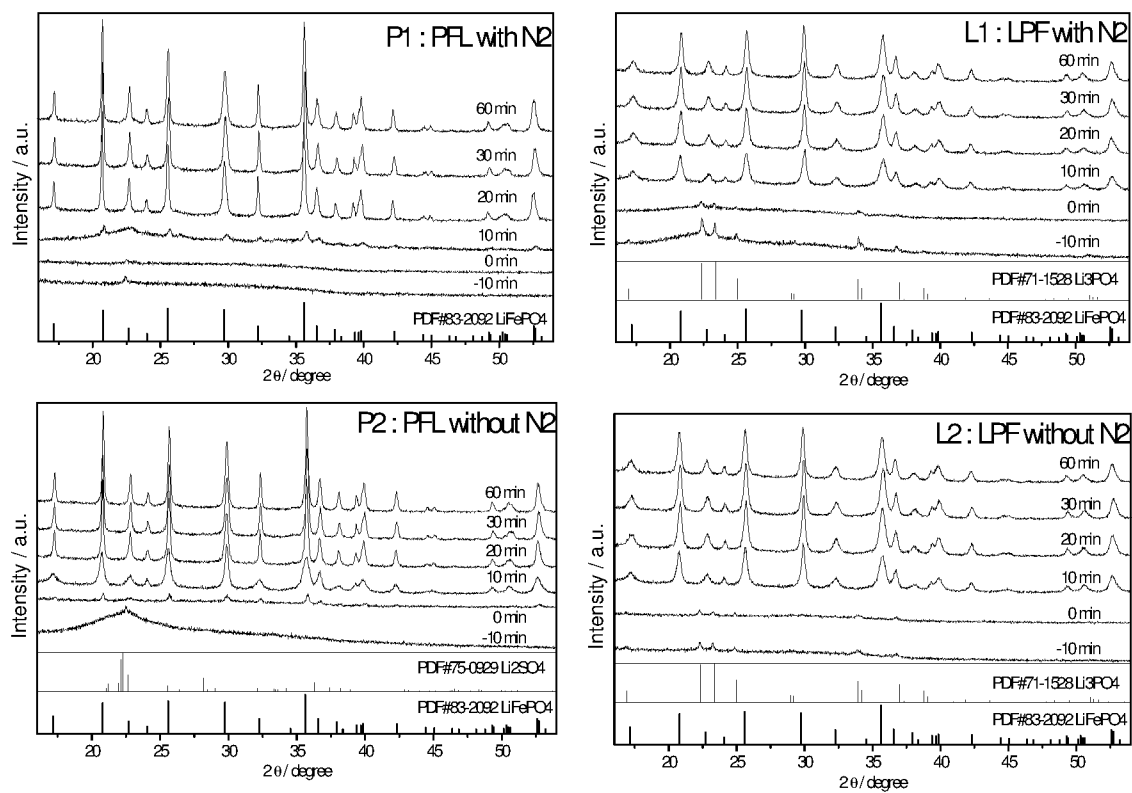


FIG. 2

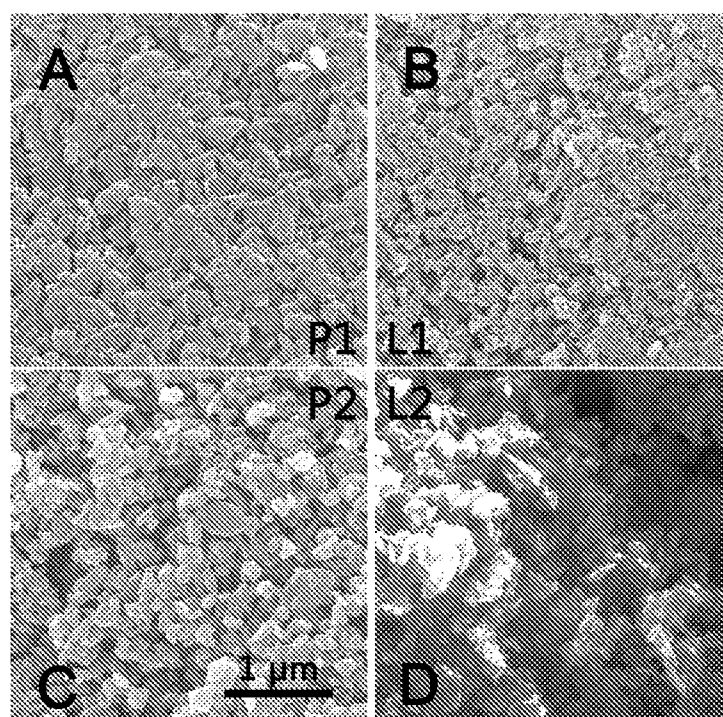


FIG. 3

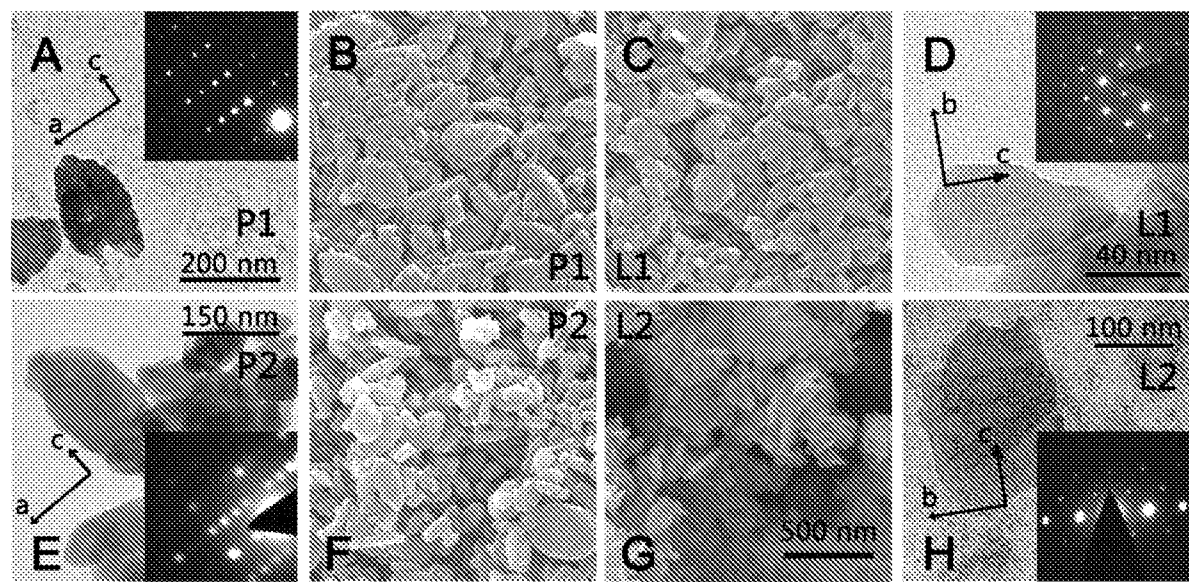


FIG. 4

Potential vs $\text{Li}/\text{Li}^+/\text{V}$

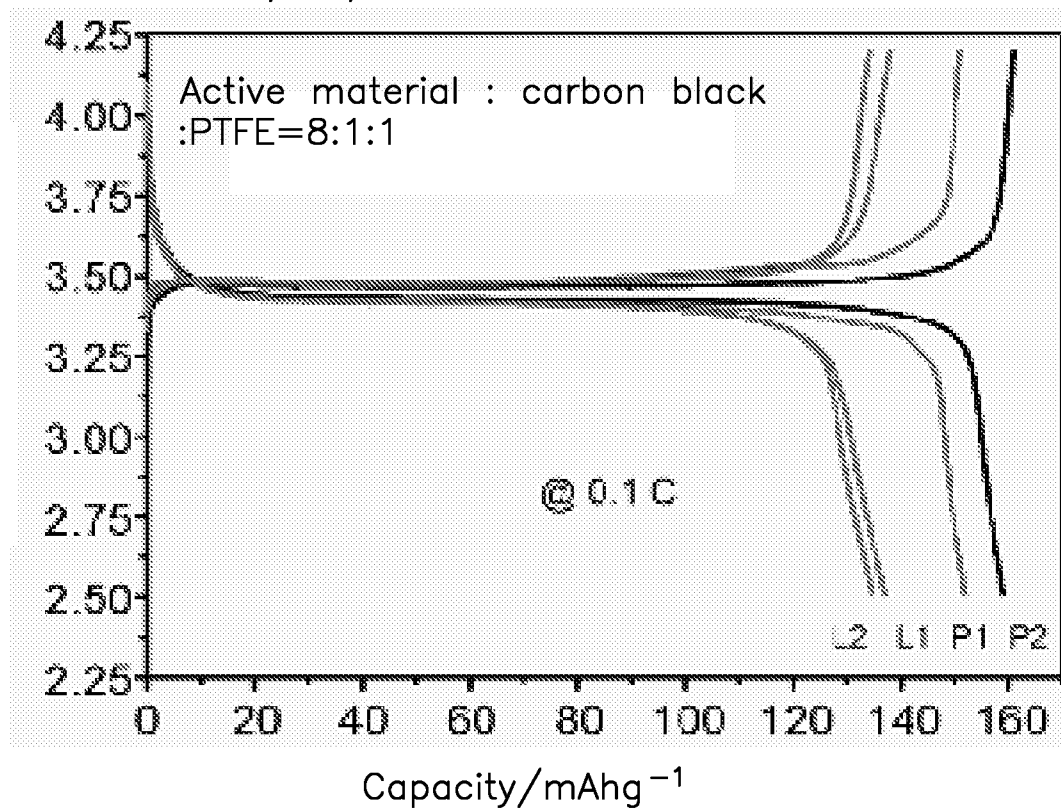


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/080954

A. CLASSIFICATION OF SUBJECT MATTER

C01B 25/45(2006.01)i; H01M 4/58(2010.01)n

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C01B 25/-; H01M 4/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNABS, WPI, EPODOC, CNKI, Web of Science: lithium iron phosphate, lithium ferrous phosphate, LiFePO₄, organic solvent?, alcohol?, polyol?, glycol, glycerol, butanetriol, erythritol, solvothermal+, coprecipitat+, co lw precipitat+**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	CN 103359701 A (UNIV TSINGHUA) 23 October 2013 (2013-10-23) description, paragraphs [0014]-[0030]	1-15
X	HUANG, Chaochao et al. "Rapid Synthesis of LiFePO ₄ by Coprecipitation" <i>CHEM. LETT.</i> , Vol. Vol. 42, No. No. 10, 20 June 2013 (2013-06-20), pages 1191-1193	1-15
X	CN 103137964 A (UNIV TSINGHUA ET AL.) 05 June 2013 (2013-06-05) description, paragraphs [0026]-[0037]	1-3, 6-12
X	CN 102593457 A (UNIV CHINA PETROLEUM ET AL.) 18 July 2012 (2012-07-18) description, paragraphs [0042]-[0063]	1-3, 6-12
X	NAN, Caiyun et al. "Solvothermal synthesis of lithium iron phosphate nanoplates" <i>J. MATER. CHEM.</i> , Vol. Vol. 21, No. No. 27, 14 January 2011 (2011-01-14), pages 9994-9996, Supporting Information	1-3, 6-12
X	SU, Chang et al. "Synthesis and Properties of Spindle-Shaped LiFePO ₄ for the Cathode Material of Lithium Ion Battery" <i>ACTA PHYS. -CHIM. SIN.</i> , Vol. Vol. 27, No. No. 3, 18 January 2011 (2011-01-18), pages 609-614	1-3, 6-12

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

03 September 2014

Date of mailing of the international search report

17 September 2014

Name and mailing address of the ISA/

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Telephone No. (86-10)62084738

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/080954**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 101415640 A (HIGH POWER LITHIUM SA ET AL.) 22 April 2009 (2009-04-22) claims 1, 6 and 8, embodiment 6	1, 2, 10-15
X	US 2012328947 A1 (CHOU, L ET AL.) 27 December 2012 (2012-12-27) claims 8, 11-13, 17 and 23	1, 2, 10-12
X	WANG, Li et al. "Nano particle LiFePO ₄ prepared by solvothermal process" <i>JOURNAL OF POWER SOURCES</i> , No. Vol. 244, 26 March 2013 (2013-03-26), pages 94-100	1, 2, 10-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/CN2014/080954

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				TW	201322525	A	01 June 2013
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