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Inventeur(s):
HAI Chao – China, YAO Yaochun – China

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Mandataire(s):
Patent42 SA – 4081 Esch-sur-Alzette (Luxembourg)

47

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Titulaire(s):
YAO Yaochun – 650500 Kunming City, Yunnan (China),
HAI Chao – 650500 Kunming City, Yunnan (China)

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Preparation Method of Battery-grade Iron Phosphate.

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The invention relates to the technical field of preparation of cathode material precursors of lithium ion batteries, in particular to a preparation method of battery-grade iron phosphate, which includes the following steps: (1) leaching iron concentrate powder with an acidic solution to obtain an iron-containing solution; (2) mixing the iron source solution with the phosphate source solution, then adding a surfactant, then adding an oxidant into the mixed solution for oxidation, and uniformly mixing again to obtain a reaction mother solution; (3) adding alkaline solution into the reaction mother solution by using a peristaltic pump to obtain iron phosphate dihydrate precipitate; (4) washing the iron phosphate dihydrate precipitate to obtain a filter cake, flash drying the iron phosphate dihydrate filter cake, and calcining to obtain battery-grade iron phosphate; and (5) evaporating and recrystallizing the wastewater generated in the general process to obtain by-products such as ammonium chloride or ammonium sulfate.

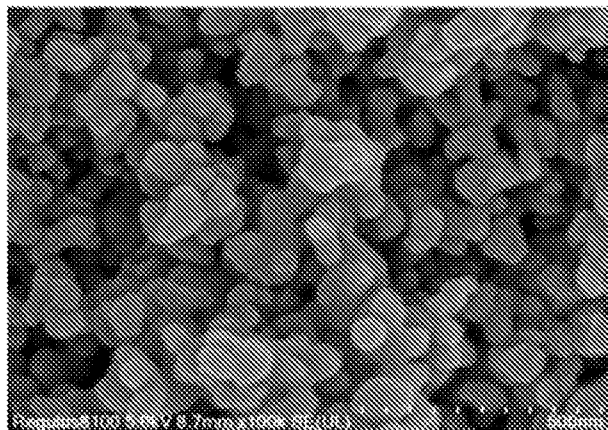


Fig. 1

PREPARATION METHOD OF BATTERY-GRADE IRON PHOSPHATE

TECHNICAL FIELD

The invention relates to the technical field of preparation of cathode material precursors of lithium ion batteries, in particular to a preparation method of battery-grade iron phosphate.

BACKGROUND

At present, with the development of new energy industry, lithium-ion batteries have attracted wide attention because of their advantages of environmental protection, large specific capacity and good cycle life. For lithium-ion battery cathode materials, iron phosphate precursor with its morphology, particle size to lithium iron phosphate can be controlled, and the synthesis process is simple, but also received great attention from scientists, and set off the research of iron phosphate as a precursor to synthesize lithium iron phosphate cathode materials. It is found that at present, the actual production mostly uses ferrous sulfate, reduced iron powder and other raw materials to synthesize battery-grade iron phosphate, which requires great cost. Therefore, it is the future development direction to seek a large amount of cheap raw materials to prepare higher quality iron phosphate materials.

At present, ferrous sulfate, iron powder, phosphoric acid, ammonium hydrogen phosphate, diammonium hydrogen phosphate, etc. are mostly used as raw materials for the synthesis of iron phosphate, which are costly, and a large amount of wastewater containing impurities will be generated after the synthesis of iron phosphate, and direct discharge will cause great environmental pollution.

SUMMARY

In The invention provides a preparation method of battery-grade iron phosphate, which can synthesize higher-quality battery-grade iron phosphate at lower cost. The invention is realized by the following technical scheme.

A preparation method of battery-grade iron phosphate includes the following steps:

(1) leaching: leaching iron concentrate powder with an acidic solution to obtain an iron source solution, where the leaching temperature is 60-90°C, and the concentration of the acidic solution is controlled at 4.5-6.0 mol/L;

(2) mix: mixing that iron source solution and the phosphate source solution according to the molar ratio of Fe:P = 0.9-1.05: 1 to obtain a mixed solution, then adding a surfactant, adding an oxidant to completely oxidize it, and uniformly mixing again to obtain a reaction mother solution, where the oxidant is H₂O₂, and the concentration is 3-30%;

(3) precipitation: adding alkaline solution into the reaction mother solution by using a peristaltic pump at a certain temperature, and adjusting the pH value to a certain value to obtain iron phosphate dihydrate precipitate;

(4) washing, drying and dewatering: washing the iron phosphate dihydrate precipitate until the conductivity is less than or equal to 200 us/cm, flash drying the iron phosphate dihydrate filter cake, and calcining to obtain battery-grade iron phosphate;

(5) tail solution treatment: evaporating and recrystallizing the wastewater in the precipitation reaction and washing process to obtain by-product ammonium chloride or ammonium sulfate;

The concentration of the surfactant in the mixed solution is 3-10g/L; the surfactant is one or more of dodecyl trimethyl ammonium bromide, sodium dodecyl sulfate and fatty acid monoglyceride.

The surfactant added in the invention can help the nucleation and growth process of iron phosphate particles, reduce the mutual attraction and agglomeration between particles, and improve the dispersibility of particles in solution, so as to control the morphology and distribution of particles more effectively. The addition of surfactant is helpful to improve the purity, crystallinity, specific surface area and other performance parameters of iron phosphate, and improve the electrochemical performance of iron phosphate in batteries.

The Fe content of the iron concentrate powder in the Step (1) is 30-79%; it contains impurities such as Ca, Mg, Al, Si and C, and the acidic solution can be one or two of hydrochloric acid and sulfuric acid. The reaction equation is: $\text{Fe}_2\text{O}_3 + 6\text{HCl} \rightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O}$, $\text{Fe}_3\text{O}_4 + 8\text{HCl} \rightarrow \text{FeCl}_2 + 2\text{FeCl}_3 + 4\text{H}_2\text{O}$ or $\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}$, $\text{Fe}_3\text{O}_4 + 4\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{FeSO}_4 + 4\text{H}_2\text{O}$.

The phosphate source in Step (2) can be one or more of phosphoric acid, diammonium hydrogen phosphate, ammonium dihydrogen phosphate and ammonium phosphate, and the reaction equation is: $\text{H}_2\text{O}_2 + 2\text{Fe}^{2+} + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + 2\text{H}_2\text{O}$, $\text{H}_2\text{O}_2 + 3\text{Fe}_2\text{SO}_4 + \text{H}_2\text{SO}_4 \rightarrow 2\text{Fe}_3(\text{SO}_4)_2 + 2\text{H}_2\text{O}$.

The alkaline solution in the Step (3) can be one or more of ammonia water, sodium hydroxide and sodium carbonate, the reaction temperature is 60-90°C, and the pH is controlled between 0.9 and 2.0; the reaction equation is $\text{Fe}^{3+} + \text{PO}_4^{3-} \rightarrow \text{FePO}_4 \downarrow$.

In Step (4), the drying temperature is 60-80°C, and the calcination process parameters are: heating rate is 5-15°C/min, heat preservation temperature is 550-800°C, calcination time is 4-6h, and the material is cooled to 25-100°C. LU507876

The evaporation temperature of that waste solution in the Step (5) is 60-180°C..

The invention also provides a battery-grade iron phosphate obtained by the preparation method.

The invention has the beneficial effects.

According to that invention, iron concentrate is used as an iron source, phosphoric acid and phosphate are use as phosphate sources, and the prepared iron phosphate is higher than industry standard in aspects of purity, iron-phosphorus ratio, morphology, particle size and the like, so that the prepared lithium iron phosphate cathode material has excellent electrochemical performance. And the waste water contains a lot of ammonium chloride and ammonium sulfate, which can be crystallized and recycled. The invention uses iron concentrate as the iron source to prepare battery-grade iron phosphate for the first time, and has almost no requirement on the purity of iron concentrate, and can utilize waste iron concentrate with high impurity content. The method has the advantages of low cost and easy control of reaction flow, and the prepared iron phosphate has good dispersibility and regular morphology. The battery grade lithium iron phosphate cathode materials prepared by this method has excellent electrochemical performance, and the wastewater generated from the preparation of iron phosphate can be recycled. The method can be widely applied to industrialized production of iron phosphate.

BRIEF DESCRIPTION OF THE FIGURES

Fig. 1 is a scanning electron microscope picture of iron phosphate prepared in Embodiment 1 of the present invention;

Fig. 2 is an XRD image of iron phosphate produced in Embodiments 1-4 of the present invention;

Fig. 3 is an electrochemical performance diagram of lithium iron phosphate cathode material prepared in Embodiment 1 of the present invention;

Fig. 4 is a process flow chart of the present invention.

DESCRIPTION OF THE INVENTION

The present invention will be further described with reference to the attached drawings and examples, but it is not limited in any way. Any transformation or

replacement based on the teaching of the present invention belongs to the protection scope of the present invention. LU507876

Embodiment 1

Step 1, leaching iron concentrate powder with 5.5 mol/L hydrochloric acid at 80°C to obtain iron source solution;

Step 2, selecting phosphoric acid as a phosphate source, mixing that phosphoric acid with the molar ratio of Fe:P = 1: 1 to obtain a mixed solution, then adding sodium dodecyl sulfate (the concentration of sodium dodecyl sulfate in the mixed solution is 7g/L), and then adding 30% H₂O₂ for oxidation and even mixing to obtain a reaction mother solution;

Step 3, under the condition of 70°C, adding ammonia water into the reaction mother solution by using a peristaltic pump, and adjusting the pH value to 1.35 to obtain iron phosphate dihydrate precipitate;

Step 4, washing the iron phosphate dihydrate with water by a vacuum filter press until the conductivity is less than or equal to 200 us/cm; And flash drying the filter cake, and calcining at 550°C to obtain battery-grade iron phosphate;

Step 5, evaporating and crystallizing the wastewater from precipitation reaction and washing at 110°C to obtain ammonium chloride;

Embodiment 2

Step 1, leaching iron concentrate powder with 5.5mol/L sulfuric acid at 80°C to obtain iron source solution;

Step 2, selecte phosphoric acid as a phosphate source, mixing that phosphoric acid in a molar ratio of Fe: P = 1: 1, adde 30% H₂O₂, and oxidizing and mixing uniformly to obtain a reaction mother solution;

Step 3, under the condition of 70°C, adding ammonia water into the reaction mother solution by using a peristaltic pump, and adjusting the pH value to 1.35 to obtain iron phosphate dihydrate precipitate;

Step 4, washing the iron phosphate dihydrate with water by a vacuum filter press until the conductivity is less than or equal to 200 us/cm; And flash drying the filter cake, and calcining at 800°C to obtain battery-grade iron phosphate;

Step 5, evaporating and crystallizing the wastewater from the precipitation reaction and washing at 110°C to obtain ammonium sulfate;

Embodiment 3

Step 1, leaching iron concentrate powder with 5.5mol/L hydrochloric acid at 80°C to obtain iron source solution;

Step 2, select phosphoric acid as a phosphate source, mixing that phosphoric acid in a molar ratio of Fe: P = 0.95: 1, add 3% H₂O₂, and oxidizing and mixing uniformly to obtain a reaction mother solution;

Step 3, adding ammonia water into the reaction mother solution by using a peristaltic pump at 70°C, and adjusting the pH value to 0.9 to obtain iron phosphate dihydrate precipitate;

Step 4, washing the iron phosphate dihydrate with water by a vacuum filter press until the conductivity is less than or equal to 200 us/cm; And flash drying the filter cake, and calcining at 550°C to obtain battery-grade iron phosphate;

Step 5, evaporating and crystallizing the wastewater from precipitation reaction and washing at 110°C to obtain ammonium chloride;

Embodiment 4

Step 1, leaching iron concentrate powder with 5.5mol/L sulfuric acid at 80°C to obtain iron source solution;

Step 2, select phosphoric acid as a phosphate source, mixing that phosphoric acid in a molar ratio of Fe: P = 1.05: 1, add 15% H₂O₂, and oxidizing and mixing uniformly to obtain a reaction mother solution;

Step 3, adding ammonia water into the reaction mother solution by using a peristaltic pump at 70°C, and adjusting the pH to 1.8 to obtain iron phosphate dihydrate precipitate;

Step 4, washing the iron phosphate dihydrate with water by a vacuum filter press until the conductivity is less than or equal to 200 us/cm; And flash drying the filter cake, and calcining at 600°C to obtain battery-grade iron phosphate;

Step 5, evaporating and crystallizing the wastewater from the precipitation reaction and washing at 110°C to obtain ammonium chloride;

Embodiment 5

Step 1, leaching iron concentrate powder with 4.5mol/L hydrochloric acid at 80°C to obtain iron source solution;

Step 2, select phosphoric acid as a phosphate source, mixing that phosphoric acid in a molar ratio of Fe: P = 1: 1, add 10% H₂O₂, and oxidizing and mixing uniformly to obtain a reaction mother solution;

Step 3, adding ammonia water into the reaction mother solution by using a peristaltic pump at 90°C, and adjusting the pH to 2.0 to obtain iron phosphate dihydrate precipitate;

Step 4, washing the iron phosphate dihydrate with water by using a vacuum filter press until the conductivity is less than or equal to 200 us/cm; And flash drying the filter cake, and calcining at 700°C to obtain battery-grade iron phosphate;

Step 5, evaporating and crystallizing the wastewater from precipitation reaction and washing at 110°C to obtain ammonium chloride; LU507876

Embodiment 6

Step 1, leaching iron concentrate powder with 6.0mol/L hydrochloric acid at 80°C to obtain iron source solution;

Step 2, select phosphoric acid as a phosphate source, mixing that phosphoric acid accord to the molar ratio of Fe: P = 1: 1, adding 30% H₂O₂, oxidizing and mixing uniformly to obtain a reaction mother solution;

Step 3, under the condition of 60°C, adding ammonia water into the reaction mother solution by using a peristaltic pump, and adjusting the pH value to 1.35 to obtain iron phosphate dihydrate precipitate;

Step 4, washing the iron phosphate dihydrate with water by a vacuum filter press until the conductivity is less than or equal to 200 us/cm; and flash drying the filter cake, and calcining at 550°C to obtain battery-grade iron phosphate;

Step 5, evaporating and crystallizing the wastewater from precipitation reaction and washing at 110°C to obtain ammonium chloride;

The iron phosphates prepared in Embodiments 1-6 are treated with lithium supplementation, and lithium iron phosphate is synthesized as the cathode of the battery, and its charge-discharge performance is tested. The lithium iron phosphate, acetylene black and 60% polytetrafluoroethylene emulsion prepared in each embodiment are mixed according to the mass ratio of 7:2:1, rolled into pieces with a thickness of 0.10-0.15mm, and pressed together with aluminum foil, and vacuum dried at 120°C for 12 hours to prepare the cathode of the battery.

CLAIMS

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1. A preparation method of battery-grade iron phosphate, characterized by comprising the following steps:

(1) leaching: leaching iron concentrate powder with an acidic solution to obtain an iron source solution, wherein the leaching temperature is 60-90°C, and the concentration of the acidic solution is controlled at 4.5-6.0 mol/L;

(2) mix: mixing that iron source solution and the phosphate source solution accord to the molar ratio of Fe:P=0.9-1.05:1 to obtain a mixed solution, then adding a surfactant, adding an oxidant to completely oxidize it, and uniformly mixing again to obtain a reaction mother solution, wherein the oxidant is H₂O₂, and the concentration is 3-30%;

(3) precipitation: adding alkaline solution into the reaction mother solution by using a peristaltic pump at a certain temperature, and adjusting the pH value to a certain value to obtain iron phosphate dihydrate precipitate;

(4) washing, drying and dewatering: washing the iron phosphate dihydrate precipitate until the conductivity is less than or equal to 200 us/cm, flash drying the iron phosphate dihydrate filter cake, and calcining to obtain battery-grade iron phosphate;

(5) tail solution treatment: evaporating and recrystallizing the wastewater in the precipitation reaction and washing process to obtain by-product ammonium chloride or ammonium sulfate;

the concentration of the surfactant in the mixed solution is 3-10g/L; the surfactant is one or more of dodecyl trimethyl ammonium bromide, sodium dodecyl sulfate and fatty acid monoglyceride.

2. The preparation method according to claim 1, characterized in that the Fe content of iron concentrate powder in step (1) is 30-79%, and the acidic solution is one or two of hydrochloric acid and sulfuric acid.

3. The preparation method according to claim 1, characterized in that the phosphate source in step (2) is one or more of phosphoric acid, diammonium hydrogen phosphate, ammonium dihydrogen phosphate and ammonium phosphate.

4. The preparation method according to claim 1, characterized in that the alkaline solution in step (3) is one or more of ammonia, sodium hydroxide and sodium carbonate, the reaction temperature is 60-90°C, and the pH is controlled between 0.9-2.0.

5. The preparation method according to claim 1, characterized in that the drying temperature in step (4) is 60-80°C, and the calcination process parameters are: heating rate is 5-15°C/min, holding temperature is 550-800°C, calcination time is 4-6h, and the material is cooled to 25-100°C. LU507876

6. The preparation method according to claim 1, characterized in that the evaporation temperature in step (5) is 60-180°C.

7. A battery-grade iron phosphate obtained by the preparation method according to any one of claims 1-6.

PATENTANSPRÜCHE

1. Ein Herstellungsverfahren von Eisenphosphat für Batterien, dadurch gekennzeichnet, dass es die folgenden Schritte umfasst:

(1) Auslaugen: Auslaugen von Eisenkonzentratpulver mit einer sauren Lösung, um eine Lösung von Eisen zu erhalten, wobei die Auslaugtemperatur 60 - 90°C beträgt und die Konzentration der sauren Lösung auf 4,5 - 6,0 mol/L eingestellt wird;

(2) Mischen: Mischen der Lösung von Eisen und der Lösung von Phosphat entsprechend dem molaren Verhältnis von Fe:P = 0,9 - 1,05: 1, um eine gemischte Lösung zu erhalten, dann Hinzufügen eines Tensids, Hinzufügen eines Oxidationsmittels, um es vollständig zu oxidieren, und erneutes gleichmäßiges Mischen, um eine Reaktionsmutterlauge zu erhalten, wobei das Oxidationsmittel H_2O_2 ist und die Konzentration 3 - 30% beträgt;

(3) Präzipitation: Zugabe von alkalischer Lösung in die Reaktionsmutterlauge mit Hilfe einer peristaltischen Pumpe bei einer bestimmten Temperatur und Einstellen des pH-Werts auf einen bestimmten Wert, um ein Präzipitat von Eisenphosphat-Dihydrat zu erhalten;

(4) Waschen, Trocknen und Entwässern: Waschen des Präzipitats von Eisenphosphat-Dihydrat, bis die Leitfähigkeit kleiner oder gleich 200 $\mu\text{S}/\text{cm}$ ist, Schnelltrocknen des Filterkuchens von Eisenphosphat-Dihydrat und Kalzinieren, um Eisenphosphat für Batterien zu erhalten;

(5) Behandlung der Tailing-Lösung: Eindampfen und Umkristallisieren des Abwassers aus der Präzipitationsreaktion und dem Waschprozess, um das Nebenprodukt Ammoniumchlorid oder Ammoniumsulfat zu erhalten;

wobei die Konzentration des Tensids in der gemischten Lösung 3 - 10 g/l beträgt; das Tensid ist eines oder mehrere von Dodecyltrimethylammonium bromid, Natriumdodecylsulfat und Fettsäuremonoglycerid.

2. Das Herstellungsverfahren nach Anspruch 1, dadurch gekennzeichnet, dass der Fe-Gehalt des Eisenkonzentratpulvers in Schritt (1) 30 - 79% beträgt und die saure Lösung eine oder zwei der Säuren Salzsäure und Schwefelsäure ist.
3. Das Herstellungsverfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Phosphat in Schritt (2) eine oder mehrere von Phosphorsäure, Diammoniumhydrogenphosphat, Ammoniumdihydrogenphosphat und Ammoniumphosphat ist.
4. Das Herstellungsverfahren nach Anspruch 1, dadurch gekennzeichnet, dass die alkalische Lösung in Schritt (3) eines oder mehrere von Ammoniak, Natriumhydroxid und Natriumcarbonat ist, wobei die Reaktionstemperatur 60 - 90°C beträgt und der pH-Wert zwischen 0,9 - 2,0 eingestellt wird.
5. Das Herstellungsverfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Trocknungstemperatur in Schritt (4) 60 - 80°C beträgt und die Parameter des Kalzinierungsprozesses sind: Aufheizgeschwindigkeit 5 - 15°C/min, Haltetemperatur 550 - 800°C, Kalzinierungszeit 4 - 6 h, und das Material wird auf 25 - 100°C abgekühlt.
6. Das Herstellungsverfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Verdampfungstemperatur in Schritt (5) 60 - 180°C beträgt.
7. Ein Eisenphosphat für Batterien, erhalten durch das Herstellungsverfahren nach einem der Ansprüche 1 - 6.

FIGURES

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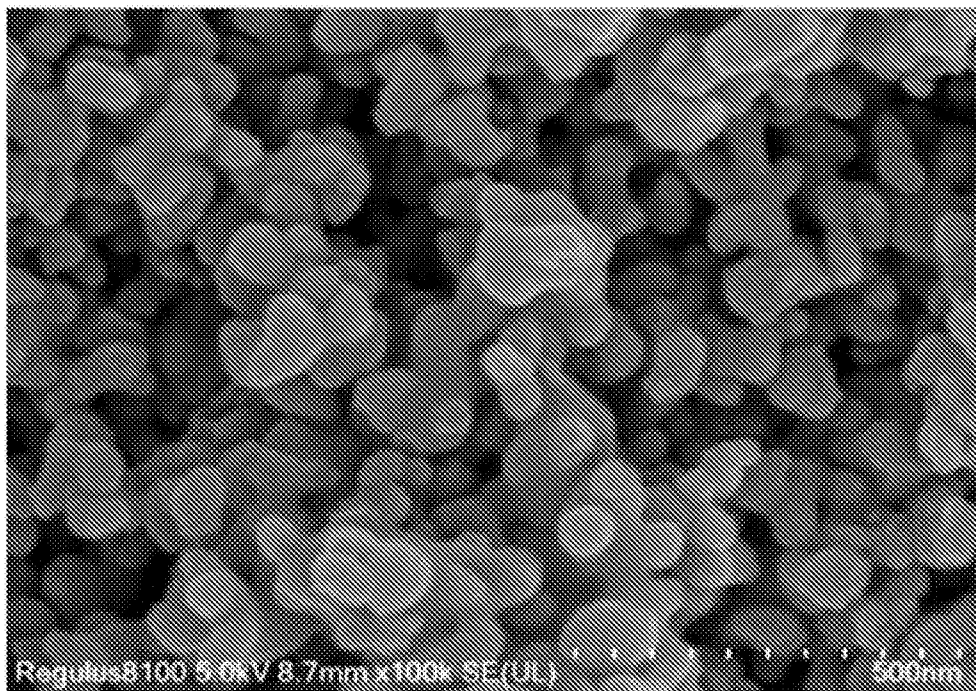


Fig. 1

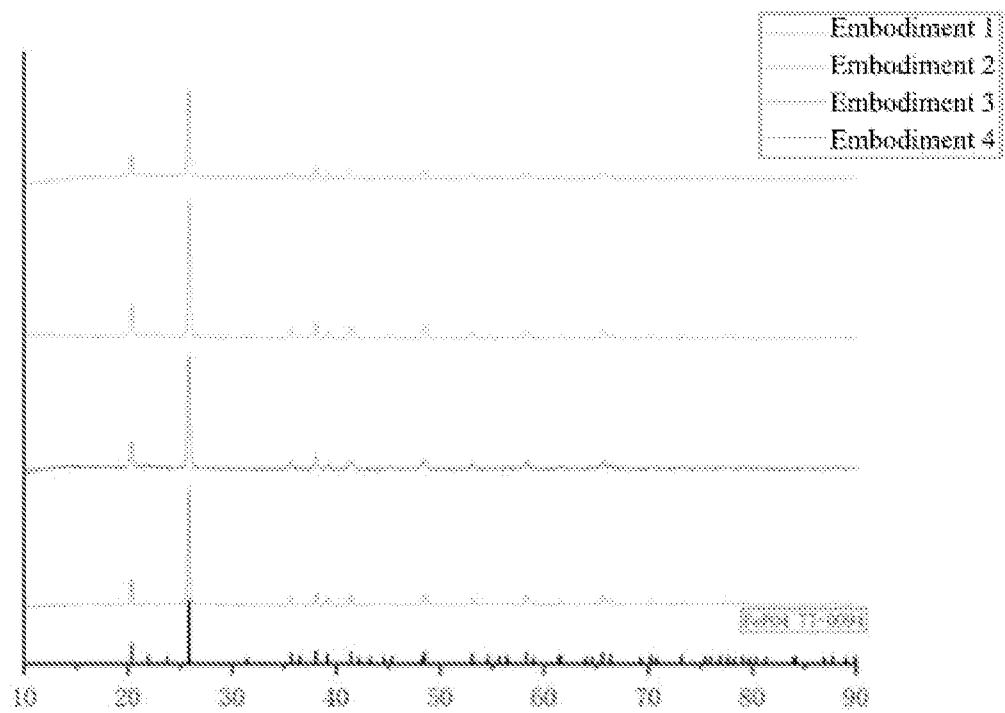


Fig. 2

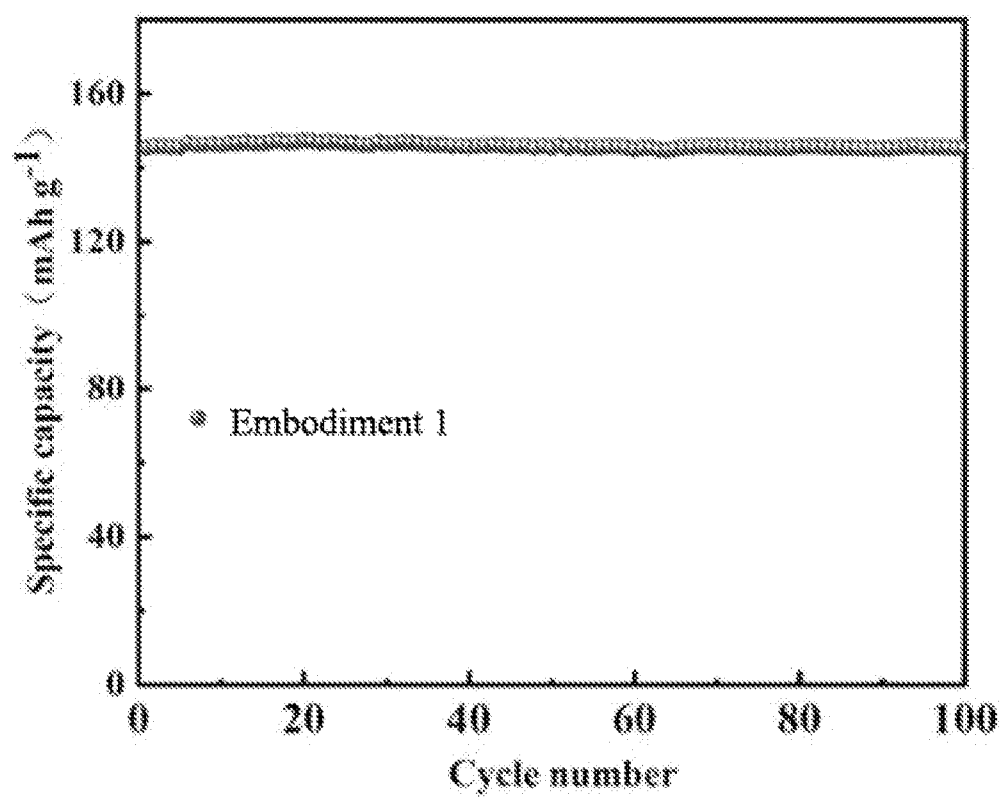


Fig. 3

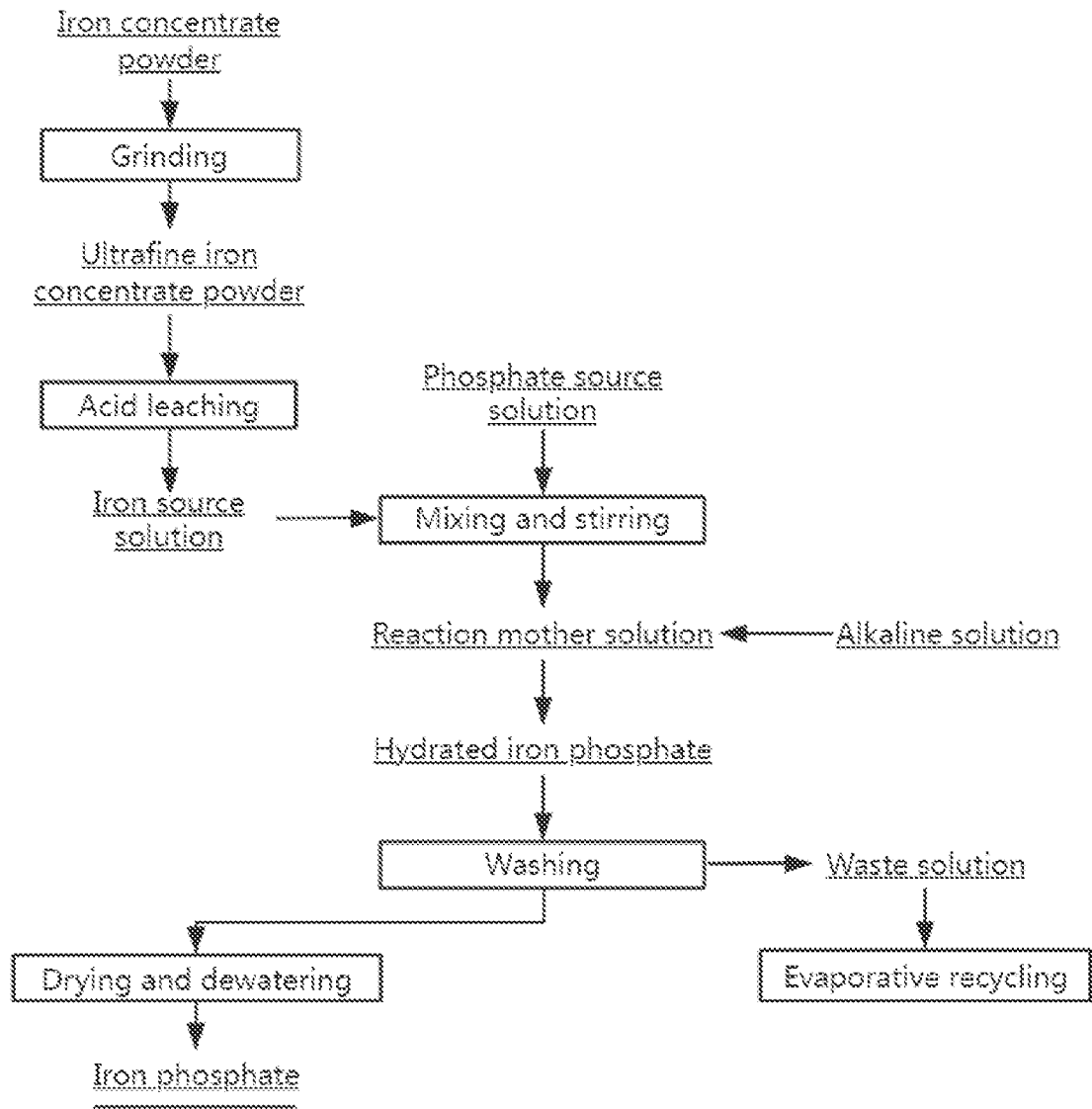


Fig. 4