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(54) Title of the Invention: **Template growth method for preparing lithium cobaltate precursor and use thereof**
Abstract Title: **Template growth method for preparing lithium cobaltate precursor and use thereof**

(57) Provided are a template growth method for preparing a lithium cobaltate precursor and use. The method comprises: S1: mixing an aqueous ammonium metavanadate solution with a polyvinylpyrrolidone solution for hydrothermal reaction, and calcining the obtained precipitate under an aerobic atmosphere to obtain a vanadium pentoxide structure-directing agent, wherein the polyvinylpyrrolidone solution is prepared by dissolving polyvinylpyrrolidone in an alcohol; S2: adding the vanadium pentoxide structure-directing agent to a cobalt salt solution to obtain a turbid liquid, adding the turbid liquid, a carbonate solution, and a complexing agent in a parallel flow mode for reaction, and performing aging when the reaction material reaches a target particle size; and S3: performing solid-liquid separation on the aged material, and anaerobically calcining the obtained precipitate before aerobic calcination to obtain a lithium cobaltate precursor. Also provided is use of the method in preparing a lithium cobaltate or lithium ion battery. Vanadium pentoxide is used as a seed crystal for coprecipitation to obtain a precursor with good crystallinity, thus improving the cycle performance of the material. Meanwhile, vanadium is doped into a lithium cobaltate material, such that the material has good lattice stability and relatively high specific capacity.

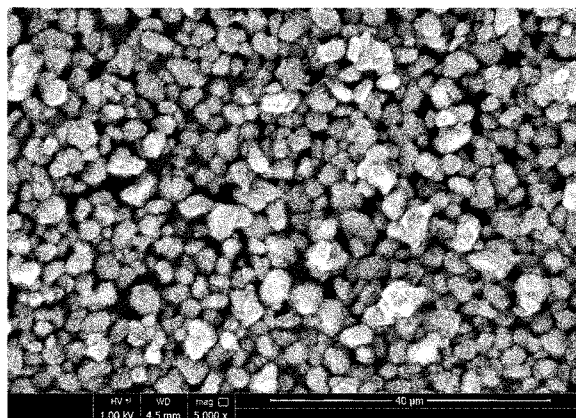


图 1

GB 2621290 A

GB 2621290 A continuation

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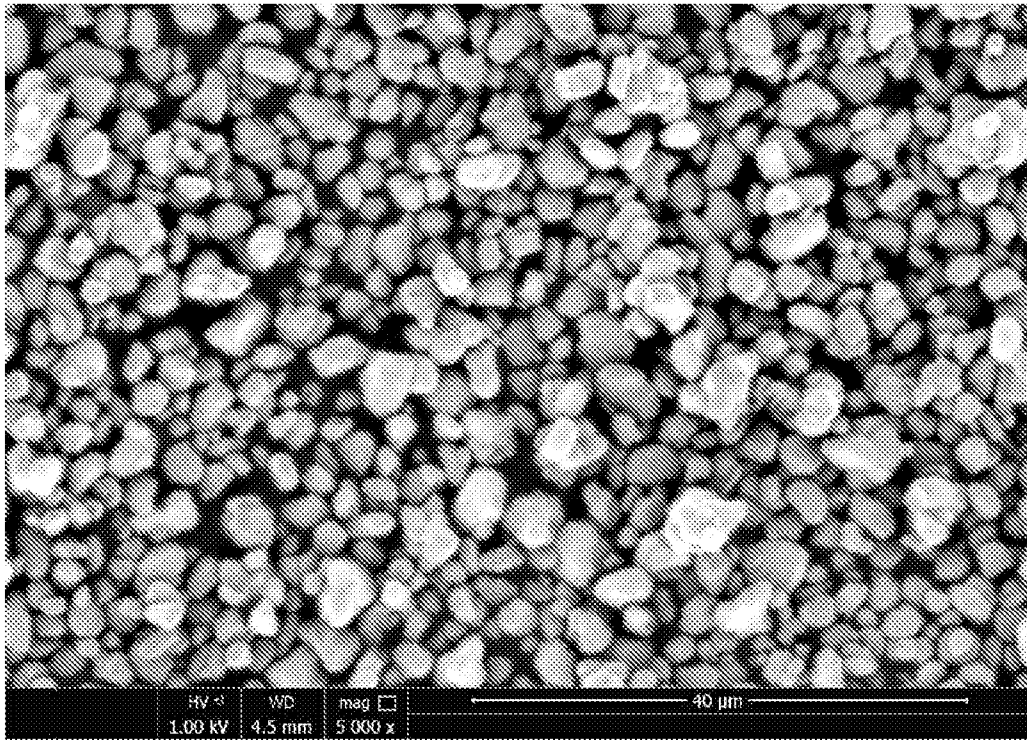


FIG. 1

TEMPLATE GROWTH METHOD FOR PREPARING LITHIUM COBALTATE PRECURSOR AND USE THEREOF

TECHNICAL FIELD

The present disclosure belongs to the technical field of lithium battery cathode materials, and specifically relates to a method for preparing a lithium cobalt oxide (LCO) precursor through template-induced growth and use thereof.

BACKGROUND

With advantages such as high specific energy, light weight, and environmental friendliness, lithium-ion batteries (LIBs) have been widely used in digital products, household appliances, electric vehicles, aerospace, satellites, weaponry, to name just a few, and play an increasingly-important role in civil, aerospace, and military fields. As portable electronic devices such as mobile phones, digital cameras, and notebook computers become increasingly more miniature, lighter, and thinner, the market places ever growing high standard on energy density, electrochemical performance, and safety of LIBs.

LiCoO₂ (Lithium cobalt oxide, LCO) cathode material has the advantages of high voltage plateau, excellent cycling performance, high compacted density, and so on, and thus is one of the first commercialized cathode materials. However, due to the structure of LCO, when a charging voltage exceeds 4.2 V, a deintercalation coefficient x of Li_{1-x}CoO₂ is greater than or equal to 0.5 and its internal structure collapses, which will lead to a series of problems such as poor charge-discharge cycles and poor high-temperature storage performance at the high voltage. Therefore, in order to improve the discharge capacity and energy density of a battery by increasing a charge cut-off voltage of the battery, it is first necessary to modify these cathode materials to solve many problems caused by the increase in charge cut-off voltage.

The doping modification of an LCO material can improve the structural stability of the material before and after a charge-discharge process, inhibit the generation of phase transition, and increase the delithiation degree, capacity, and electric conductivity of the material. According to the theory of crystal chemistry, sometimes the doping of a small amount of a foreign element leads to crystal defects, which can increase the diffusion rate of ions in a bulk phase. According to the energy band theory, a p-type or n-type semiconductor can be produced by doping a semiconductor compound with high-valent or low-valent ions, which can increase the electric conductivity of the crystal. In recent years, the influence of doping with different metal elements (Mg, Al, and Zr) on the electrochemical performance of an LCO cathode material has been explored by researchers. However, there are few reports on LCO cathode materials doped with a small amount of vanadium.

SUMMARY

The present disclosure is intended to solve at least one of the technical problems existing in the prior art. In view of this, the present disclosure provides a method for preparing an LCO precursor through template-induced growth and use thereof. In the method, a vanadium pentoxide particle is prepared as a template, and then vanadium is doped during co-precipitation to obtain a vanadium-doped LCO precursor.

According to an aspect of the present disclosure, a method for preparing an LCO precursor through template-induced growth is provided, including the following steps:

10 S1: mixing an ammonium metavanadate (AMV) aqueous solution with a polyvinylpyrrolidone (PVP) solution to allow a hydrothermal reaction, and subjecting a resulting precipitate to calcination in an aerobic atmosphere to obtain a vanadium pentoxide template, where the PVP solution is prepared by dissolving PVP in an alcohol;

15 S2: adding the vanadium pentoxide template to a cobalt salt solution to obtain a suspension, concurrently feeding the suspension, a carbonate solution, and a complexing agent to allow a reaction, and when a particle size of a resulting reaction system reaches a target value, aging; and

S3: conducting solid-liquid separation (SLS) to obtain a precipitate, and subjecting the precipitate first to anaerobic calcination and then to aerobic calcination to obtain the LCO precursor.

20 In some embodiments of the present disclosure, in the step S1, the AMV aqueous solution may be prepared by dissolving AMV in water; and the AMV, the water, the PVP, and the alcohol may be in a ratio of (1-3) g : (25-35) mL : (8-12) g : (90-110) mL.

In some preferred embodiments of the present disclosure, in the step S1, the alcohol may be ethylene glycol (EG).

25 In some embodiments of the present disclosure, in the step S1, the hydrothermal reaction may be conducted at 170°C to 190°C for 20 h to 28 h.

30 In some embodiments of the present disclosure, in the step S1, the vanadium pentoxide template may have a particle size of 50 nm to 100 nm. The vanadium pentoxide template is micro-spherical, and a particle size of the vanadium pentoxide template cannot be too large or too small. If the template has a too-small particle size, it will dissolve too fast, and cannot play a role of seed crystal well. If the template has a too-large particle size, the dissolution will be too slow, and less cobalt vanadate will be produced. Therefore, when the vanadium pentoxide has a particle size of 50 nm to 100 nm, it can be ensured that the vanadium pentoxide dissolves and produces a cobalt vanadate precipitate at the same time, while it also serves as a template.

In some embodiments of the present disclosure, in the step S1, the calcination may be conducted

at 450°C to 550°C for 1 h to 3 h.

In some embodiments of the present disclosure, in the step S2, the cobalt salt solution may have a concentration of 1.0 mol/L to 2.0 mol/L; and a molar ratio of cobalt in the cobalt salt solution to vanadium in the vanadium pentoxide template may be 10:(0.1-2).

5 In some embodiments of the present disclosure, in the step S2, the cobalt salt solution may be at least one selected from the group consisting of a cobalt sulfate solution, a cobalt nitrate solution, and a cobalt chloride solution.

In some embodiments of the present disclosure, in the step S2, the carbonate solution may be a sodium carbonate solution with a concentration of 1.0 mol/L to 2.0 mol/L.

10 In some embodiments of the present disclosure, in S2, the complexing agent may be ammonium hydroxide with a concentration of 6.0 mol/L to 12.0 mol/L.

In some embodiments of the present disclosure, in the step S2, the reaction may be conducted at a pH of 8 to 9, a temperature of 70°C to 80°C, and an ammonia concentration of 5 g/L to 10 g/L.

15 In some embodiments of the present disclosure, in the step S2, the reaction may be conducted at a stirring speed of 200 r/min to 500 r/min.

In some embodiments of the present disclosure, in the step S2, the aging may be conducted for 48 h to 72 h.

In some embodiments of the present disclosure, in the step S2, the target value of the particle size of the reaction system may be 4.0 μm to 8.0 μm.

20 In some embodiments of the present disclosure, in the step S3, before the anaerobic calcination, the method further comprises washing the precipitate with water and then drying; and the drying may be conducted at 100°C to 200°C for 10 h to 30 h.

In some embodiments of the present disclosure, in the step S3, the anaerobic calcination may be conducted as follows: introducing an inert gas, heating the precipitate from room temperature to a temperature of 200°C to 300°C at a heating rate of 0.5°C/min to 10°C/min and holding the temperature for 4 h to 6 h, and then heating the precipitate to a temperature of 600°C to 800°C and holding the temperature for 1 h to 2 h; and the aerobic calcination may be conducted as follows: introducing an oxidizing gas, and holding the temperature of 600°C to 800°C for 4 h to 6 h.

30 The present disclosure also provides use of the method described above in the preparation of LCO or an LIB.

In some embodiments of the present disclosure, a method for preparing the LCO may include: mixing the LCO precursor with a lithium source, and roasting a resulting mixture in an aerobic atmosphere.

In some embodiments of the present disclosure, the lithium source may be at least one selected

from the group consisting of lithium carbonate, lithium hydroxide, lithium nitrate, and lithium oxalate.

In some embodiments of the present disclosure, a molar ratio of cobalt in the LCO precursor to lithium in the lithium source may be 1:(1.0-1.2).

In some embodiments of the present disclosure, the roasting may be conducted at 900°C to
5 1,200°C for 6 h to 18 h.

According to a preferred embodiment of the present disclosure, the present disclosure at least has the following beneficial effects.

1. In the present disclosure, a nano-scale vanadium pentoxide template is first prepared through a hydrothermal reaction, then the vanadium pentoxide is mixed with a cobalt salt solution, a resulting
10 mixture is subjected to co-precipitation with a carbonate solution and complexing agent to obtain vanadium-doped basic cobalt carbonate, and the vanadium-doped basic cobalt carbonate is subjected to calcination to obtain an LCO precursor. The LCO precursor can be sintered with a lithium source to obtain an LCO cathode material.

2. The vanadium pentoxide template can hardly be dissolved in the cobalt salt solution. Thus,
15 during the co-precipitation, cobalt ions react with carbonate ions and hydroxide ions to produce basic cobalt carbonate, and co-precipitation carries on with the vanadium pentoxide template as a seed crystal to obtain a cobalt carbonate precipitate with prominent crystallinity. When an LCO cathode material is prepared by the subsequent sintering, the prominent crystallinity can be maintained to avoid cracking of the LCO material and improve the cycling performance of the material. In addition, during
20 the co-precipitation, vanadium pentoxide easily dissolves in a slightly-alkaline solution to produce metavanadate, and the metavanadate further reacts with cobalt ions in the solution to produce cobalt vanadate, such that the anion is replaced by vanadium to obtain a vanadium-doped LCO precursor. When the LCO precursor is sintered with a lithium source, the cobalt vanadate further undergoes a crystallization reaction to obtain a vanadium-doped LCO cathode material.

3. Due to the doping of high-valent vanadium, the prepared LCO cathode material exhibits
25 excellent lattice stability and high specific capacity during a charge-discharge process.

BRIEF DESCRIPTION OF DRAWINGS

The present disclosure is further described below with reference to accompanying drawings and
30 examples.

FIG. 1 is a scanning electron microscopy (SEM) image of the LCO prepared in Example 1 of the present disclosure.

DETAILED DESCRIPTION

The concepts and technical effects of the present disclosure are clearly and completely described below in conjunction with examples, such as to allow the objectives, features and effects of the present disclosure to be fully understood. Apparently, the described examples are merely some rather than all of the examples of the present disclosure. All other examples obtained by those skilled in the art based on the examples of the present disclosure without creative efforts should fall within the protection scope of the present disclosure.

Preparation of a vanadium pentoxide template:

AMV, deionized water, PVP K30, and EG were taken according to a ratio of 1 g : 30 mL : 10 g : 100 mL; AMV was dissolved in deionized water to obtain an AMV solution, and PVP K30 was dissolved in EG to obtain a PVP solution; the AMV solution and the PVP solution were mixed and transferred to a hydrothermal reactor to undergo a reaction at 180°C for 24 h; and a resulting precipitate was washed and then calcined at 500°C for 2 h in an air atmosphere to obtain the micro-spherical vanadium pentoxide template with a particle size of 50 nm to 100 nm.

Example 1

An LCO cathode material was prepared in this example, and a specific preparation process was as follows:

Step 1. According to a cobalt-to-vanadium molar ratio of 10:0.1, the vanadium pentoxide template was added to a cobalt sulfate solution with a concentration of 2.0 mol/L, and a resulting mixture was thoroughly mixed to obtain a mixed solution.

Step 2. A sodium carbonate solution with a concentration of 2.0 mol/L was prepared as a precipitating agent.

Step 3. Ammonium hydroxide with a concentration of 12.0 mol/L was prepared as a complexing agent.

Step 4. The mixed solution prepared in step 1, the sodium carbonate solution prepared in step 2, and the ammonium hydroxide prepared in step 3 were concurrently fed into a reactor to allow a reaction at a stirring speed of 200 r/min, a pH of 8, a temperature of 70°C, and an ammonia concentration of 5 g/L.

Step 5. When it was detected that D50 of a resulting precipitate in the reactor reached 8.0 μm, the feeding was stopped and aging was conducted for 48 h.

Step 6. The precipitate in the reactor was separated through SLS, washed with pure water, and dried at 100°C for 30 h.

Step 7. The dried precipitate was placed in a tube furnace; an inert gas was introduced into the tube furnace for protection, and a temperature was raised from room temperature to a temperature of 200°C at a heating rate of 10°C/min and held for 6 h, and then raised to 600°C and held for 2 h; then

an oxidizing gas was introduced instead of the inert gas, and the temperature of 600°C was held for 6 h; and a product was cooled, crushed, and sieved to obtain an LCO precursor material.

Step 8. According to a cobalt-to-lithium molar ratio of 1:1, the LCO precursor material obtained in step 7 was mixed with lithium carbonate, and a resulting mixture was roasted at 900°C for 18 h in an air atmosphere, then crushed, sieved, and subjected to iron removal to obtain the LCO cathode material. FIG. 1 is an SEM image of the LCO prepared in this example, and it can be seen from the figure that the LCO particles have a very-compact blocky structure and are not easy to crack.

Example 2

An LCO cathode material was prepared in this example, and a specific preparation process was as follows:

Step 1. According to a cobalt-to-vanadium molar ratio of 10:1, the vanadium pentoxide template was added to a cobalt nitrate solution with a concentration of 1.5 mol/L, and a resulting mixture was thoroughly mixed to obtain a mixed solution.

Step 2. A sodium carbonate solution with a concentration of 1.5 mol/L was prepared as a precipitating agent.

Step 3. Ammonium hydroxide with a concentration of 9.0 mol/L was prepared as a complexing agent.

Step 4. The mixed solution prepared in step 1, the sodium carbonate solution prepared in step 2, and the ammonium hydroxide prepared in step 3 were concurrently fed into a reactor to allow a reaction at a stirring speed of 350 r/min, a pH of 8.5, a temperature of 75°C, and an ammonia concentration of 8 g/L.

Step 5. When it was detected that D50 of a resulting precipitate in the reactor reached 6.0 μm, the feeding was stopped and aging was conducted for 60 h.

Step 6. The precipitate in the reactor was separated through SLS, washed with pure water, and dried at 150°C for 20 h.

Step 7. The dried precipitate was placed in a tube furnace; an inert gas was introduced into the tube furnace for protection, and a temperature was raised from room temperature to a temperature of 250°C at a heating rate of 5°C/min and held for 5 h, and then raised to 700°C and held for 1.5 h; then an oxidizing gas was introduced instead of the inert gas, and the temperature of 700°C was held for 5 h; and a product was cooled, crushed, and sieved to obtain an LCO precursor material.

Step 8. According to a cobalt-to-lithium molar ratio of 1:1.1, the LCO precursor material obtained in step 7 was mixed with lithium hydroxide, and a resulting mixture was roasted at 1,050°C for 12 h in an air atmosphere, then crushed, sieved, and subjected to iron removal to obtain the LCO cathode material.

Example 3

An LCO cathode material was prepared in this example, and a specific preparation process was as follows:

Step 1. According to a cobalt-to-vanadium molar ratio of 10:2, the vanadium pentoxide template
5 was added to a cobalt chloride solution with a concentration of 1.0 mol/L, and a resulting mixture was thoroughly mixed to obtain a mixed solution.

Step 2. A sodium carbonate solution with a concentration of 1.0 mol/L was prepared as a precipitating agent.

Step 3. Ammonium hydroxide with a concentration of 6.0 mol/L was prepared as a complexing
10 agent.

Step 4. The mixed solution prepared in step 1, the sodium carbonate solution prepared in step 2, and the ammonium hydroxide prepared in step 3 were concurrently fed into a reactor to allow a reaction at a stirring speed of 500 r/min, a pH of 9, a temperature of 80°C, and an ammonia concentration of 10 g/L.

Step 5. When it was detected that D50 of a resulting precipitate in the reactor reached 4.0 μm, the
15 feeding was stopped and aging was conducted for 72 h.

Step 6. The precipitate in the reactor was separated through SLS, washed with pure water, and dried at 200°C for 10 h.

Step 7. The dried precipitate was placed in a tube furnace; an inert gas was introduced into the
20 tube furnace for protection, and a temperature was raised from room temperature to a temperature of 300°C at a heating rate of 10°C/min and held for 4 h, and then raised to 800°C and held for 1 h; then an oxidizing gas was introduced instead of the inert gas, and the temperature of 800°C was held for 4 h; and a product was cooled, crushed, and sieved to obtain an LCO precursor material.

Step 8. According to a cobalt-to-lithium molar ratio of 1:1, the LCO precursor material obtained
25 in step 7 was mixed with lithium nitrate, and a resulting mixture was roasted at 1,200°C for 6 h in an air atmosphere, then crushed, sieved, and subjected to iron removal to obtain the LCO cathode material.

Comparative Example 1

An LCO cathode material was prepared in this comparative example, which was different from
30 Example 1 in that the vanadium pentoxide template was not added. A specific preparation process was as follows:

Step 1. A cobalt sulfate solution with a concentration of 2.0 mol/L was prepared.

Step 2. A sodium carbonate solution with a concentration of 2.0 mol/L was prepared as a precipitating agent.

Step 3. Ammonium hydroxide with a concentration of 12.0 mol/L was prepared as a complexing

agent.

Step 4. The cobalt sulfate solution prepared in step 1, the sodium carbonate solution prepared in step 2, and the ammonium hydroxide prepared in step 3 were concurrently fed into a reactor to allow a reaction at a stirring speed of 200 r/min, a pH of 8, a temperature of 70°C, and an ammonia concentration of 5 g/L.

Step 5. When it was detected that D50 of a resulting precipitate in the reactor reached 8.0 μm, the feeding was stopped and aging was conducted for 48 h.

Step 6. The precipitate in the reactor was separated through SLS, washed with pure water, and dried at 100°C for 30 h.

Step 7. The dried precipitate was placed in a tube furnace; an inert gas was introduced into the tube furnace for protection, and a temperature was raised from room temperature to a temperature of 200°C at a heating rate of 10°C/min and held for 6 h, and then raised to 600°C and held for 2 h; then an oxidizing gas was introduced instead of the inert gas, and the temperature of 600°C was held for 6 h; and a product was cooled, crushed, and sieved to obtain an LCO precursor material.

Step 8. According to a cobalt-to-lithium molar ratio of 1:1, the LCO precursor material obtained in step 7 was mixed with lithium carbonate, and a resulting mixture was roasted at 900°C for 18 h in an air atmosphere, then crushed, sieved, and subjected to iron removal to obtain the LCO cathode material.

Comparative Example 2

An LCO cathode material was prepared in this comparative example, which was different from Example 2 in that the vanadium pentoxide template was not added. A specific preparation process was as follows:

Step 1. A cobalt nitrate solution with a concentration of 1.5 mol/L was prepared.

Step 2. A sodium carbonate solution with a concentration of 1.5 mol/L was prepared as a precipitating agent.

Step 3. Ammonium hydroxide with a concentration of 9.0 mol/L was prepared as a complexing agent.

Step 4. The cobalt nitrate solution prepared in step 1, the sodium carbonate solution prepared in step 2, and the ammonium hydroxide prepared in step 3 were concurrently fed into a reactor to allow a reaction at a stirring speed of 350 r/min, a pH of 8.5, a temperature of 75°C, and an ammonia concentration of 8 g/L.

Step 5. When it was detected that D50 of a resulting precipitate in the reactor reached 6.0 μm, the feeding was stopped and aging was conducted for 60 h.

Step 6. The precipitate in the reactor was separated through SLS, washed with pure water, and

dried at 150°C for 20 h.

Step 7. The dried precipitate was placed in a tube furnace; an inert gas was introduced into the tube furnace for protection, and a temperature was raised from room temperature to a temperature of 250°C at a heating rate of 5°C/min and held for 5 h, and then raised to 700°C and held for 1.5 h; then an oxidizing gas was introduced instead of the inert gas, and the temperature of 700°C was held for 5 h; and a product was cooled, crushed, and sieved to obtain an LCO precursor material.

Step 8. According to a cobalt-to-lithium molar ratio of 1:1.1, the LCO precursor material obtained in step 7 was mixed with lithium hydroxide, and a resulting mixture was roasted at 1,050°C for 12 h in an air atmosphere, then crushed, sieved, and subjected to iron removal to obtain the LCO cathode material.

Comparative Example 3

An LCO cathode material was prepared in this comparative example, which was different from Example 3 in that the vanadium pentoxide template was not added. A specific preparation process was as follows:

Step 1. A cobalt chloride solution with a concentration of 1.0 mol/L was prepared.

Step 2. A sodium carbonate solution with a concentration of 1.0 mol/L was prepared as a precipitating agent.

Step 3. Ammonium hydroxide with a concentration of 6.0 mol/L was prepared as a complexing agent.

Step 4. The cobalt chloride solution prepared in step 1, the sodium carbonate solution prepared in step 2, and the ammonium hydroxide prepared in step 3 were concurrently fed into a reactor to allow a reaction at a stirring speed of 500 r/min, a pH of 9, a temperature of 80°C, and an ammonia concentration of 10 g/L.

Step 5. When it was detected that D50 of a resulting precipitate in the reactor reached 4.0 μm, the feeding was stopped and aging was conducted for 72 h.

Step 6. The precipitate in the reactor was separated through SLS, washed with pure water, and dried at 200°C for 10 h.

Step 7. The dried precipitate was placed in a tube furnace; an inert gas was introduced into the tube furnace for protection, and a temperature was raised from room temperature to a temperature of 300°C at a heating rate of 10°C/min and held for 4 h, and then raised to 800°C and held for 1 h; then an oxidizing gas was introduced instead of the inert gas, and the temperature of 800°C was held for 4 h; and a product was cooled, crushed, and sieved to obtain an LCO precursor material.

Step 8. According to a cobalt-to-lithium molar ratio of 1:1, the LCO precursor material obtained in step 7 was mixed with lithium nitrate, and a resulting mixture was roasted at 1,200°C for 6 h in an

air atmosphere, then crushed, sieved, and subjected to iron removal to obtain the LCO cathode material.

Test Example

The LCO cathode material obtained from each of Examples 1-3 and Comparative Examples 1-3, acetylene black (as a conductive agent), and polyvinylidene fluoride (PVDF) (as a binder) were weighed and mixed in a ratio of 92:4:4, then a specified amount of an organic solvent N-methylpyrrolidone (NMP) was added, and a resulting mixture was stirred and coated on an aluminum foil to obtain a cathode; and then with a metal lithium sheet as an anode, a CR2430 button battery was assembled in an argon-filled glove box. An electrical performance test was conducted on a CT2001A L test system under the following conditions: voltage: 3.0 V to 4.48 V, current density: 1 C = 180 mAh/g, and test temperature: 25 ± 1°C. Test results were shown in Table 1.

Table 1 Electrochemical performance of LCO

	Discharge capacity at 0.1 C/4.48 V, mAh/g	Capacity retention after 600 cycles at 0.1 C/4.48 V
Example 1	232.6	88%
Example 2	247.3	85%
Example 3	258.6	82%
Comparative Example 1	208.2	72%
Comparative Example 2	208.6	71%
Comparative Example 3	208.8	68%

It can be seen from Table 1 that the discharge capacity and cycling performance of the examples are significantly superior to the discharge capacity and cycling performance of the comparative examples, which is attributed to the addition of the vanadium pentoxide template in the examples. When vanadium pentoxide is used as a seed crystal for co-precipitation, a precursor with prominent crystallinity is obtained, and an LCO cathode material obtained by the sintering of the precursor inherits the prominent crystallinity, which makes the LCO cathode material difficult to crack and improves the cycling performance of the cathode material. In addition, vanadium pentoxide can be dissolved to produce metavanadate during the co-precipitation, and the metavanadate reacts with

cobalt ions to produce cobalt vanadate, such that vanadium is doped into the LCO material smoothly, which makes the cathode material have prominent lattice stability and high specific capacity.

The examples of the present disclosure are described in detail with reference to the accompanying drawings, but the present disclosure is not limited to the above examples. Within the scope of
5 knowledge possessed by those of ordinary skill in the technical field, various changes can also be made without departing from the purpose of the present disclosure. In addition, the examples in the present disclosure and features in the examples may be combined with each other in a non-conflicting situation.

CLAIMS

1. A method for preparing a lithium cobalt oxide (LCO) precursor through template-induced growth, comprising the following steps:

5 S1: mixing an ammonium metavanadate aqueous solution with a polyvinylpyrrolidone solution to allow a hydrothermal reaction, and subjecting a resulting precipitate to calcination in an aerobic atmosphere to obtain a vanadium pentoxide template, wherein the polyvinylpyrrolidone solution is prepared by dissolving polyvinylpyrrolidone in an alcohol;

S2: adding the vanadium pentoxide template to a cobalt salt solution to obtain a suspension, concurrently feeding the suspension, a carbonate solution, and a complexing agent to allow a reaction, and when a particle size of a resulting reaction system reaches a target value, aging; and

10 S3: conducting solid-liquid separation to obtain a precipitate, and subjecting the precipitate first to anaerobic calcination and then to aerobic calcination to obtain the LCO precursor.

2. The method according to claim 1, wherein in the step S1, the ammonium metavanadate aqueous solution is prepared by dissolving ammonium metavanadate in water; and the ammonium metavanadate, the water, the polyvinylpyrrolidone, and the alcohol are in a ratio of (1-3) g : (25-35) mL : (8-12) g : (90-110) mL.

3. The method according to claim 1, wherein in the step S1, the hydrothermal reaction is conducted at 170°C to 190°C for 20 h to 28 h.

4. The method according to claim 1, wherein in the step S1, the vanadium pentoxide template has a particle size of 50 nm to 100 nm.

5. The method according to claim 1, wherein in the step S2, the cobalt salt solution has a concentration of 1.0 mol/L to 2.0 mol/L; and a molar ratio of cobalt in the cobalt salt solution to vanadium in the vanadium pentoxide template is 10:(0.1-2).

6. The method according to claim 1, wherein in the step S2, the carbonate solution is a sodium carbonate solution with a concentration of 1.0 mol/L to 2.0 mol/L.

7. The method according to claim 1, wherein in the step S2, the reaction is conducted at a pH of 8 to 9, a temperature of 70°C to 80°C, and an ammonia concentration of 5 g/L to 10 g/L.

8. The method according to claim 1, wherein in the step S2, the aging is conducted for 48 h to 72 h.

9. The method according to claim 1, wherein in the step S3, the anaerobic calcination is conducted as follows: introducing an inert gas, heating the precipitate from room temperature to a temperature of 200°C to 300°C at a heating rate of 0.5°C/min to 10°C/min and holding the temperature for 4 h to 6 h, and then heating the precipitate to a temperature of 600°C to 800°C and holding the temperature for 1 h to 2 h; and the aerobic calcination is conducted as follows: introducing

an oxidizing gas, and holding the temperature of 600°C to 800°C for 4 h to 6 h.

10. Use of the method according to any one of claims 1 to 9 in the preparation of LCO or a lithium-ion battery.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2023/077217

A. CLASSIFICATION OF SUBJECT MATTER

C01G51/00(2006.01)i;C01G31/02(2006.01)i;H01M10/052(2010.01)i;H01M4/525(2010.01)i

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)

IPC: C01G51/-, C01G31/-, H01M10/-, H01M4/-

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)

CNXTX, CNKI, VEN, ENTXT, WEB OF SCIENCE: 钒酸铵, 偏钒酸铵, 聚乙烯吡咯烷酮, 水热, 五氧化二钒, 模板, 钴盐, 硝酸钴, 硫酸钴, 氯化钴, 碳酸盐, 碳酸钠, 沉淀剂, 络合剂, 氨水, 钴酸锂, 四氧化三钴, 前驱体; vanadium ammonium, polyvinylpyrrolidone, polyvinyl pyrrolidone, hydrothermal, vanadium pentoxide, template, cobalt salt, cobalt nitrate, cobalt sulfate, cobalt chloride, carbonate, sodium carbonate, precipitant, complex, ammonia, lithium cobaltate, lithium cobalt oxide, lithium cobaltite, cobalt tetroxide, tricobalt tetraoxide, precursor; NH₄VO₃, PVP, Na₂CO₃, NH₃·H₂O, Co₃O₄, Co^{???}M^{???}O^{???}, Co^{???}M^{???}O^{???}

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	CN 114735757 A (GUANGDONG BRUNP RECYCLING TECHNOLOGY CO., LTD. et al.) 12 July 2022 (2022-07-12) claims 1-10	1-10
A	CN 105047906 A (HUNAN SHANSHAN NEW MATERIAL CO., LTD.) 11 November 2015 (2015-11-11) claims 1-10	1-10
A	CN 112255279 A (SHENYANG UNIVERSITY OF CHEMICAL TECHNOLOGY) 22 January 2021 (2021-01-22) claims 1-2	1-10
A	US 2020227742 A1 (NINGDE AMPEREX TECHNOLOGY LTD.) 16 July 2020 (2020-07-16) entire document	1-10

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

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance
 “D” document cited by the applicant in the international application
 “E” earlier application or patent but published on or after the international filing date
 “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 “O” document referring to an oral disclosure, use, exhibition or other means
 “P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

24 March 2023

Date of mailing of the international search report

24 May 2023

Name and mailing address of the ISA/CN

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Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2023/077217

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2004010375 A (NIPPON CHEM IND. CO., LTD.) 15 January 2004 (2004-01-15) entire document	1-10
A	孟琳等 (MENG, Lin et al.). "五氧化二钒纳米颗粒的制备及其电化学性能研究 (Vanadium Pentoxide nanorods mixed Solvent Hydrothermal Process metal-doping anode electrochemical Performance)" 北京化工大学学报 (自然科学版) (<i>Journal of Beijing University of Chemical Technology (Natural Science Edition)</i>), Vol. 43, No. (3), 31 May 2016 (2016-05-31), pp. 60-65	1-10