



(12) PATENT APPLICATION FOR INVENTION



(10) Application Publication No.: CN 102456881 A

(43) Application Publication Date: 16 May 2012

(21) Application No.: 201010517761.6

HO1M 10/052 (2010.01)

(22) Filing Date: 18 October 2010

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(51) Int. Cl.

HO1M 4/58 (2010.01)

HO1M 4/1397 (2010.01)

HO1M 4/136 (2010.01)

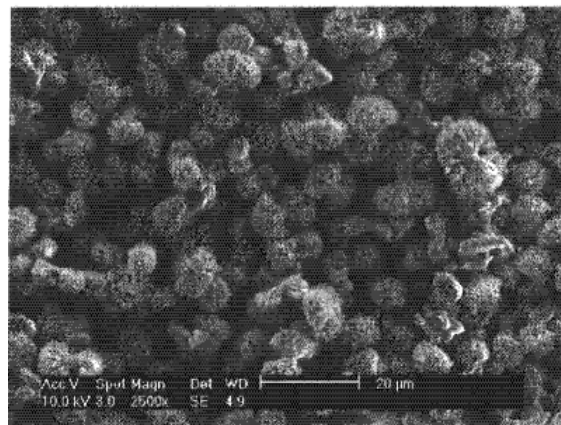
Claims: 2 pages; Description: 10 pages; Drawings: 3 pages

(54) Title of Invention

OLIVINE PHOSPHATE POSITIVE ELECTRODE
MATERIAL, PREPARATION METHOD THEREFOR,
AND POSITIVE ELECTRODE AND BATTERY
COMPRISING POSITIVE ELECTRODE MATERIAL

(57) Abstract

Provided in the present invention are an olivine phosphate positive electrode material, a preparation method therefor, and a positive electrode and a battery including the positive electrode material. The positive electrode material includes: a carbon nanotube cluster formed by tangling carbon nanotubes, a secondary particle formed by agglomeration of sheet-like primary particles attached to an outer side of the carbon nanotube cluster, and a carbon layer covering an outer surface of the secondary particle, the sheet-like primary particles having an olivine crystal structure, and having the following chemical composition: $\text{Li}_x\text{A}_a\text{M}_m\text{B}_b\text{PO}_z\text{N}_n$. The positive electrode material has the advantages of a good carbon coating effect, small primary particles, and large secondary particles, and is prepared by selecting a suitable precursor and suitable reaction conditions, adding raw materials according to a chemical molar ratio to an organic solvent to perform an ultrasonic solvothermal reaction, and then performing high-temperature annealing. The preparation method has few steps, low energy consumption, convenient operations, and low raw material costs. The positive electrode material of the present invention may be directly used as a positive electrode material of a secondary lithium battery or



may be mixed with an existing positive electrode material as an additive and used together with the same.

OLIVINE PHOSPHATE POSITIVE ELECTRODE MATERIAL, PREPARATION METHOD THEREFOR, AND POSITIVE ELECTRODE AND BATTERY COMPRISING POSITIVE ELECTRODE MATERIAL

TECHNICAL FIELD

The present invention relates to a positive electrode material for a secondary lithium battery, a preparation method therefor, and a positive electrode and a battery including the positive electrode material, and specifically relates to an olivine phosphate positive electrode material, a preparation method therefor, and a positive electrode and a battery including the positive electrode material.

BACKGROUND

Transition metal lithium phosphates (LiMPO_4 , $\text{M} = \text{Fe, Co, Mn, or Ni}$) having an olivine structure are positive electrode active materials that are mainly used for secondary lithium batteries, and have advantages such as low prices and rich reserves of raw materials, no environmental pollution, good chemical stability, very good safety performance, high lithium storage capacity, good cycle performance, high voltage, etc. The most studied at present is lithium iron phosphate (LiFePO_4), which is considered an ideal candidate for future power supply applications. Disadvantages of such a material are low electron conductivity and low ion conductivity. When the material is used as the positive electrode active material of a secondary lithium battery, rate characteristics of the battery are poor. That is, when the battery is charged/discharged at a large current, the battery capacity is significantly reduced compared to when the battery is charged/discharged at a small current.

To solve this problem, a common method includes: covering surfaces of material particles with carbon and another conductive material or directly combining the material particles with a conductive material to improve electrical contact between the particles and between the particles and a current collector; reducing the particle size to shorten a diffusion path of lithium ions in the particles; doping Li sites or Fe sites with aliovalent ions to improve the electron conductivity and ion conductivity of the material; replacing oxygen with nitrogen; and forming oxygen vacancies to improve the intrinsic electron conductivity and ion conductivity of the material.

In the above modification method, the effect of doping with an aliovalent element needs to be further evaluated, and carbon coating and particle size reduction are more common, but in actual production, some difficulties are incurred. To prepare particles of a small size, a template and a

dispersing agent are often needed, which introduces other impurities, thereby reducing the specific capacity of the material. Furthermore, synthesis often needs to be performed at a low temperature, which results in poor crystallization of the material, thereby affecting properties of the material. In addition, complete carbon coating on particles of a small size having a high specific surface area requires a very large carbon content, which greatly reduces the tap density of the material. Previous studies have shown that lithium ions are transported along a one-dimensional channel, i.e., the (010) direction, in a material. In most hydrothermal or solvothermal experiments, the thinnest direction of an obtained sheet-like material is exactly the (010) direction, i.e., the direction of the path of lithium ion migration, which provides a method for designing a material. That is, the effect achieved by reducing the overall particle size can be achieved by just reducing as much as possible the particle size of the dimension in the lithium ion diffusion direction. However, most hydrothermal or solvothermal samples have poor properties due to the absolute particle size of primary particles of such samples being too large. Agglomeration reduces channels for intercalation and deintercalation of lithium ions, and also makes it difficult for the electrolyte solution to be in sufficient contact with the material. Too low of electrical conductivity results in poor electrical contact between particles and between the particles and a current collector. It is very difficult to ensure uniformity of subsequent carbon coating, and the process is relatively complex. These reasons described above limit applications of transition metal phosphate compounds having relatively reasonable lamellar morphologies and having the olivine structure in the field of secondary batteries.

SUMMARY

The inventors of the present invention have found via studies that the absolute length in the (010) direction of the material particles, the 3D microstructure formed by sheet-like primary particles, and electrical contact of the material are important factors affecting the performance of the positive electrode material. A material having a suitable microstructure can be obtained by optimizing synthesis conditions of an ultrasonic solvothermal method and adding an appropriate quantity of carbon nanotubes to a precursor, and has both primary sheet-like particles that are very thin in the (010) direction and secondary particles that can prevent agglomeration from reducing lithium ion channels and facilitate electrode fabrication. The carbon nanotubes are tangled to form carbon nanotube clusters (particles in the shape of clusters). A carbon nanotube cluster forms an inner core of each secondary particle, and sheet-like primary particles of a phosphate material are

attached to an outer side thereof. Some of the carbon nanotubes forming the cluster are relatively long, and extend to an outer portion of the secondary particle, so that some of the carbon nanotubes are distributed inside the secondary particle. After annealing, a very uniform carbon film is formed on the surface of the material, and forms a conductive network together with the carbon nanotube clusters. The inventors of the present invention have also found that by selecting the combination and ratios of precursors used, a transition metal lithium phosphate positive electrode material having the olivine structure can be prepared by using a simple ultrasonic solvothermal method. The material has a special lamellar spherical microstructure formed by nanosheet-like primary particles and a carbon nanotube cluster core, and no template is needed.

Therefore, an objective of the present invention is to overcome the disadvantages of the existing LiMPO_4 materials prepared hydrothermally or solvothermally and having a lamellar morphology and the olivine structure, i.e., too large primary particles, severe agglomeration, and poor electrical contact, and to provide a phosphate positive electrode material having a lamellar spherical microstructure morphology and an olivine structure. The positive electrode material has a conductive carbon nanotube cluster as a core, and has the advantages of a good carbon coating effect, small primary particles, and large secondary particles.

Another objective of the present invention is to overcome disadvantages of existing phosphate positive electrode materials having the olivine structure, i.e., having a difficult preparation process, the process being complex, and high costs, and to provide a method for preparing a phosphate positive electrode material having the olivine crystal structure and a lamellar spherical microstructure morphology. By selecting a solvent and a precursor and using a simple ultrasonic solvothermal method, the preparation method can obtain a phosphate positive electrode material having the olivine crystal structure and the lamellar spherical microstructure morphology.

Still another objective of the present invention is to provide uses of the positive electrode material. The positive electrode material can be directly used in a secondary lithium battery as a positive electrode active material, and can also be used as an additive used by being mixed with an existing positive electrode material. That is, the positive electrode material of the present invention can be used for a positive electrode of a secondary lithium battery, and to form a secondary lithium battery together with a negative electrode, an electrolyte solution, and a separator.

The technical solution of the present invention is as follows:

provided in the present invention is an olivine phosphate positive electrode material, the positive electrode material comprising: a carbon nanotube cluster formed by tangling carbon nanotubes, a secondary particle formed by agglomeration of sheet-like primary particles attached to an outer side of the carbon nanotube cluster, and a carbon layer covering an outer surface of the secondary particle;

the sheet-like primary particles having an olivine crystal structure, and having the following chemical composition:



wherein a doping element A is selected from at least one of Na, Mg, Ti, V, Cr, Cu, Mn, Co, Ni, Zn, Ga, In, Ge, W, Hg, Au, Ag, Nb, and Zr;

a transition metal M is selected from at least one of Fe, Co, Mn, Ni, and V;

a doping element B is selected from at least one of Li, Na, K, Ca, Mg, Ti, V, Cr, Cu, Mn, Co, Ni, Zn, Ga, In, Ge, Ag, Nb, Hg, Au, Zr, and W;

M and B are not the same element at the same time; and

x, a, m, b, z, and n represent molar ratios, where $0.9 \leq x \leq 1.8$, $0 \leq a \leq 0.1$, $0.5 \leq m \leq 1$, $0 \leq b \leq 0.5$, $3 \leq z \leq 4$, and $0 \leq n \leq 1$.

In the positive electrode material, the thinnest direction of the sheet-like primary particles is the (010) direction of olivine, and the average thickness is 10 to 200 nm. In the positive electrode material, the geometric shape of the secondary particle is spherical, ellipsoidal, spindle-shaped, or dumbbell-shaped, and the average particle size is 1 to 50 μm .

In the positive electrode material, the thickness of the carbon layer is 1 to 10 nm, and the content of carbon accounts for 0.1-25 wt% of the total weight of the positive electrode material.

Also provided in the present invention is a method for preparing the positive electrode material, the method comprising the following steps:

(1) weighing a lithium salt, a transition metal salt, a phosphate, a salt of a doping element, a pH-adjusting agent, a nitrogen source, a carbon source, and carbon nanotubes according to a molar ratio of (0.9 to 1.8):(0.5 to 1):(0.75 to 1):(0 to 0.5):(0 to 2):(0 to 1):(0 to 0.3):(0 to 0.3), and dissolving the same in a solvent to form a solution comprising carbon nanotubes;

(2) placing, in a sealed high-pressure reaction kettle, the solution comprising carbon nanotubes obtained in step (1), introducing a protective gas, and reacting at a temperature of 100°C to 400°C for 1 to 72 hours, preferably reacting for 1 to 10 hours;

(3) cooling the product obtained in step (2), separating a precipitate, and washing the same; and

(4) drying, at a temperature of 40°C to 150°C for 1 to 24 hours, the washed precipitate from step (3), to obtain the positive electrode material.

In the preparation method, the lithium salt is selected from one or a plurality of lithium fluoride, lithium acetate, lithium carbonate, lithium citrate, lithium nitrate, and lithium oxalate, the transition metal salt is selected from one or a plurality of the acetate, carbonate, citrate, nitrate, and oxalate of a transition metal, the salt of the doping element is selected from one or a plurality of the acetate, citrate, nitrate, and oxalate of the doping element, the pH-adjusting agent is selected from one or a plurality of aqueous ammonia, urea, methylamine, ethylenediamine, diisopropylamine, triethanolamine, and tetrabutylammonium bromide, the nitrogen source is selected from one or a plurality of a transition metal nitride, a lithium nitride, an ammonium salt, melamine, ammonia, and nitrogen, the carbon source is selected from one or a plurality of a vitamin, glucose, polyethylene glycol, polyacrylic acid, ascorbic acid, sucrose, citric acid, graphite, acetylene black, and carbon black, and the carbon nanotube is a single-walled or multi-walled carbon nanotube having a diameter of 0.5 to 200 nm and an aspect ratio of 20 to 10000.

In step (1), the solvent is selected from one or a plurality of water, methanol, ethanol, propanol, ethylene glycol, acetone, glycerol, isopropanol, n-butanol, benzyl alcohol, dimethyl sulfoxide, and polyethylene glycol.

In step (2), the protective gas is one or a plurality of argon, nitrogen, hydrogen, and carbon monoxide.

In step (3), a solvent for washing is selected from one or a plurality of water, ethanol, acetone, dichloromethane, chloroform, ethyl acetate, and tetrahydrofuran.

The preparation method further comprises: after introducing the protective gas in step (2), pre-reacting first at a reaction temperature of 60°C to 120°C, preferably 80°C, for 0.5 to 12 hours, preferably 2 hours.

The preparation method further comprises: performing ultrasonic treatment in the reaction of step (2) at an ultrasonic frequency of 20K to 100 kHz and a power of 0 to 3000 W.

The preparation method further comprises: sintering the dried product from step (4) at a temperature of 200°C to 400°C in an inert atmosphere or an inert atmosphere comprising a reducing gas for 1 to 10 hours; and then sintering the resulting product at a temperature of 400°C to 800°C, preferably 550°C to 700°C, for 1 to 24 hours, preferably 3 to 10 hours.

Preferably, the inert atmosphere is argon or nitrogen, and the reducing gas is hydrogen or carbon monoxide.

In the preparation method, the heating rate in the reaction or sintering step is 1°C/min to 10°C/min.

Also provided in the present invention is a lithium positive electrode for a secondary lithium battery, the lithium positive electrode comprising a current collector and a positive electrode material coated on the current collector, wherein the positive electrode material comprises the above positive electrode material of the present invention.

Also provided in the present invention is a secondary lithium battery, the lithium battery comprising a positive electrode, a negative electrode, an electrolyte solution, and a separator, wherein the positive electrode is the above lithium positive electrode of the present invention.

Compared with the prior art, the present invention has at least the following beneficial effects:

1) the olivine phosphate material (i.e., the positive electrode material of the present invention) having the lamellar spherical microstructure can improve the rate performance, energy density, and capacity of existing phosphate material batteries. The microscopic morphology of the material is constructed, so that the material has sheet-like primary particles that facilitate lithium ion transport. The carbon nanotube cluster forms the core. The primary particles are agglomerated on the outer side of the carbon nanotube cluster to form the secondary particle. Some carbon nanotubes are distributed inside the entire secondary particle, and combination thereof not only can maintain good communication between the primary particles and the exterior in the (010) direction which allows the electrolyte solution to permeate easily, provides a fast ion transport channel, and results in a large reaction interface, but also can effectively maintain a large specific surface area in a plane perpendicular to the (010) direction of the primary particles and form good contact with the carbon nanotubes, thereby overcoming the disadvantages of poor interface

transport properties and slow interface reaction of the olivine material. The outer surface of the material particle is covered with a thin and uniform carbon film, and the conductive carbon film can form a continuous and uniform graded conductive network by bridging the entire secondary particle with the carbon nanotube cluster core and the distribution in the particle, so that the material maintains good electrochemical performance.

2) In the present invention, the phosphate positive electrode material having the lamellar spherical microstructure morphology and the olivine crystal structure is prepared for the first time by selecting the suitable precursor, solvent, and reaction conditions and by using the simple ultrasonic solvothermal reaction method. The preparation process is very simple, and can prepare a material having a three-dimensional microstructure having good performance without involving other complex processes and expensive raw materials.

3) The olivine phosphate material having the lamellar spherical microstructure provided by the present invention has relatively large secondary particles, can greatly reduce the amount of a binder used in the manufacturing process of an electrode sheet of the battery, and can effectively increase the content of the active material per unit volume of the electrode sheet.

4) The olivine phosphate material having the lamellar spherical microstructure provided in the present invention is also very safe.

5) The secondary lithium battery comprising the olivine positive electrode material having the lamellar spherical microstructure of the present invention has significant advantages such as high power density, high energy density, and a large capacity, and is applicable to various mobile electronic devices or devices that need to be driven by a mobile energy source, for example, mobile phones, notebook computers, portable video recorders, electronic toys, and particularly devices requiring high-power power batteries, for example, electric tools, electric vehicles, hybrid vehicles, electric torpedoes, energy storage power supplies, etc., but is not limited thereto.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the present invention will be described in detail below with reference to the accompanying drawings, wherein:

FIG. 1 is an XRD diagram of an LiFePO_4 sample of the present invention;

FIG. 2 is an SEM diagram of the LiFePO_4 sample of the present invention;

FIG. 3 is an SEM diagram of the LiFePO_4 sample of the present invention;

FIG. 4 is a TEM diagram of the LiFePO_4 sample of the present invention;

FIG. 5 is a diagram of the comparison between a first-cycle charge-discharge curve of an LiFePO_4 sample of the present invention and a sheet-like LiFePO_4 sample prepared by using a common hydrothermal method with or without a carbon coating; and

FIG. 6 is a diagram of the comparison between charge-discharge curves of an LiFePO_4 sample of the present invention at different rates.

DETAILED DESCRIPTION

The present invention will be further described below with reference to specific examples. However, these examples are merely intended to describe the present invention rather than limiting the scope of the present invention.

Example 1: preparation of pure phase LiFePO_4 of the present invention used for a secondary lithium battery and having a lamellar spherical microstructure morphology and an olivine crystal structure.

LiFePO_4 having the olivine structure of the present invention was prepared via the following steps: $\text{LiOH}\cdot\text{H}_2\text{O}$, H_3PO_4 , $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, $(\text{NH}_2)_2\text{CO}$ (urea), ascorbic acid, and carbon nanotubes in a molar ratio of 1:1:1:1.2:0.1:0.1 were weighed first, and sequentially dissolved into an ethylene glycol solvent. Each precursor was added only after the former precursor was completely dissolved to form a transparent solution. After all of the precursors except the carbon nanotubes were dissolved, the solution was placed in a high-pressure reaction kettle including a polytetrafluoroethylene inner container. The filling rate was 90%. The high-pressure reaction kettle was sealed, and high-purity Ar gas was introduced. An ultrasonic apparatus was turned on. The temperature was raised from room temperature to 80°C over 1 hour, maintained at a constant temperature of 80°C for two hours, then raised to 200°C over 1 hour, maintained at a constant temperature of 200°C for 24 hours, and then lowered to room temperature over 10 hours. The ultrasonic apparatus was turned off, and the reaction kettle was opened. A precipitate was separated by using a centrifugation method, and sequentially washed three times each using ethanol and acetone. The precipitate was baked in a vacuum oven at 60°C for 10 hours, and the resulting dry powder was pure phase LiFePO_4 having a lamellar spherical microstructure morphology and an

olivine crystal structure, and was annealed under the protection of high-purity Ar gas (steps were as follows: the dry powder prepared in the above step was placed in a tube furnace; high-purity Ar gas was introduced; the temperature was maintained at room temperature for 4 hours, then raised to 250°C over 1 hour, maintained at a constant temperature of 250°C for 3 hours, then raised to 600°C over 1 hour, maintained at a constant temperature of 600°C for 5 hours, and then lowered to room temperature over 10 hours; introduction of the gas was stopped; and the powder was taken out), thereby obtaining pure phase LiFePO_4 covered by a nano carbon layer and having the lamellar spherical microstructure. XRD, SEM, TEM, and a constant current charge and discharge instrument were used to test the discharge capacity and efficiency thereof. XRD of the obtained material sample is shown in FIG. 1. Electron micrographs of the obtained material sample are shown in FIG. 2, FIG. 3, and FIG. 4. It can be seen that the prepared material had sheet-like primary particles, and carbon nanotubes formed the core of a secondary particle, and were distributed throughout the secondary particle. The surface of the sample was covered by a thin carbon film. Data of the average particle size in the thinnest direction of the primary particles thereof, the average particle size of the secondary particles, the discharge capacity, and the first-cycle efficiency is shown in Table 1.

Example 2: preparation of olivine pure phase LiMnPO_4 of the present invention used for a secondary lithium battery and having a lamellar spherical microstructure.

LiMnPO_4 having the olivine structure of the present invention was prepared via the following steps: $\text{LiOH}\cdot\text{H}_2\text{O}$, H_3PO_4 , $\text{MnSO}_4\cdot 7\text{H}_2\text{O}$, $(\text{NH}_2)_2\text{CO}$ (urea), ascorbic acid, and carbon nanotubes in a molar ratio of 1:1:1:1.2:0.1:0.1 were weighed first, and sequentially dissolved into an ethylene glycol solvent. Each precursor was added only after the former precursor was completely dissolved to form a transparent solution. After all of the precursors except the carbon nanotubes were dissolved, the solution was placed in a high-pressure reaction kettle including a polytetrafluoroethylene inner container. The filling rate was 90%. The high-pressure reaction kettle was sealed, and N_2 gas was introduced. An ultrasonic apparatus was turned on. The temperature was raised from room temperature to 80°C over 1 hour, maintained at a constant temperature of 80°C for 2 hours, then raised to 200°C over 1 hour, maintained at a constant temperature of 200°C for 24 hours, and then lowered to room temperature over 10 hours. The ultrasonic apparatus was turned off, and the reaction kettle was opened. A precipitate was separated by using a centrifugation method, and sequentially washed three times each using ethanol and

acetone sequentially. The precipitate was baked in a vacuum oven at 60°C for 10 hours, and the resulting dry powder was pure phase LiMnPO_4 having a lamellar spherical microstructure morphology and an olivine crystal structure, and was annealed under the protection of high-purity Ar gas (steps were as follows: the dry powder prepared in the above step was placed in a tube furnace; high-purity Ar gas was introduced; the temperature was maintained at room temperature for 4 hours, then raised to 250°C over 1 hour, maintained at a constant temperature of 250°C for 3 hours, then raised to 650°C over 1 hour, maintained at a constant temperature of 650°C for 5 hours, and then lowered to room temperature over 10 hours; introduction of the gas was stopped; and the powder was taken out), thereby obtaining pure phase LiMnPO_4 covered by a nano carbon layer and having the lamellar spherical microstructure. XRD, SEM, TEM, and a constant current charge and discharge instrument were used to measure the average thickness of primary particles in the (010) direction, the average particle size of the secondary particles, the carbon content, the first-cycle discharge capacity, and first-cycle discharge rate. The obtained data is shown in Table 1.

Example 3: preparation of olivine pure phase $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ of the present invention used for a secondary lithium battery and having a lamellar spherical microstructure.

$\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ having the olivine structure of the present invention was prepared via the following steps: $\text{LiOH}\cdot\text{H}_2\text{O}$, H_3PO_4 , $\text{MnSO}_4\cdot 4\text{H}_2\text{O}$, $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, $(\text{NH}_2)_2\text{CO}$ (urea), ascorbic acid, and carbon nanotubes in a molar ratio of 1:1:0.8:0.2:1.2:0.1:0.1 were weighed first, and sequentially dissolved into an ethylene glycol solvent. Each precursor was added only after the former precursor was completely dissolved to form a transparent solution. After all of the precursors except the carbon nanotubes were dissolved, the solution was placed in a high-pressure reaction kettle including a polytetrafluoroethylene inner container. The filling rate was 90%. The high-pressure reaction kettle was sealed, and high-purity Ar gas was introduced. An ultrasonic apparatus was turned on. The temperature was raised from room temperature to 80°C over 1 hour, maintained at a constant temperature of 80°C for two hours, then raised to 200°C over 1 hour, maintained at a constant temperature of 200°C for 24 hours, and then lowered to room temperature over 10 hours. The ultrasonic apparatus was turned off, and the reaction kettle was opened. A precipitate was separated by using a centrifugation method, and sequentially washed three times each using ethanol and acetone. The precipitate was baked in a vacuum oven at 60°C for 10 hours, and the resulting dry powder was pure phase $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ having a lamellar spherical microstructure morphology and an olivine crystal structure, and was annealed under the protection

of high-purity Ar gas (steps were as follows: the dry powder prepared in the above step was placed in a tube furnace; high-purity Ar gas was introduced; the temperature was maintained at room temperature for 4 hours, then raised to 250°C over 1 hour, maintained at a constant temperature of 250°C for 3 hours, then raised to 650°C over 1 hour, maintained at a constant temperature of 650°C for 5 hours, and then lowered to room temperature over 10 hours; introduction of the gas was stopped; and the powder was taken out), thereby obtaining pure phase olivine $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ covered by a nano carbon layer and having the lamellar spherical microstructure. XRD, SEM, TEM, and a constant current charge and discharge instrument were used to measure the average thickness of primary particles in the (010) direction, the average particle size of the secondary particles, the carbon content, the first-cycle discharge capacity, and first-cycle discharge rate. The obtained data is shown in Table 1.

Example 4: preparation of olivine nitrogen-doped phosphate positive electrode material $\text{Li}_{1.1}\text{FePO}_{3.9}\text{N}_{0.1}$ of the present invention used for a secondary lithium battery and having a lamellar spherical microstructure morphology.

Olivine $\text{Li}_{1.1}\text{FePO}_{3.9}\text{N}_{0.1}$ of the present invention was prepared via the following steps: $\text{LiOH}\cdot\text{H}_2\text{O}$, H_3PO_4 , $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, $(\text{NH}_2)_2\text{CO}$ (urea), ascorbic acid, and carbon nanotubes in a molar ratio of 1.1:1:1:1.1:0.1:0.1 were weighed first, and sequentially dissolved into an ethylene glycol solvent. Each precursor was added only after the former precursor was completely dissolved to form a transparent solution. After all of the precursors except the carbon nanotubes were dissolved, the solution was placed in a high-pressure reaction kettle including a polytetrafluoroethylene inner container. The filling rate was 90%. The high-pressure reaction kettle was sealed, and high-purity Ar gas was introduced. An ultrasonic apparatus was turned on. The temperature was raised to 200°C over 1 hour, maintained at a constant temperature of 200°C for 24 hours, and then lowered to room temperature over 10 hours. The ultrasonic apparatus was turned off, and the reaction kettle was opened. A precipitate was separated by using a centrifugation method, and sequentially washed three times each using ethanol and acetone. The precipitate was baked in a vacuum oven at 60°C for 10 hours, and the resulting dry powder was phosphate $\text{Li}_{1.1}\text{FePO}_4(\text{OH})_{0.1}$ having a lamellar spherical microstructure morphology, and was annealed under the protection of high-purity Ar gas (steps were as follows: the dry powder prepared in the above step was placed in a tube furnace; a gas mixture of ammonia and nitrogen at a ratio of 1:1 (in volume) was introduced; the temperature was maintained at room temperature for 4 hours, then raised to 250°C over 1 hour,

maintained at a constant temperature of 250°C for 3 hours, then raised to 650°C over 1 hour, maintained at a constant temperature of 650°C for 5 hours, and then lowered to room temperature over 10 hours; introduction of the gas was stopped; and the powder was taken out), thereby obtaining olivine nitrogen-phosphate $\text{Li}_{1.1}\text{FePO}_{3.9}\text{N}_{0.1}$ covered by a nano carbon layer and having the lamellar spherical microstructure. XRD, SEM, TEM, and a constant current charge and discharge instrument were used to measure the average thickness of primary particles in the (010) direction, the average particle size of the secondary particles, the carbon content, the first-cycle discharge capacity, and first-cycle discharge rate. The obtained data is shown in Table 1.

Example 5: preparation of olivine Na-doped lithium iron phosphate material $\text{LiFe}_{0.95}\text{Na}_{0.05}\text{PO}_4$ of the present invention used for a secondary lithium battery and having a lamellar spherical microstructure.

Olivine Na-doped lithium iron phosphate material $\text{LiFe}_{0.95}\text{Na}_{0.05}\text{PO}_4$ of the present invention was prepared via the following steps: $\text{LiOH}\cdot\text{H}_2\text{O}$, H_3PO_4 , $\text{MnSO}_4\cdot 7\text{H}_2\text{O}$, Na_2SO_4 , $(\text{NH}_2)_2\text{CO}$ (urea), ascorbic acid, and carbon nanotubes in a molar ratio of 1:1:0.95:0.025:1.2:carbon nanotube 0.1 were weighed first, and sequentially dissolved into an ethylene glycol solvent. Each precursor was added only after the former precursor was completely dissolved to form a transparent solution. After of all the precursors except the carbon nanotubes were dissolved, the solution was placed in a high-pressure reaction kettle including a polytetrafluoroethylene inner container. The filling rate was 90%. The high-pressure reaction kettle was sealed, and high-purity Ar gas was introduced. An ultrasonic apparatus was turned on. The temperature was raised from room temperature to 80°C over 1 hour, maintained at a constant temperature of 80°C for two hours, then raised to 200°C over 1 hour, maintained at a constant temperature of 200°C for 24 hours, and then lowered to room temperature over 10 hours. The ultrasonic apparatus was turned off, and the reaction kettle was opened. A precipitate was separated by using a centrifugation method, and sequentially washed three times each using ethanol and acetone. The precipitate was baked in a vacuum oven at 60°C for 10 hours, and the resulting dry powder was pure phase $\text{LiFe}_{0.95}\text{Na}_{0.05}\text{PO}_4$ having a lamellar spherical microstructure morphology and an olivine crystal structure, and was annealed under the protection of high-purity Ar gas (steps were as follows: the dry powder prepared in the above step was placed in a tube furnace; high-purity Ar gas was introduced; the temperature was maintained at room temperature for 4 hours, then raised to 250°C over 1 hour, maintained at a constant temperature of 250°C for 3 hours, then raised to 650°C over 1 hour, maintained at a constant

temperature of 650°C for 5 hours, and then lowered to room temperature over 10 hours; introduction of the gas was stopped; and the powder was taken out), thereby obtaining pure phase olivine $\text{LiFe}_{0.95}\text{Na}_{0.05}\text{PO}_4$ covered by a nano carbon layer and having the lamellar spherical microstructure. XRD, SEM, TEM, and a constant current charge and discharge instrument were used to measure the average thickness of primary particles in the (010) direction, the average particle size of the secondary particles, the carbon content, the first-cycle discharge capacity, and first-cycle discharge rate. The obtained data is shown in Table 1.

Example 6: preparation of olivine oxygen vacancy lithium iron phosphate material $\text{LiFePO}_{3.98}$ of the present invention used for a secondary lithium battery and having a lamellar spherical microstructure.

$\text{LiFePO}_{3.98}$ having the olivine structure of the present invention was prepared via the following steps: $\text{LiOH}\cdot\text{H}_2\text{O}$, H_3PO_4 , $\text{MnSO}_4\cdot 7\text{H}_2\text{O}$, $(\text{NH}_2)_2\text{CO}$ (urea), ascorbic acid, and carbon nanotubes in a molar ratio of 1:1:1:1.2:0.1:0.1 were weighed first, and sequentially dissolved into an ethylene glycol solvent. Each precursor was added only after the former precursor was completely dissolved to form a transparent solution. After all of the precursors except the carbon nanotubes were dissolved, the solution was placed in a high-pressure reaction kettle including a polytetrafluoroethylene inner container. The filling rate was 90%. The high-pressure reaction kettle was sealed, and high-purity Ar gas was introduced. An ultrasonic apparatus was turned on. The temperature was raised from room temperature to 80°C over 1 hour, maintained at a constant temperature of 80°C for two hours, then raised to 200°C over 1 hour, maintained at a constant temperature of 200°C for 24 hours, and then lowered to room temperature over 10 hours. The ultrasonic apparatus was turned off, and the reaction kettle was opened. A precipitate was separated by using a centrifugation method, and sequentially washed three times each using ethanol and acetone. The precipitate was baked in a vacuum oven at 60°C for 10 hours, and the resulting dry powder was pure phase olivine LiFePO_4 having a lamellar spherical microstructure, and was annealed under the protection of an Ar/ H_2 gas mixture (H_2 accounted for 8% in volume) (steps were as follows: the dry powder prepared in the above step was placed in a tube furnace; an Ar/ H_2 gas mixture was introduced; the temperature was maintained at room temperature for 4 hours, then raised to 250°C over 1 hour, maintained at a constant temperature of 250°C for 3 hours, then raised to 650°C over 1 hour, maintained at a constant temperature of 650°C for 5 hours, and then lowered to room temperature over 10 hours; introduction of the gas was stopped; and the powder was taken

out), thereby obtaining olivine $\text{LiFePO}_{3.98}$ covered by a nano carbon layer and having the lamellar spherical microstructure morphology. XRD, SEM, TEM, and a constant current charge and discharge instrument were used to measure the average thickness of primary particles in the (010) direction, the average particle size of the secondary particles, the carbon content, the first-cycle discharge capacity, and first-cycle discharge rate. The obtained data is shown in Table 1.

Examples 7 to 50: preparation of doped phosphate materials 7-50 of the present invention used for a secondary lithium battery and having a lamellar spherical microstructure morphology and an olivine crystal structure.

The preparation methods were similar to those in Examples 1 to 6, and differences were as follows: doped LiMPO_4 base materials including different doping elements at different ratios and LiMPO_4 base materials including oxygen vacancies were prepared, and the expression thereof could be written as $\text{Li}_x\text{A}_a\text{M}_m\text{B}_b\text{PO}_z\text{N}_n$. A was at least one of Na, Mg, Ti, V, Cr, Cu, Mn, Co, Ni, Zn, Ga, In, Ge, Ag, Hg, Au, Zr, Nb, or W. M was at least one of Fe, Co, Mn, Ni, or V. B was at least one of Li, Na, K, Ca, Mg, Ti, V, Cr, Cu, Mn, Co, Ni, Zn, Ga, In, Ge, Ag, Hg, Au, Zr, Nb, and W. M and B were not the same element at the same time. x, a, m, b, z, and n represent molar ratios, where $0.9 \leq x \leq 4$, $0 \leq a \leq 0.1$, $0.5 \leq m \leq 1$, $0 \leq b \leq 0.5$, $3 \leq z \leq 4$, and $0 \leq n \leq 1$. Moreover, XRD, SEM, TEM, BET, and a constant current charge and discharge instrument were used to measure the average particle size, the average pore diameter, the carbon content, the first-cycle discharge capacity, and the first-cycle discharge rate. The obtained data is shown in Table 1.

Table 1 Main features of olivine phosphate positive electrode materials having the lamellar spherical microstructure morphology[0001]

Examples	Olivine transition metal phosphate having the lamellar spherical microstructure				Discharge capacity	First-cycle efficiency
	Chemical formula	Average particle size of primary sheet-like particles in (010) direction	Average particle size of secondary particles	Carbon content		
1	LiFePO_4	70 nm	10 μm	3%	165 mAh/g	99%
2	LiMnPO_4	80 nm	5 μm	8%	100 mAh/g	80%
3	$\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$	75 nm	15 μm	7%	125 mAh/g	95%
4	$\text{Li}_{1.1}\text{FePO}_{3.9}\text{N}_{0.1}$	50 nm	7 μm	1%	130 mAh/g	92%

5	$\text{LiFe}_{0.95}\text{Na}_{0.05}\text{PO}_4$	20 nm	20 μm	4%	155 mAh/g	93%
6	$\text{LiFePO}_{3.98}$	40 nm	3 μm	4%	140 mAh/g	90%
7	$\text{Li}_{0.9}\text{Zr}_{0.1}\text{Fe}_{0.9}\text{Mg}_{0.1}\text{PO}_{3.9}\text{N}_{0.17}$	80 nm	2 μm	6%	144 mAh/g	85%
8	$\text{Li}_{0.95}\text{Na}_{0.05}\text{Fe}_{0.9}\text{Cr}_{0.067}\text{PO}_{3.99}\text{N}_{0.01}$	25 nm	1 μm	20%	125 mAh/g	89%
9	$\text{Li}_{0.95}\text{Nb}_{0.01}\text{Fe}_{0.9}\text{Cu}_{0.1}\text{PO}_{3.99}\text{N}_{0.1}$	63 nm	0.7 μm	15%	110 mAh/g	90%
10	$\text{Li}_{0.95}\text{W}_{0.01}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{PO}_{3.99}\text{N}_{0.1}$	40 nm	16 μm	2%	137 mAh/g	88%
11	$\text{LiMg}_{0.05}\text{Fe}_{0.9}\text{Zn}_{0.1}\text{PO}_{3.9}\text{N}_{0.1}$	15 nm	3 μm	23%	122 mAh/g	87%
12	$\text{Li}_{0.92}\text{Ge}_{0.06}\text{Fe}_{0.9}\text{Na}_{0.2}\text{PO}_{3.9}\text{N}_{0.12}$	70 nm	8 μm	9%	115 mAh/g	90%
13	$\text{Li}_{0.95}\text{V}_{0.02}\text{Fe}_{0.9}\text{Ag}_{0.2}\text{PO}_{3.9}\text{N}_{0.1}$	14 nm	14 μm	14%	100 mAh/g	95%
14	$\text{Li}_{0.95}\text{Co}_{0.02}\text{Fe}_{0.9}\text{Cu}_{0.1}\text{PO}_{3.9}\text{N}_{0.1}$	30 nm	9 μm	0.2%	154 mAh/g	92%
15	$\text{Li}_{0.95}\text{Ga}_{0.02}\text{Fe}_{0.7}\text{V}_{0.2}\text{PO}_{3.9}\text{N}_{0.1}$	80 nm	5 μm	4%	120 mAh/g	97%
16	$\text{LiCu}_{0.1}\text{Co}_{0.7}\text{In}_{0.2}\text{PO}_{3.4}\text{N}_{0.43}$	100 nm	24 μm	6%	148 mAh/g	88%
17	$\text{Li}_{1.1}\text{Mn}_{0.8}\text{Zr}_{0.1}\text{PO}_{3.9}\text{N}_{0.1}$	47 nm	1 μm	9%	160 mAh/g	90%
18	$\text{Li}_{1.1}\text{Ni}_{0.75}\text{Nb}_{0.1}\text{PO}_{3.9}\text{N}_{0.1}$	68 nm	27 μm	2.6%	130 mAh/g	91%
19	$\text{Li}_{1.8}\text{FePO}_4\text{N}$	90 nm	7 μm	7.2%	160 mAh/g	92%
20	$\text{Li}_{0.95}\text{Na}_{0.05}\text{Fe}_{0.9}\text{Co}_{0.1}\text{PO}_{3.99}\text{N}_{0.01}$	42 nm	40 μm	16%	109 mAh/g	86%
21	$\text{Li}_{1.8}\text{Co}_{0.1}\text{FePO}_3\text{N}$	35 nm	0.2 μm	0.9%	155 mAh/g	93%
22	$\text{Li}_{1.04}\text{Cr}_{0.02}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{PO}_{3.9}\text{N}_{0.1}$	60 nm	6 μm	3%	100 mAh/g	85%
23	$\text{Li}_{0.96}\text{Ti}_{0.05}\text{Fe}_{0.9}\text{Ca}_{0.1}\text{PO}_{3.9}\text{N}_{0.12}$	50 nm	5 μm	4.9%	133 mAh/g	95%
24	$\text{Li}_{0.94}\text{Hg}_{0.08}\text{Fe}_{0.9}\text{Li}_{0.2}\text{PO}_{3.98}\text{N}_{0.02}$	20 nm	11 μm	9.7%	150 mAh/g	94%
25	$\text{Li}_{0.94}\text{Au}_{0.08}\text{Fe}_{0.9}\text{K}_{0.2}\text{PO}_{3.98}\text{N}_{0.02}$	180 nm	3 μm	2%	130 mAh/g	88%
26	$\text{Li}_{0.95}\text{Mn}_{0.02}\text{Fe}_{0.9}\text{Hg}_{0.2}\text{PO}_{3.9}\text{N}_{0.1}$	60 nm	5 μm	4.2%	146 mAh/g	89%
27	$\text{Li}_{0.95}\text{Ni}_{0.02}\text{Fe}_{0.9}\text{Au}_{0.2}\text{PO}_{3.9}\text{N}_{0.1}$	70 nm	8 μm	6%	128 mAh/g	93%
28	$\text{Li}_{0.95}\text{In}_{0.02}\text{Fe}_{0.7}\text{Ga}_{0.2}\text{PO}_{3.9}\text{N}_{0.1}$	30 nm	15 μm	1%	110 mAh/g	96%

29	LiZn _{0.05} Fe _{0.8} Ti _{0.1} PO _{3.9} N _{0.1}	55 nm	10 μm	7%	125 mAh/g	98%
30	Li _{1.1} Fe _{0.8} Ge _{0.1} PO _{3.9} N _{0.1}	42 nm	12 μm	3%	128 mAh/g	94%
31	Li _{1.1} V _{0.5} W _{0.1} PO _{3.9} N _{0.1}	25 nm	9 μm	24%	157 mAh/g	91%
32	LiFePO _{3.998}	64 nm	3 μm	9%	160 mAh/g	95%
33	LiFePO _{3.7}	85 nm	8 μm	4.1%	165 mAh/g	93%
34	LiFePO _{3.5}	30 nm	2 μm	8%	148 mAh/g	95%
35	LiFePO _{3.97} N _{0.02}	175 nm	40 μm	5%	164 mAh/g	91%
36	LiFePO _{3.25} N _{0.5}	190 nm	45 μm	17%	120 mAh/g	89%
37	LiFePO ₃ N _{0.5}	30 nm	7 μm	8%	108 mAh/g	90%
38	LiFe _{0.9} Na _{0.1} PO _{3.95}	100 nm	6 μm	6.6%	161 mAh/g	94%
39	LiFe _{0.97} Li _{0.03} PO _{3.98}	80 nm	4 μm	4%	160 mAh/g	96%
40	LiFe _{0.95} K _{0.05} PO _{3.97}	60 nm	3 μm	3%	162 mAh/g	97%
41	LiFe _{0.9} Cu _{0.1} PO _{3.95}	55 nm	7 μm	20%	155 mAh/g	92%
42	LiFe _{0.95} Na _{0.05} PO _{3.925} N _{0.1}	30 nm	0.5 μm	22%	135 mAh/g	91%
43	LiFe _{0.9} Cu _{0.1} PO _{3.1} N _{0.5}	85 nm	4 μm	6%	150 mAh/g	90%
44	LiFe _{0.9} Ag _{0.1} PO _{3.6} N _{0.2}	77 nm	6 μm	7%	144 mAh/g	88%
45	LiFe _{0.97} Na _{0.03} PO _{3.8} N _{0.1}	96 nm	10 μm	9%	158 mAh/g	96%
46	LiCoPO ₄	100 nm	8 μm	2%	110 mAh/g	92%
47	LiFe _{0.5} Mn _{0.5} PO ₄	60 nm	5 μm	5%	100 mAh/g	97%
48	LiFe _{0.8} Co _{0.2} PO ₄	45 nm	2 μm	10%	115 mAh/g	90%
49	LiFe _{0.8} Mn _{0.2} PO ₄	30 nm	0.7 μm	12%	150 mAh/g	93%
50	LiMn _{0.5} Co _{0.5} PO ₄	80 nm	8 μm	3%	90 mAh/g	89%

Example 51: electrochemical measurements of the LiFePO₄ material of the present invention having the three-dimensional microstructure and covered by carbon

The LiFePO₄ positive electrode material (the active material, prepared in Example 1) having the three-dimensional microstructure was mixed with acetylene black and an N-methylpyrrolidinone solution including 5% of polyvinidylene fluoride (PVDF) at normal temperature and pressure to form a slurry (active material:acetylene black:PVDF = 80:10:10). The slurry was uniformly coated on an aluminum foil substrate, and then vacuum-dried at 100°C for 8 hours. A resulting film was compacted at a pressure of 10 MPa to achieve a film thickness of about 100 μm, and was cut into a 1 cm × 1 cm electrode sheet used as a positive electrode of a simulated battery. The same method

was also used to prepare a positive electrode including a sheet-like material prepared by using a common hydrothermal method (for the method, please refer to the document: J. Chen, S. Wang, and M. Stanley, *Journal of Power Sources*, 174(2007), 442-448) and having a carbon coating and a positive electrode including a sheet-like material prepared by using the common hydrothermal method and having no carbon coating.

A lithium sheet was used as a negative electrode of the simulated battery, and an electrolyte solution was 1 mol of LiPF_6 dissolved in 1 L of a mixed solvent of EC and DMC (a volume ratio of 1:1). Each of the two positive electrodes was assembled with the negative electrode, the electrolyte solution, and a separator in an argon-protected glovebox to form the simulated battery.

Electrochemical test steps of the simulated battery were as follows:

the simulated battery was charged at a rate of C/10 to 4.2 V, and was then discharged at the same current rate to 2.6 V. The obtained charge-discharge curves are shown in FIG. 5. At a rate of C/10, the discharged capacity reached 160 mAh/g calculated in terms of the mass of LiFePO_4 (the positive electrode material of the present invention) having the lamellar spherical microstructure. However, the capacity of the sheet-like, carbon-coated LiFePO_4 material that was prepared by using the common hydrothermal method was only 120 mAh/g under the same test conditions, and the capacity of the sheet-like LiFePO_4 material without a carbon coating that was prepared by using the common hydrothermal method was only 70 mAh/g under the same test conditions. Therefore at the same rate, the capacity of the microstructure material of the present invention was much higher than that of the positive electrode material without a carbon coating that was prepared by using the common hydrothermal method and the carbon-coated positive electrode material that was prepared by using the common hydrothermal method.

In addition, the simulated battery was respectively charged at rates of 10C, 5C, 2C, 1C, 0.5C, 0.2C, and 0.1C to 4.2 V, and was discharged at the same rates to 2.6 V. The obtained charge-discharge curves are shown in FIG. 6. As can be seen from the drawing, the microstructure material of the present invention has a morphology that facilitates deintercalation of lithium ions and a conductive network formed by carbon nanotubes and a surface carbon layer, so that electron conductivity and ion conductivity of the olivine phosphate material are improved, and the material still has a high capacity even when charged and discharged at a large current, and is applicable to some devices

requiring high-power power batteries, for example, electric tools, electric vehicles, hybrid vehicles, electric torpedoes, energy storage power supplies, etc.

CLAIMS

1. An olivine phosphate positive electrode material, the positive electrode material comprising: a carbon nanotube cluster formed by tangling carbon nanotubes, a secondary particle formed by agglomeration of sheet-like primary particles attached to an outer side of the carbon nanotube cluster, and a carbon layer covering an outer surface of the secondary particle;

the sheet-like primary particles having an olivine crystal structure, and having the following chemical composition:



wherein a doping element A is selected from at least one of Na, Mg, Ti, V, Cr, Cu, Mn, Co, Ni, Zn, Ga, In, Ge, W, Hg, Au, Ag, Nb, and Zr;

a transition metal M is selected from at least one of Fe, Co, Mn, Ni, and V;

a doping element B is selected from at least one of Li, Na, K, Ca, Mg, Ti, V, Cr, Cu, Mn, Co, Ni, Zn, Ga, In, Ge, Ag, Nb, Hg, Au, Zr, and W;

M and B are not the same element at the same time; and

x, a, m, b, z, and n represent molar ratios, where $0.9 \leq x \leq 1.8$, $0 \leq a \leq 0.1$, $0.5 \leq m \leq 1$, $0 \leq b \leq 0.5$, $3 \leq z \leq 4$, and $0 \leq n \leq 1$.

2. The positive electrode material according to claim 1, wherein the thinnest direction of the sheet-like primary particles is the (010) direction of olivine, and the average thickness is 10 to 200 nm.

3. The positive electrode material according to claim 1 or 2, wherein the geometric shape of the secondary particle is spherical, ellipsoidal, spindle-shaped, or dumbbell-shaped, and the average particle size is 1 to 50 μm .

4. The positive electrode material according to any one of claims 1 to 3, wherein the thickness of the carbon layer is 1 to 10 nm, and the content of carbon accounts for 0.1-25 wt% of the total weight of the positive electrode material.

5. A method for preparing the positive electrode material according to any one of claims 1 to 4, the method comprising the following steps:

(1) weighing a lithium salt, a transition metal salt, phosphate, a salt of a doping element, a pH-adjusting agent, a nitrogen source, a carbon source, and carbon nanotubes according to a molar ratio of (0.9 to 1.8):(0.5 to 1):(0.75 to 1):(0 to 0.5):(0 to 2):(0 to 1):(0 to 0.3):(0 to 0.3), and dissolving the same in a solvent to form a solution comprising carbon nanotubes;

(2) placing, in a sealed high-pressure reaction kettle, the solution comprising carbon nanotubes obtained in step (1), introducing a protective gas, and reacting at a temperature of 100°C to 400°C for 1 to 72 hours, preferably reacting for 1 to 10 hours;

(3) cooling the product obtained in step (2), separating a precipitate, and washing the same; and

(4) drying, at a temperature of 40°C to 150°C for 1 to 24 hours, the washed precipitate from step (3), to obtain the positive electrode material.

6. The preparation method according to claim 5, wherein the lithium salt is selected from one or a plurality of lithium fluoride, lithium acetate, lithium carbonate, lithium citrate, lithium nitrate, and lithium oxalate; the transition metal salt is selected from one or a plurality of the acetate, carbonate, citrate, nitrate, and oxalate of a transition metal; the salt of the doping element is selected from one or a plurality of the acetate, citrate, nitrate, and oxalate of the doping element; the pH-adjusting agent is selected from one or a plurality of aqueous ammonia, urea, methylamine, ethylenediamine, diisopropylamine, triethanolamine, and tetrabutylammonium bromide; the nitrogen source is selected from one or a plurality of a transition metal nitride, a lithium nitride, an ammonium salt, melamine, ammonia, and nitrogen; the carbon source is selected from one or a plurality of a vitamin, glucose, polyethylene glycol, polyacrylic acid, ascorbic acid, sucrose, citric acid, graphite, acetylene black, and carbon black; and the carbon nanotube is a single-walled or multi-walled carbon nanotube having a diameter of 0.5 to 200 nm and an aspect ratio of 20 to 10000.

7. The preparation method according to claim 5 or 6, wherein in step (1), the solvent is selected from one or a plurality of water, methanol, ethanol, propanol, ethylene glycol, acetone, glycerol, isopropanol, n-butanol, benzyl alcohol, dimethyl sulfoxide, and polyethylene glycol.
8. The preparation method according to any one of claims 5 to 7, wherein in step (2), the protective gas is one or a plurality of argon, nitrogen, hydrogen, and carbon monoxide.
9. The preparation method according to any one of claims 5 to 8, wherein in step (3), a solvent for washing is selected from one or a plurality of water, ethanol, acetone, dichloromethane, chloroform, ethyl acetate, and tetrahydrofuran.
10. The preparation method according to any one of claims 5 to 9, further comprising: after introducing the protective gas in step (2), pre-reacting first at a reaction temperature of 60°C to 120°C, preferably 80°C, for 0.5 to 12 hours, preferably 2 hours.
11. The preparation method according to any one of claims 5 to 10, further comprising: performing ultrasonic treatment in the reaction of step (2) at an ultrasonic frequency of 20K to 100 kHz and a power of 0 to 3000 W.
12. The preparation method according to any one of claims 5 to 11, further comprising: sintering the dried product from step (4) at a temperature of 200°C to 400°C in an inert atmosphere or an inert atmosphere comprising a reducing gas for 1 to 10 hours; and then sintering the resulting product at a temperature of 400°C to 800°C, preferably 550°C to 700°C, for 1 to 24 hours, preferably 3 to 10 hours;
- preferably, the inert atmosphere is argon or nitrogen, and the reducing gas is hydrogen or carbon monoxide.
13. The preparation method according to any one of claims 5 to 12, wherein the heating rate in the reaction or sintering step is 1°C/min to 10°C/min.

14. A lithium positive electrode for a secondary lithium battery, the lithium positive electrode comprising a current collector and a positive electrode material coated on the current collector, characterized in that the positive electrode material comprises the positive electrode material according to any one of claims 1 to 4.

15. A secondary lithium battery, the lithium battery comprising a positive electrode, a negative electrode, an electrolyte solution, and a separator, characterized in that the positive electrode is the lithium positive electrode according to claim 14.

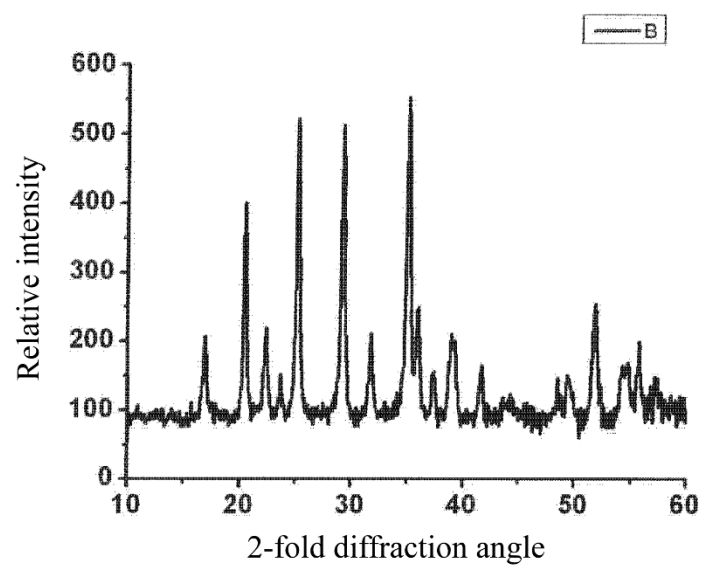


FIG. 1

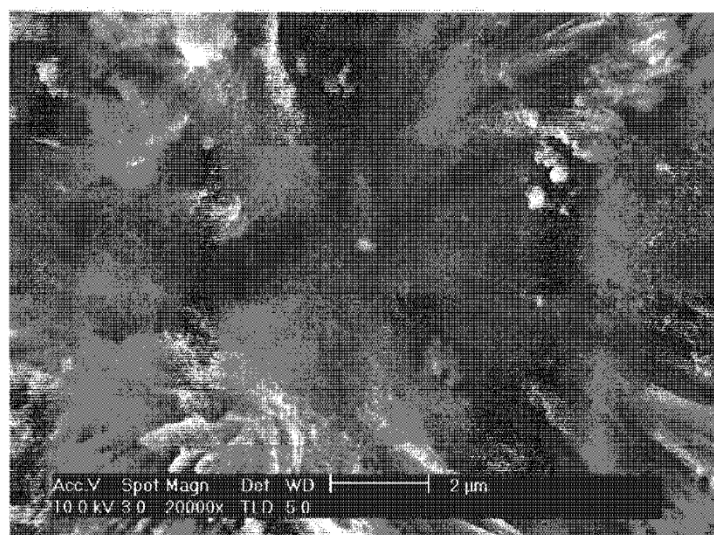


FIG. 2

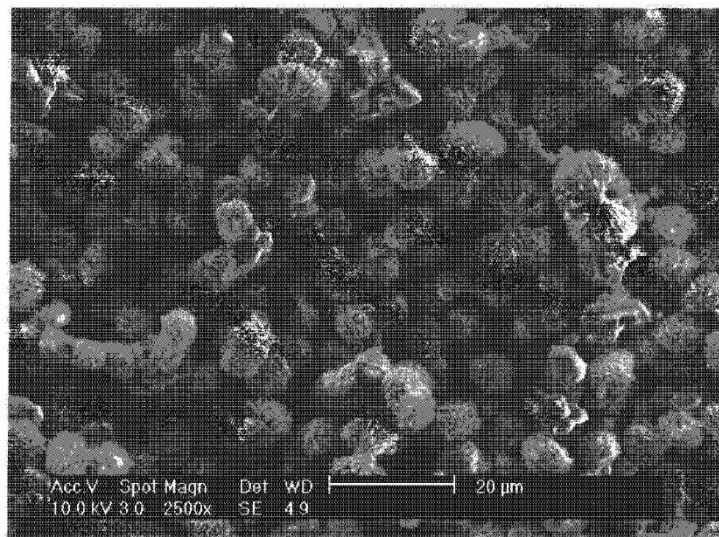


FIG. 3

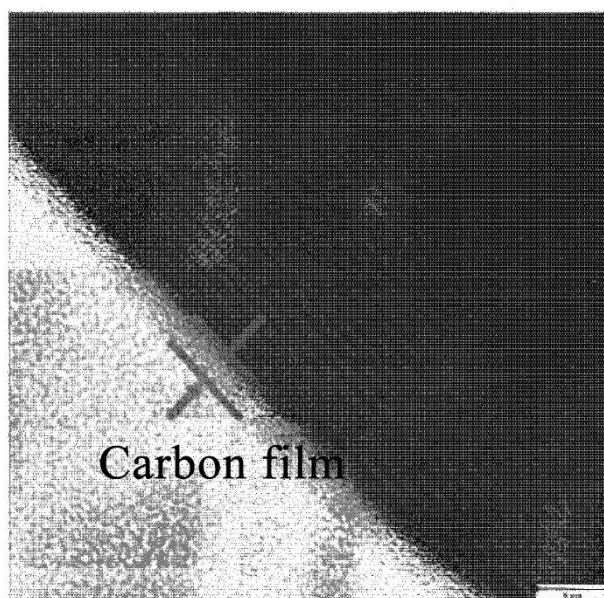


FIG. 4

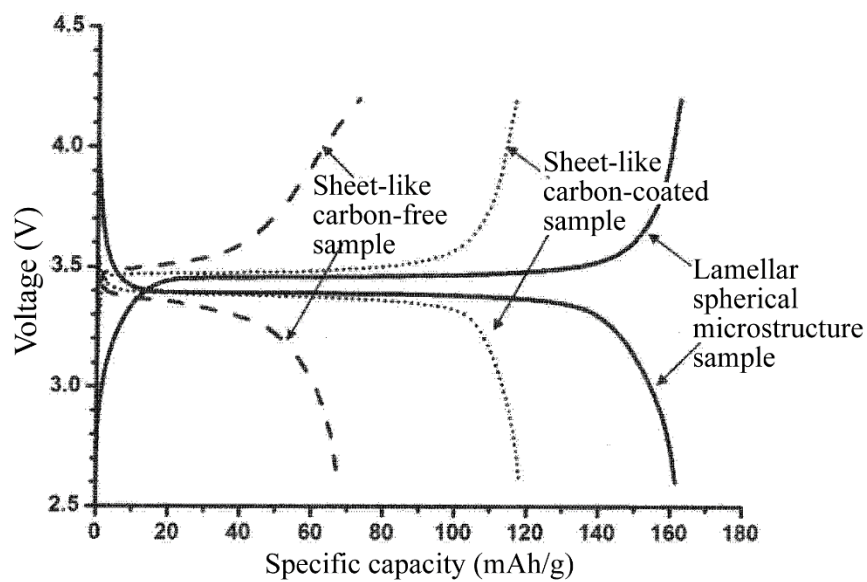


FIG. 5

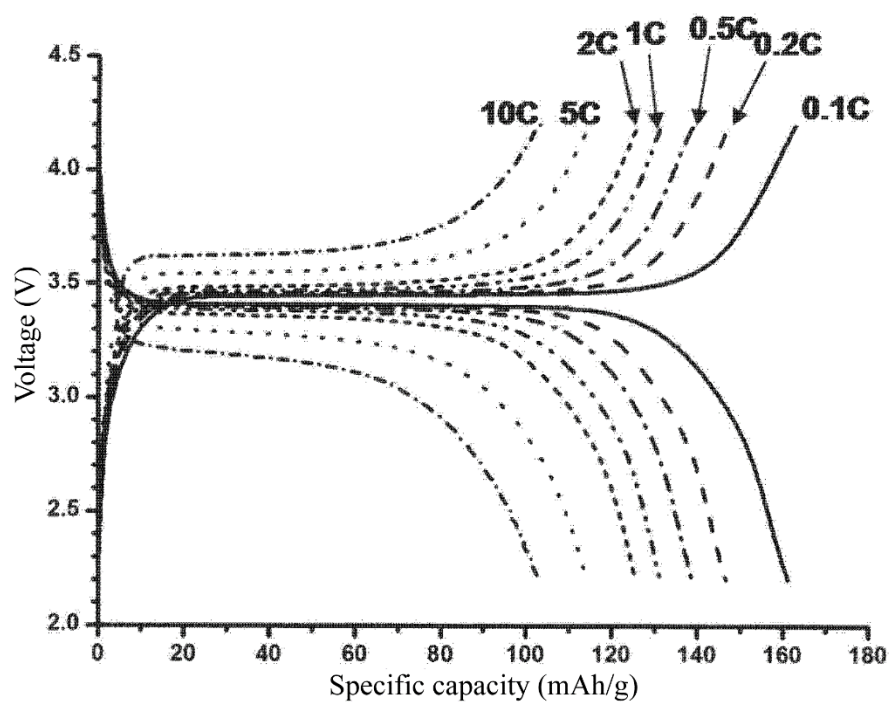


FIG. 6



TRANSLATOR'S CERTIFICATE OF TRANSLATION

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Date: May 21, 2024

To whom it may concern:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true. I further declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

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Name