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(54) Title of Invention

Conductive Agent for Lithium-Iron-Phosphate Battery and
Preparation Method Thereof

(57) Abstract

Disclosed in the present invention is a conductive agent for a lithium-iron-phosphate battery, and also disclosed is a preparation method of the conductive agent. The conductive agent of the present invention consists of a carbon nanotube/carbon black composite material, graphene, and a binder, and the weight ratio of the components is: carbon nanotube/carbon black composite material : graphene : binder = 1 : (0.001 to 0.1) : (0.01 to 1). The preparation method includes: first performing pretreatment on a carbon nanotube/carbon black composite material, then placing the carbon nanotube/carbon black composite material and a binder in re-distilled water to ultrasonically dispersing the same, then adding, under ultrasonic conditions, graphene to the re-distilled water, and performing ultrasonic dispersion, thereby obtaining a conductive agent. The preparation method of the conductive agent of the present invention is simple, and the prepared conductive agent is uniformly dispersed and has good stability. The conductive agent has good electron conductivity and uniform heat conductivity. A lithium-iron-phosphate battery prepared by using the conductive agent of the present invention has significantly improved electrochemical performance and significantly reduced AC internal resistance.

CLAIMS

1. A conductive agent for a lithium-iron-phosphate battery, characterized by consisting of a carbon nanotube/carbon black composite material, graphene, and a binder, the weight ratio of the carbon nanotube/carbon black composite material, the graphene, and the binder being: carbon nanotube/carbon black composite material : graphene : binder = 1 : (0.001 to 0.1) : (0.01 to 1).

2. The conductive agent for a lithium-iron-phosphate battery according to claim 1, wherein the weight ratio of the carbon nanotube/carbon black composite material, the graphene, and the binder is: carbon nanotube/carbon black composite material : graphene : binder = 1 : 0.1 : 1.

3. The conductive agent for a lithium-iron-phosphate battery according to claim 1 or 2, wherein the binder is polyacrylic acid and/or polyacrylic cyanide, and when the binder is polyacrylic acid and polyacrylic cyanide, the weight ratio of the polyacrylic acid to the polyacrylic cyanide is: polyacrylic acid : polyacrylic cyanide = (0.5 to 5) : 1.

4. A preparation method of the conductive agent for a lithium-iron-phosphate battery according to claim 1, characterized in that specific steps are as follows:

(1) pretreatment of the carbon nanotube/carbon black composite material: placing the carbon nanotube/carbon black composite material in a freeze drier, maintaining the temperature at -20°C to 30°C for 1 to 2 hours, then vacuumizing to 100 Pa, performing drying for 2 to 4 hours, then maintaining a vacuum degree, adjusting the temperature to room temperature, and then removing the carbon nanotube/carbon black composite material from the freeze drier, thereby completing the pretreatment; and

(2) preparation of the conductive agent for a lithium-iron-phosphate battery: weighing the carbon nanotube/carbon black composite material, graphene, and a binder, wherein the weight ratio of the carbon nanotube/carbon black composite material, the graphene, and the binder is: carbon nanotube/carbon black composite material : graphene : binder = 1 : (0.001 to 0.1) : (0.01 to 1), placing the weighed carbon nanotube/carbon black composite material and binder in re-distilled water, performing ultrasonic dispersion for 5 to 15 minutes with an ultrasonic frequency

being 20 kHz and power being 130 W, then adding, under ultrasonic conditions, the graphene to the re-distilled water, and further performing ultrasonic dispersion for 5 to 15 minutes with the ultrasonic frequency being 20 kHz and the power being 130 W, thereby obtaining the conductive agent for a lithium-iron-phosphate battery.

5. The preparation method of the conductive agent for a lithium-iron-phosphate battery according to claim 4, wherein the amount of the re-distilled water in step (2) is: the weight of the re-distilled water : the weight of the binder = (200 to 20000) : 1.

CONDUCTIVE AGENT FOR LITHIUM-IRON-PHOSPHATE BATTERY AND PREPARATION METHOD THEREOF

TECHNICAL FIELD

[0001] The present invention relates to the technical field of lithium ion secondary batteries, in particular to a conductive agent for a lithium-iron-phosphate battery and a preparation method thereof.

BACKGROUND

[0002] The lithium ion secondary battery is a novel high-energy secondary power source, and has advantages such as a large specific capacity, a high and stable discharge voltage, good low-temperature performance, environmental-friendliness, safety, a long life, and slight self-discharge. The above-described advantages of the lithium ion secondary battery have won the favor of scientists all over the world, thereby promoting rapid development of the lithium ion secondary battery. There are many types of cathode materials for the lithium ion secondary battery, mainly including lithium cobaltate, lithium manganate, lithium nickelate, lithium iron phosphate, etc. The lithium-iron-phosphate battery is a lithium ion secondary battery wherein lithium iron phosphate is used as the cathode material. The lithium-iron-phosphate battery is a high-performance battery that has emerged in recent years, and has significantly better safety performance and cycle life than those of other lithium ion secondary batteries. The cycle life of the lithium-iron-phosphate battery is 2000 cycles. A single battery does not burn at an overcharge voltage of 30V. The lithium-iron-phosphate battery does not explode when punctured, is non-toxic, non-polluting, and safe, and has advantages such as widely available raw materials, a low price, and a long life.

[0003] Electrode reaction of the lithium ion secondary battery includes transport of electrons and transport of ions, so that the electrode needs to have good conductivity to ensure a clear electron transport channel. In addition, some pore structures are further needed, and may hold an electrolyte to ensure smooth ion transport. Only when the two requirements are satisfied, can it be ensured that the electrode active material has a high utilization rate and good cycle stability. A positive electrode of the lithium-iron-phosphate battery uses lithium iron phosphate as an active material, but lithium iron phosphate has poor conductivity, so that a conductive agent is usually added to the active material during formation of the electrode to improve the conductivity thereof.

Currently, a carbon nanotube/carbon black composite material is commonly used as a conductive agent for the lithium-iron-phosphate battery. The carbon nanotube/carbon black composite material as the conductive agent can not only improve the probability of contacting the active material, i.e., lithium iron phosphate to reduce internal resistance and polarization, but also serve to improve binding stability of the cathode material and increase pore structures of the electrode to facilitate holding of the electrolyte and improve the cycle stability of the electrode, so that an effective conductive network is formed in the electrode, and the electrode material is fixed. However, the carbon nanotube/carbon black composite material as the conductive agent has limited electron conductivity, and heat conductivity thereof is not uniform, thereby affecting overall heat distribution of the battery, and finally adversely affecting the battery.

SUMMARY

[0004] An objective of the present invention is to provide a conductive agent for a lithium-iron-phosphate battery, the conductive agent having high electron conductivity and uniform heat conductivity.

[0005] Also, the objective of the present invention is to further provide a preparation method of the conductive agent for a lithium-iron-phosphate battery.

[0006] In order to achieve the above objective, the technical solution adopted by the present invention is as follows: A conductive agent for a lithium-iron-phosphate battery, consisting of a carbon nanotube/carbon black composite material, graphene, and a binder, the weight ratio of the carbon nanotube/carbon black composite material, the graphene, and the binder being: carbon nanotube/carbon black composite material : graphene : binder = 1 : (0.001 to 0.1) : (0.01 to 1).

[0007] Preferably, the weight ratio of the carbon nanotube/carbon black composite material, the graphene, and the binder is: carbon nanotube/carbon black composite material : graphene : binder = 1 : 0.1 : 1.

[0008] The binder is polyacrylic acid and/or polyacrylic cyanide, and when the binder is polyacrylic acid and polyacrylic cyanide, the weight ratio of the polyacrylic acid to the polyacrylic cyanide is: polyacrylic acid : polyacrylic cyanide = (0.5 to 5) : 1.

[0009] A preparation method of the conductive agent for a lithium-iron-phosphate battery specifically comprises the following steps:

(1) pretreatment of the carbon nanotube/carbon black composite material: placing the carbon nanotube/carbon black composite material in a freeze drier, maintaining the temperature at -20°C to 30°C for 1 to 2 hours, then vacuumizing to 100 Pa, performing drying for 2 to 4 hours, then maintaining a vacuum degree, adjusting the temperature to room temperature, and then removing the carbon nanotube/carbon black composite material from the freeze drier, thereby completing the pretreatment; and

(2) preparation of the conductive agent for a lithium-iron-phosphate battery: weighing the carbon nanotube/carbon black composite material, graphene, and a binder, wherein the weight ratio of the carbon nanotube/carbon black composite material, the graphene, and the binder is: carbon nanotube/carbon black composite material : graphene : binder = 1 : (0.001 to 0.1) : (0.01 to 1), placing the weighed carbon nanotube/carbon black composite material and binder in re-distilled water, performing ultrasonic dispersion for 5 to 15 minutes with an ultrasonic frequency being 20 kHz and power being 130 W, then adding, under ultrasonic conditions, the graphene to the re-distilled water, and further performing ultrasonic dispersion for 5 to 15 minutes with the ultrasonic frequency being 20 kHz and the power being 130 W, thereby obtaining the conductive agent for a lithium-iron-phosphate battery.

[0010] The amount of the re-distilled water in step (2) is: the weight of the re-distilled water : the weight of the binder = (200 to 20000) : 1.

[0011] In the conductive agent for a lithium-iron-phosphate battery provided in the present invention, graphene has a greater electron transport rate and better heat dissipation performance than carbon nanotubes, so that further addition of graphene to the carbon nanotube/carbon black composite material can not only reduce the internal resistance of the carbon nanotube/carbon black composite material, but also improve heat dissipation performance of a unit cell. After combination of the graphene and the carbon nanotube/carbon black composite material, multi-dimensional conduction of electrons between lithium iron phosphate as the active material can also be achieved, and complementary advantages can be achieved by means of fibrous, spherical, and sheet-like characteristics achieved by the combination of the carbon nanotube/carbon black composite material and the graphene, thereby improving physical and chemistry properties of the active material, and playing an important role in the consistency of the battery. Addition of the binder to the conductive agent for a lithium-iron-phosphate battery provided in the present invention not

only can reduce sinking speed of the conductive agent and improve a dispersion effect of the conductive agent, but also can improve compatibility between carbon nanotubes and the active material. In addition, the addition of the binder plays an important role in improving stability of the conductive agent and process stability in a subsequent slurry preparation process, and can also simplify the slurry preparation process.

[0012] The conductive agent for a lithium-iron-phosphate battery provided in the present invention effectively utilizes respective advantages of fibrous carbon nanotubes, spherical carbon black, and sheet-like graphene, and cause the same to achieve a synergistic effect, thereby significantly improving electrochemical performance of the battery. In addition, the addition of the binder not only can reduce the falling speed of the conductive agent and improve the storage stability of the prepared conductive agent, but also can improve the compatibility between carbon nanotubes and the lithium iron phosphate as the active material in the slurry preparation process.

[0013] The preparation method of the conductive agent for a lithium-iron-phosphate battery of the present invention is simple, and the prepared conductive agent is uniformly dispersed and has good stability. The conductive agent for a lithium-iron-phosphate battery provided in the present invention has good electron conductivity and uniform heat conductivity. The electrochemical performance of the lithium-iron-phosphate battery prepared by using the conductive agent of the present invention is significantly improved, and is stable.

DETAILED DESCRIPTION

[0014] Example 1

A conductive agent for a lithium-iron-phosphate battery in the present embodiment consisted of a carbon nanotube/carbon black composite material, graphene, and polyacrylic acid, the weight ratio of the carbon nanotube/carbon black composite material, the graphene, and the polyacrylic acid was: carbon nanotube/carbon black composite material : graphene : polyacrylic acid = 1 : 0.1 : 1.

[0015] A preparation method of the conductive agent for a lithium-iron-phosphate battery of the present embodiment specifically included the following steps:

(1) pretreatment of the carbon nanotube/carbon black composite material: placing the carbon nanotube/carbon black composite material in a freeze drier, rapidly cooling the same to -

20°C, maintaining the temperature for 2 hours, then vacuumizing to 100 Pa, performing drying for 2 hours, then maintaining a vacuum degree, raising the temperature gradually to room temperature, and then removing the carbon nanotube/carbon black composite material from the freeze drier, thereby completing the pretreatment; and

(2) preparation of the conductive agent for a lithium-iron-phosphate battery: weighing 1g of the carbon nanotube/carbon black composite material treated in step (1), weighing 0.1g of polyacrylic acid, then placing the weighed carbon nanotube/carbon black composite material and polyacrylic acid in 50 ml of re-distilled water, performing ultrasonic dispersion for 5 minutes with an ultrasonic frequency being 20 kHz and power being 130 W, then adding, under ultrasonic conditions, 1g of graphene to the re-distilled water, and further performing ultrasonic dispersion for 15 minutes with the ultrasonic frequency being 20 kHz and the power being 130 W, thereby obtaining the conductive agent for a lithium-iron-phosphate battery.

[0016] Example 2

A conductive agent for a lithium-iron-phosphate battery in the present embodiment consisted of a carbon nanotube/carbon black composite material, graphene, and polyacrylic acid, the weight ratio of the carbon nanotube/carbon black composite material, the graphene, and the polyacrylic acid was: carbon nanotube/carbon black composite material : graphene : polyacrylic acid = 1 : 0.1 : 1.

[0017] A preparation method of the conductive agent for a lithium-iron-phosphate battery of the present embodiment specifically included the following steps:

(1) pretreatment of the carbon nanotube/carbon black composite material: placing the carbon nanotube/carbon black composite material in a freeze drier, rapidly cooling the same to -20°C, maintaining the temperature for 1 hour, then vacuumizing to 100 Pa, performing drying for 4 hours, then maintaining a vacuum degree, raising the temperature gradually to room temperature, and then removing the carbon nanotube/carbon black composite material from the freeze drier, thereby completing the pretreatment; and

(2) preparation of the conductive agent for a lithium-iron-phosphate battery: weighing 2.5g of the carbon nanotube/carbon black composite material treated in step (1), weighing 0.25g of polyacrylic acid, then placing the weighed carbon nanotube/carbon black composite material and

polyacrylic acid in 50 ml of re-distilled water, performing ultrasonic dispersion for 15 minutes with an ultrasonic frequency being 20 kHz and power being 130 W, then adding, under ultrasonic conditions, 2.5g of graphene to the re-distilled water, and further performing ultrasonic dispersion for 5 minutes with the ultrasonic frequency being 20 kHz and the power being 130 W, thereby obtaining the conductive agent for a lithium-iron-phosphate battery.

[0018] Example 3

A conductive agent for a lithium-iron-phosphate battery in the present embodiment consisted of a carbon nanotube/carbon black composite material, graphene, and polyacrylic cyanide, the weight ratio of the carbon nanotube/carbon black composite material, the graphene, and the polyacrylic cyanide was: carbon nanotube/carbon black composite material : graphene : polyacrylic cyanide = 1 : 0.1 : 1.

[0019] A preparation method of the conductive agent for a lithium-iron-phosphate battery of the present embodiment specifically included the following steps:

(1) pretreatment of the carbon nanotube/carbon black composite material: placing the carbon nanotube/carbon black composite material in a freeze drier, raising the temperature to 30°C, maintaining the temperature for 1 hour, then vacuumizing to 100 Pa, performing drying for 3 hours, then maintaining a vacuum degree, lowering the temperature gradually to room temperature, and then removing the carbon nanotube/carbon black composite material from the freeze drier, thereby completing the pretreatment; and

(2) preparation of the conductive agent for a lithium-iron-phosphate battery: weighing 0.025g of the carbon nanotube/carbon black composite material treated in step (1), weighing 0.0025g of polyacrylic cyanide, then placing the weighed carbon nanotube/carbon black composite material and polyacrylic cyanide in 50 ml of re-distilled water, performing ultrasonic dispersion for 10 minutes with an ultrasonic frequency being 20 kHz and power being 130 W, then adding, under ultrasonic conditions, 0.025g of graphene to the re-distilled water, and further performing ultrasonic dispersion for 10 minutes with the ultrasonic frequency being 20 kHz and the power being 130 W, thereby obtaining the conductive agent for a lithium-iron-phosphate battery.

[0020] Example 4

A conductive agent for a lithium-iron-phosphate battery in the present embodiment consisted of a carbon nanotube/carbon black composite material, graphene, and polyacrylic cyanide, the weight ratio of the carbon nanotube/carbon black composite material, the graphene, and the polyacrylic cyanide was: carbon nanotube/carbon black composite material : graphene : polyacrylic cyanide = 1 : 0.001 : 1.

[0021] A preparation method of the conductive agent for a lithium-iron-phosphate battery of the present embodiment specifically included the following steps:

(1) pretreatment of the carbon nanotube/carbon black composite material: placing the carbon nanotube/carbon black composite material in a freeze drier, raising the temperature to 30°C, maintaining the temperature for 1 hour, then vacuumizing to 100 Pa, performing drying for 3 hours, then maintaining a vacuum degree, lowering the temperature gradually to room temperature, and then removing the carbon nanotube/carbon black composite material from the freeze drier, thereby completing the pretreatment; and

(2) preparation of the conductive agent for a lithium-iron-phosphate battery: weighing 2.5g of the carbon nanotube/carbon black composite material treated in step (1), weighing 0.0025g of polyacrylic cyanide, then placing the weighed carbon nanotube/carbon black composite material and polyacrylic cyanide in 50 ml of re-distilled water, performing ultrasonic dispersion for 15 minutes with an ultrasonic frequency being 20 kHz and power being 130 W, then adding, under ultrasonic conditions, 2.5g of graphene to the re-distilled water, and further performing ultrasonic dispersion for 10 minutes with the ultrasonic frequency being 20 kHz and the power being 130 W, thereby obtaining the conductive agent for a lithium-iron-phosphate battery.

[0022] Example 5

A conductive agent for a lithium-iron-phosphate battery in the present embodiment consisted of a carbon nanotube/carbon black composite material, graphene, polyacrylic cyanide, and polyacrylic acid, the weight ratio of the carbon nanotube/carbon black composite material, the graphene, the polyacrylic cyanide, and the polyacrylic acid was: carbon nanotube/carbon black composite material : graphene : (polyacrylic cyanide + polyacrylic acid) = 1 : 0.1 : 0.01.

[0023] A preparation method of the conductive agent for a lithium-iron-phosphate battery of the present embodiment specifically included the following steps:

(1) pretreatment of the carbon nanotube/carbon black composite material: placing the carbon nanotube/carbon black composite material in a freeze drier, rapidly cooling the same to -20°C, maintaining the temperature for 1 hour, then vacuumizing to 100 Pa, performing drying for 4 hours, then maintaining a vacuum degree, raising the temperature gradually to room temperature, and then removing the carbon nanotube/carbon black composite material from the freeze drier, thereby completing the pretreatment; and

(2) preparation of the conductive agent for a lithium-iron-phosphate battery: weighing 0.25g of the carbon nanotube/carbon black composite material treated in step (1), weighing 0.0083g of polyacrylic acid and 0.0167g of polyacrylic cyanide, then placing the weighed carbon nanotube/carbon black composite material, polyacrylic acid, and polyacrylic cyanide in 50 ml of re-distilled water, performing ultrasonic dispersion for 10 minutes with an ultrasonic frequency being 20 kHz and power being 130 W, then adding, under ultrasonic conditions, 0.0025g of graphene to the re-distilled water, and further performing ultrasonic dispersion for 10 minutes with the ultrasonic frequency being 20 kHz and the power being 130 W, thereby obtaining the conductive agent for a lithium-iron-phosphate battery.

[0024] Example 6

A conductive agent for a lithium-iron-phosphate battery in the present embodiment consisted of a carbon nanotube/carbon black composite material, graphene, polyacrylic cyanide, and polyacrylic acid, the weight ratio of the carbon nanotube/carbon black composite material, the graphene, the polyacrylic cyanide, and the polyacrylic acid was: carbon nanotube/carbon black composite material : graphene : (polyacrylic cyanide + polyacrylic acid) = 1 : 0.1 : 0.1.

[0025] A preparation method of the conductive agent for a lithium-iron-phosphate battery of the present embodiment specifically included the following steps:

(1) pretreatment of the carbon nanotube/carbon black composite material: placing the carbon nanotube/carbon black composite material in a freeze drier, rapidly cooling the same to -20°C, maintaining the temperature for 1 hour, then vacuumizing to 100 Pa, performing drying for 4 hours, then maintaining a vacuum degree, raising the temperature gradually to room temperature, and then removing the carbon nanotube/carbon black composite material from the freeze drier, thereby completing the pretreatment; and

(2) preparation of the conductive agent for a lithium-iron-phosphate battery: weighing 2.5g of the carbon nanotube/carbon black composite material treated in step (1), weighing 0.2083g of polyacrylic acid and 0.0417g of polyacrylic cyanide, then placing the weighed carbon nanotube/carbon black composite material, polyacrylic acid, and polyacrylic cyanide in 50 ml of re-distilled water, performing ultrasonic dispersion for 10 minutes with an ultrasonic frequency being 20 kHz and power being 130 W, then adding, under ultrasonic conditions, 0.25g of graphene to the re-distilled water, and further performing ultrasonic dispersion for 10 minutes with the ultrasonic frequency being 20 kHz and the power being 130 W, thereby obtaining the conductive agent for a lithium-iron-phosphate battery.

[0026] The conductive agents of Example 1 to Example 6 of the present invention were used to respectively prepare 5AH pouch lithium-iron-phosphate batteries of No. 1 to No. 6, and AC internal resistance thereof was measured. Results are shown in Table 1. A contrast sample lithium-iron-phosphate battery was also a 5AH pouch lithium-iron-phosphate battery, and the conductive agent was the carbon nanotube/carbon black composite material. As can be seen from Table 1, the lithium-iron-phosphate batteries prepared by using the conductive agent of the present invention had significantly reduced AC internal resistance and significantly improved electrochemical performance.

[0027] Table 1 Measurement data of AC internal resistance of lithium-iron-phosphate batteries

Test Item	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	Contrast sample
AC internal resistance (milliohm)	4.5	4.7	4.4	4.6	4.8	4.5	5.9



TRANSLATOR'S CERTIFICATE OF TRANSLATION

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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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Signed this 21st day of May, 2024

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