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(54) Title of Invention

Carbon Nanotube/Lithium Iron Phosphate Composite Cathode Material and In Situ Preparation Method Thereof

(57) Abstract

The present invention belongs to the technical field of lithium ion battery materials, and in particular relates to a carbon nanotube/lithium iron phosphate composite cathode material and an in situ preparation method thereof. The method includes: ultrasonically dispersing carbon nanotubes, acetylene black, and a dispersing agent in water or an organic solvent to obtain a mixture; mixing a lithium source, an iron source, and a phosphate salt, simultaneously adding an organic carbon source and the mixture, and performing ball-milling and drying; and drying the same, then calcining the same in an inert protective atmosphere, and performing sieving to obtain a composite cathode material wherein carbon nanotubes are uniformly dispersed in a bulk phase and on surfaces of lithium iron phosphate, wherein the carbon nanotubes account for 0.5-15% by weight, and the lithium iron phosphate accounts for 85-99.5% by weight. When the obtained composite cathode material is used as a positive electrode of a lithium ion battery, the power output and the cycle characteristics can be significantly improved, and in addition, the capability of binding with an aluminum foil current collector is strong. An electrode sheet has high compacted density. The flexibility and winding property of the electrode sheet are good.

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CARBON NANOTUBE/LITHIUM IRON PHOSPHATE COMPOSITE CATHODE MATERIAL AND IN SITU PREPARATION METHOD THEREOF

TECHNICAL FIELD

[0001] The present invention belongs to the technical field of lithium ion battery materials, and in particular relates to a carbon nanotube/lithium iron phosphate composite cathode material and an in situ preparation method thereof.

BACKGROUND

[0002] As a next-generation high-energy secondary battery product, lithium ion batteries have outstanding features such as a high discharge voltage, high specific energy and specific power, small self-discharge, a long cycle life, etc., and have been widely used in the fields of mobile communication devices, notebook computers, mobile phones, instruments, and apparatuses, etc. Since commercialization in the 1990s, lithium ion battery products have continued to develop rapidly at a rate of about 30% per year, and the market share thereof has rapidly exceeded other secondary batteries such as nickel-hydrogen batteries and nickel-cadmium batteries in a few years. According to statistics from the China Industrial Association of Power Sources, the production of rechargeable lithium batteries in Chinese Mainland was 950,000,000 in 2006, accounting for 16.9% of the global total production, and the production was greater than 1 billion in 2007, an increase of 11% over 2006. With the continuous advancement of lithium ion battery technology, lithium ion power batteries used as power have made breakthroughs from time to time in recent years, and are increasingly widely used in the fields of electric bicycles, electric motorcycles, electric golf carts, electric vehicles for carrying passengers or goods in public places, electric vehicles, etc. Lithium ion power batteries also have increasingly competitive advantages in the fields of smart robots, electric scooters, toy vehicles, lawn mowers, cotton pickers, field exploration tools, hand tools, etc. In addition, lithium ion power batteries have immeasurable markets in the fields of military, space flight and aviation, etc. Unlike portable communication devices, lithium ion power batteries have high requirements on power. Therefore, novel lithium ion battery materials must be developed to meet requirements on power lithium ion batteries.

[0003] Lithium iron phosphate is one of cathode materials for power batteries that are currently receiving much attention. Conventional lithium iron phosphate cathode materials are typically

uniform micron or sub-micron particles. Due to the large particle size, in cases of large-current charging and discharging, it is difficult to release stress generated in the process of lithium ion intercalation and deintercalation, causing an active material to be broken or exfoliated from an electrode sheet in a cycle process, deactivating the active material, and thus rapidly reducing the cycle life. In addition, it is difficult to further increase the power density because of the poor conductivity of the electrode material. The discharge rate of a current lithium ion battery is typically about the 3C current. By improving the battery fabrication process, the highest discharge rate of a high-power lithium ion battery can reach about 10C, but at the same time, the energy density and the cycle life of the battery are significantly reduced. In order to satisfy the requirements on both the high power density and the long cycle life, a further breakthrough in technology related to lithium ion battery materials is urgently needed.

[0004] During fabrication of an electrode sheet of a lithium ion battery, a certain amount of acetylene black is typically added as an electrically conductive additive to improve electron conductivity. The electrically conductive additive is an important component of the electrode sheet of the lithium ion battery, and although the proportion thereof is not large, the crystallinity, the form, the amount of addition, and the like thereof greatly affect the charge/discharge performance of the battery. As an electrically conductive additive that has emerged recently, carbon nanotubes have many excellent properties, and have the following outstanding advantages compared with electrically conductive additives such as acetylene black that are commonly used:

[0005] 1) Carbon nanotubes have good electrical conductivity, and the fibrous structure thereof can better connect electrode active materials into a continuous “network” that is electrically conductive, thereby improving the electrical conductivity of the electrode and the utilization rate of the active material.

[0006] 2) The carbon nanotubes have good mechanical properties, and the added carbon nanotubes provide high toughness to the electrode sheet, so that exfoliation caused by a change in the volume of the material during charging and discharging can be effectively suppressed, and particles of the active material can always maintain good electrical contact during charging and discharging, thereby improving the cycle life of the electrode.

[0007] 3) Uniform dispersion of carbon nanotubes can also significantly improve infiltration of the electrolyte in the electrode material.

[0008] Due to the above advantages, introducing an appropriate quantity of carbon nanotubes into the electrode material and dispersing the same uniformly can greatly improve both the power density and the cycle performance of the lithium ion battery, thereby achieving high use value. Endo et al. in Japan has found that the addition of vapor grown carbon fibers having good elastic properties helps to alleviate expansion and contraction of graphite particles during charging and discharging and to form a well electrically conductive network, thereby improving the cycle performance of negative electrode materials for lithium ion batteries. Nishizawa et al. believes that the conductivity of the composite electrode is the most important factor in designing a high performance battery, and the addition of carbon fibers as an electrically conductive agent maintains electrically conductive channels between particles well during charging and discharging cycles. Yoshiyuki et al. added carbon fibers to mesophase carbon microspheres, thereby well improving binding stability and cycle stability of the active material for the negative electrode. Kato et al. compared the effects of addition of the same quantity of carbon nanotubes, acetylene black, vapor grown carbon fibers, and graphite flakes as the electrically conductive agent on the cycle stability of the graphite negative electrode, and found that the cycle stability of the graphite negative electrode was the best when carbon nanotubes were used as the electrically conductive agent for the negative electrode. Lee et al. added nano carbon fibers to the $LiCoO_2$ battery. It was found in the research that the addition of a small quantity of vapor grown carbon fibers can improve the conductivity and flexibility of the electrode sheet, and also improve the cycle stability and low-temperature discharge performance. KANG Feiyu et al., in Tsinghua University used carbon nanotubes as an electrically conductive additive, and simply mixed the same with $LiNi_{0.8}Co_{0.2}O_2$ and $LiFePO_4$, rather than using electrically conductive carbon black. It was found that multi-walled carbon nanotubes can significantly improve the discharge capacity of the material and reduce interface resistance.

[0009] At present, conventional methods of adding carbon nanotubes into an electrode material of a lithium battery are as follows: As disclosed in U.S. Pat. No. US 20050106466 A1, US 6528211 B1, WO 2005011027-A2, and WO 2007/004728-A1 and the Chinese patent for invention CN 200510100831.7 (publication number CN 1956245 A), the methods are mainly as follows: carbon nanotubes are used as an electrically conductive additive instead of carbon black. The carbon nanotubes are all directly added to the active material, and are distributed only on surfaces of the electrode material, but cannot form a continuously connected three-dimensional electrically

conductive network or ore structure both in the bulk phase and on surfaces of the electrode material, and in addition, the dispersion problem of the carbon nanotubes cannot be completely solved, thereby hindering full utilization of properties of the carbon nanotubes.

SUMMARY

[0010] In view of the problems in the prior art, provided in the present invention is a high performance carbon nanotube/lithium iron phosphate composite cathode material and an in situ preparation method thereof, which can improve the high-power discharge capacity, cycle life, and compressibility of existing lithium iron phosphate cathode materials by fully utilizing properties of carbon nanotubes. Uniform dispersion of carbon nanotubes in the bulk phase and on surfaces of lithium iron phosphate is achieved by means of an in situ solid phase reaction process, thereby solving the problem in the prior art in which carbon nanotubes are distributed only on the surface of the electrode material and cannot form a continuously connected three-dimensional electrically conductive network structure both in the interior and on the surface of the material, and also solving the problem in which the properties of carbon nanotubes cannot be fully utilized because the carbon nanotubes cannot be fully dispersed.

[0011] The technical solutions employed by the present invention are as follows:

[0012] An in situ preparation method of a carbon nanotube/lithium iron phosphate composite cathode material comprises carbon nanotube dispersion (dispersion of carbon nanotubes and dispersion in a precursor) and an in situ solid phase reaction process. A specific preparation process comprises:

[0013] (1) Carbon nanotube dispersion: weighing a certain quantity of carbon nanotubes, acetylene black, and a dispersing agent, ultrasonically dispersing the same in water or an organic solvent to obtain a mixture, a low-concentration mother liquor containing totally 0.5-8% of carbon nanotubes and acetylene black by weight, the ratio of the weight of carbon (the sum of the weight of the carbon nanotubes and the weight of the acetylene black) to the weight of the dispersing agent being (20 to 5) : 1, the weight ratio of the carbon nanotubes to the acetylene black being (0.1 to 10) : 1, and the dispersing agent being polyvinylpyrrolidone (PVP) or polyvinyl alcohol (PVA).

[0014] (2) Precursor dispersion: according to a method of preparing a lithium iron phosphate material, selecting a raw material, mixing the raw material with the mixture from step (1), and

simultaneously adding an appropriate organic carbon source, pyrolytic carbon formed by the organic carbon source in a subsequent heat treatment process being capable of acting synergistically with the carbon nanotubes in performance to improve performance of the electrode material.

[0015] Mixing a lithium source, an iron source, and a phosphate salt at an atom ratio of Li : Fe : P = 1 : 1 : 1 at one time, and simultaneously adding an organic carbon source and the mixture from step (1), the weight of carbon (the sum of the weight of the carbon nanotubes and the weight of the acetylene black) accounting for 0.1-10% of the weight of a composite electrode material, the organic carbon source accounting for 3-25% of the final phosphoric acid composite electrode material by weight, adding a mixing and milling medium to perform mixing and ball-milling for 6 to 24 hours, and performing drying at 60°C to 110°C to obtain precursor powder.

[0016] The particle size of the precursor powder is 0.1-15 μm.

[0017] The mixing medium is at least one of deionized water, industrial alcohol, or absolute ethyl alcohol.

[0018] The organic carbon source mainly comprises: sucrose, glucose, a phenolic resin, or the like. Depending on a synthetic method, the lithium source mainly comprises: lithium carbonate, lithium hydroxide, lithium acetate, lithium dihydrogen phosphate, lithium citrate, or the like. The iron source mainly comprises: iron oxalate, iron acetate, ferric citrate, ferric oxide, ferroferric oxide, ferrous phosphate, or the like. A phosphate radical mainly comprises: ammonium dihydrogen phosphate, diammonium hydrogen phosphate, ferrous phosphate, lithium dihydrogen phosphate, or the like.

[0019] (3) In situ solid phase reaction: after the mixed precursor powder is dried in step (2), calcining the same at 600°C to 850°C in an inert protective atmosphere for 4 to 48 hours, pulverizing the burned material, and then sieving the same through a sieve of 150 to 400 meshes, thereby obtaining the carbon nanotube lithium iron phosphate composite cathode material.

[0020] The carbon nanotube dispersion of the present invention may comprise: adding the carbon nanotubes and the dispersing agent to water or the organic solvent, the weight ratio of the water, the carbon nanotubes, and the dispersing agent being 100 : (0.3 to 10) : (0.2 to 1); and after

ultrasonic dispersion, adding acetylene black, followed by ultrasonic or high-speed stirring and mixing to obtain a homogeneous mixture of the carbon nanotubes and the acetylene black.

[0021] The high-performance carbon nanotube lithium iron phosphate composite material obtained in the present invention has the following features: carbon nanotubes or carbon nanofibers are uniformly distributed on the surface of and in the lithium iron phosphate material by means of an in situ solid phase reaction. In the present invention, it has been found that the tube diameter and length of the carbon nanotubes have a considerable effect on utilization of the properties of the composite electrode material. Thus, the carbon nanotubes used in the present invention need to have the tube diameter of 10 to 200 nm and the length of 5 to 20 μm, and the optimal effect is achieved when the carbon nanotubes have the tube diameter of 50 to 150 nm and the length of 10 to 15 μm. Compared with carbon nanotubes having a smaller tube diameter and a greater length, the carbon nanotubes are less entangled with each other and are more easily dispersed. Therefore, formation of an effective conductive network is facilitated. Only when the effective conductive network is formed, the conductive network and the acetylene black can act on each other to achieve a synergistic effect.

[0022] The carbon nanotube/lithium iron phosphate composite cathode material obtained in the present invention has the following structure:

[0023] The composite cathode material obtained in the present invention is the particulate homogeneous composite of the carbon nanotubes and the lithium iron phosphate cathode material. The carbon nanotubes not only are present on the surface of the material, but also form a uniformly distributed network structure inside the material. The carbon nanotubes account for 0.5-15% by weight, and the lithium iron phosphate accounts for 85-99.5% by weight, the balance being coating carbon introduced during synthesis of the lithium iron phosphate, and accounting for 0-6% by weight. Preferably, the carbon nanotubes account for 0.5-3% by weight, and the lithium iron phosphate accounts for 92-97% by weight, the coating carbon accounting for 1-5% by weight.

[0024] The carbon nanotube/lithium iron phosphate composite cathode material obtained in the present invention has the following properties:

[0025] (1) The first discharge specific capacity is greater than 150 mAh/g.

[0026] (2) Apparent density: 0.5 g/cm^3.

[0027] Tap density: 1.0 g/cm^3.

[0028] Median diameter: about 4 μm.

[0029] Specific surface area: < 20 m^2/g.

[0030] Advantageous effects of the present invention are as follows:

[0031] (1) The carbon nanotube lithium iron phosphate composite cathode material prepared in the present invention has good electrochemical performance: the capacity > 150 mAh/g, the cycle life > 1500 times under high current use conditions, and discharge performance satisfying 10C/0.5C > 90%.

[0032] (2) When the carbon nanotube lithium iron phosphate composite cathode material prepared in the present invention is used as a positive electrode sheet of a lithium ion battery, the power output and the cycle characteristics can be significantly improved, and in addition, the capability of binding with an aluminum foil current collector is strong. The electrode sheet has high compacted density. Surface density of the compressed positive electrode sheet ≥ 2.3 g/cm^3. The flexibility and winding property of the positive electrode sheet are good.

[0033] (3) A lithium battery comprising the carbon nanotube lithium iron phosphate composite cathode material prepared in the present invention has a high specific capacity and a long cycle life.

[0034] (4) The present invention is inexpensive, and is easy to industrialize.

BRIEF DESCRIPTION OF THE DRAWINGS

[0035] FIG. 1 is a carbon nanotube lithium iron phosphate composite cathode material prepared in Example 1 of the present invention.

[0036] FIG. 2 is an XRD diagram of a carbon nanotube lithium iron phosphate composite cathode material prepared in Example 1 of the present invention.

[0037] FIG. 3 is a first charge/discharge curve of Example 1 of the present invention, a charge/discharge current being 0.1C.

[0038] FIG. 4 is a life curve of 100 times of 2.5V to 4.2V 100% DOD charge/discharge in Example 1 of the present invention, a discharge current being 1.5C.

DETAILED DESCRIPTION

[0039] Example 1: a carbon nanotube lithium iron phosphate composite cathode material was prepared by using in situ solid phase reaction (carbon thermal reduction).

[0040] (1) Carbon nanotubes having a length of 10-15 μm and a tube diameter of 50-150 nm were selected as a raw material. 10g of carbon nanotubes and 6g of polyvinylpyrrolidone (PVP) as a dispersing agent were added to 500 ml of deionized water. After ultrasonic dispersion, 20g of acetylene black were further added, followed by ultrasonic or high-speed stirring and mixing to obtain a homogeneous mixture of the carbon nanotubes and the acetylene black.

[0041] (2) 2 Kg of deionized water were added to a ball-milling tank, 1000g of LiH_2PO_4, 769.2g of Fe_2O_3, and 360g of sucrose were added, and then the mixture from step (1) was added thereto. After wet ball-milling was performed for 24h, a homogeneous suspension fluid slurry was obtained, and was spray-dried (100°C) to obtain quasi-spherical solid-phase precursor powder having a particle size of about 2 μm. The precursor was calcined at 700°C under protection of an inert gas for 15 hours, crushed, and then sieved through a 200-mesh sieve to obtain a carbon nanotube lithium iron phosphate composite sample. An electrode sheet was soft when the carbon nanotube lithium iron phosphate composite sample had tap density of 1.25 g/cm^3 and compacted density of 2.3 g/cm^3. A scanning electron microscope image thereof is shown in FIG. 1, and it can be seen that the carbon nanotubes were uniformly dispersed in the lithium iron phosphate material. The carbon nanotubes accounted for 0.6% by weight, and the lithium iron phosphate accounted for 95% by weight, the balance being coating carbon accounting for 4.4% by weight. An X-ray diffraction pattern is shown in FIG. 2, and it can be seen that the material was pure phase lithium iron phosphate. The first charge/discharge curve is shown in FIG. 3, and an initial charge capacity and an initial discharge capacity at 0.1C were respectively 160.2 mAh/g and 150.1 mAh/g. The cycle performance is shown in FIG. 4. The initial specific capacity of discharge at 1.5C was 120.1 mAh/g. Under the 2.5-4.2V, 100% DOD condition, and after 100 cycles at 1.5C, the capacity retention ratio was 98.8%, and capacity loss was only 1.2%.

[0042] Example 2: a carbon nanotube lithium iron phosphate composite cathode material was prepared by using an in situ solid phase reaction method.

[0043] Differences from Example 1 were as follows:

[0044] (1) Carbon nanotubes having a length of 10-15 μm and a tube diameter of 50-150 nm were selected as a raw material. 10g of carbon nanotubes and 6g of polyvinylpyrrolidone (PVP) as a dispersing agent were added to 500 ml of deionized water. After ultrasonic dispersion, 20g of acetylene black were further added, followed by ultrasonic or high-speed stirring and mixing to obtain a homogeneous mixture of the carbon nanotubes and the acetylene black.

[0045] (2) 2 Kg of deionized water were added to a ball-milling tank, 355.2g of Li_2CO_3, 1730g of $FeC_2O_4 \cdot 2H_2O$, 1106g of ammonium dihydrogen phosphate, and 83g of sucrose were added, and then the mixture from step (1) was added thereto. After wet ball-milling was performed for 24h, a homogeneous suspension fluid slurry was obtained, and was spray-dried (100°C) to obtain quasi-spherical solid-phase precursor powder having a particle size of 2 μm. The precursor was calcined at 700°C under protection of an inert gas for 24 hours, crushed, and then sieved through a sieve of 150 to 300 meshes to obtain a carbon nanotube lithium iron phosphate composite material. The carbon nanotubes accounted for 0.6% by weight, and the lithium iron phosphate accounted for 95% by weight, the balance being coating carbon accounting for 4.4% by weight.

[0046] Example 3: a carbon nanotube lithium iron phosphate composite cathode material was prepared by using $FePO_4$ as a raw material and by using a carbon thermal reduction - in situ solid phase reaction method.

[0047] Differences from Example 1 were as follows:

[0048] (1) Carbon nanotubes having a length of 10-15 μm and a tube diameter of 50-150 nm were selected as a raw material. 20g of carbon nanotubes and 6g of polyvinylpyrrolidone (PVP) as a dispersing agent were added to 500 ml of deionized water. After ultrasonic dispersion, 40g of acetylene black were further added, followed by ultrasonic or high-speed stirring and mixing to obtain a homogeneous mixture of the carbon nanotubes and the acetylene black.

[0049] (2) 2 Kg of deionized water were added to a ball-milling tank, 355.2g of Li_2CO_3, 1450g of $FePO_4 \cdot 2H_2O$, 1106g of diammonium hydrogen phosphate, and 360g of sucrose were added, and then the mixture from step (1) was added thereto. After wet ball-milling was performed for 24h, a homogeneous suspension fluid slurry was obtained, and was spray-dried (90°C) to obtain quasi-spherical solid-phase precursor powder having a particle size of 2 μm. The precursor was calcined at 800°C under protection of an inert gas for 6 hours, crushed, and then sieved through a 400-mesh sieve to obtain a carbon nanotube lithium iron phosphate composite material. The

carbon nanotubes accounted for 1.2% by weight, and the lithium iron phosphate accounted for 94% by weight, the balance being coating carbon accounting for 4.8% by weight.

[0050] Example 4: a carbon nanotube doped-lithium iron phosphate composite cathode material was synthesized by using a technique of doping in Li sites.

[0051] Differences from Example 2 were as follows: during synthesis of a lithium iron phosphate cathode material, a certain quantity of high-valent metal elements were introduced to Li sites. That is, $Li_{1-x}M_xFePO_4$ was synthesized, where M was Nd, Ti, Zr, W, V, etc. The added quantity X was 0.005 to 0.03.The above-mentioned elements were introduced to improve electron conductivity of the material, thereby further improving large-current discharge performance. For example, M was Zr:

[0052] (1) was the same as step 1 of Example 2.

[0053] (2) 2 Kg of deionized water were added to a ball-milling tank, 351.6g of lithium carbonate, 16g of zirconium dioxide, 1730g of iron oxalate, 1106g of ammonium dihydrogen phosphate, and 83g of sucrose were added, and then the mixture from step (1) was added thereto. After wet ball-milling was performed for 24h, a homogeneous suspension fluid slurry was obtained, and was spray-dried (100°C) to obtain quasi-spherical solid-phase precursor powder having a particle size of 2 μm. The precursor was calcined at 700°C under protection of an inert gas for 24 hours, crushed, and then sieved through a sieve of 150 to 300 meshes to obtain a carbon nanotube lithium iron phosphate composite material. The molecular formula of the obtained material was $Li_{0.99}Zr_{0.01}FePO_4$. The carbon nanotubes accounted for 0.6% by weight, and the lithium iron phosphate accounted for 95% by weight, the balance being coating carbon accounting for 4.4% by weight.

[0054] Example 5: a carbon nanotube doped-lithium iron phosphate composite cathode material was synthesized by using a technique of doping in Fe sites.

[0055] Differences from Example 1 were as follows: during synthesis of a lithium iron phosphate cathode material, a certain quantity of high-valent metal elements were introduced to Fe sites. That is, $LiM_xFe_{1-x}PO_4$ was synthesized, where M was Mg, Ti, Co, Ni, Mn, etc. The added quantity X was 0.01 to 0.10. The above-mentioned elements were introduced to improve ion

conductivity of the material, thereby further improving large-current discharge performance. For example, M was Mg:

[0056] (1) was the same as step 1 of Example 1.

[0057] (3) (2) 2 Kg of deionized water were added to a ball-milling tank, 1000g of LiH_2PO_4, 769.2g of Fe_2O_3, 28g of $Mg(OH)_2$, and 360g of sucrose were added, and then the mixture from step (1) was added thereto. After wet ball-milling was performed for 24h, a homogeneous suspension fluid slurry was obtained, and was spray-dried (100°C) to obtain quasi-spherical solid-phase precursor powder having a particle size of about 2 μm. The precursor was calcined at 700°C under protection of an inert gas for 15 hours, crushed, and then sieved through a 200-mesh sieve to obtain a carbon nanotube lithium iron phosphate composite sample. The molecular formula of the material was $LiFe_{0.95}Mg_{0.05}PO_4$. The carbon nanotubes accounted for 0.6% by weight, and the lithium iron phosphate accounted for 95% by weight, the balance being coating carbon accounting for 4.4% by weight.

[0058] Comparative Example 1:

[0059] Lithium iron phosphate cathode material was directly synthesized without introduction of carbon nanotubes or acetylene black.

[0060] 2 Kg of deionized water were added to a ball-milling tank, and 1000g of LiH_2PO_4, 769.2g of Fe_2O_3, and 360g of sucrose were added. After wet ball-milling was performed for 24h, a homogeneous suspension fluid slurry was obtained, and was spray-dried to obtain a quasi-spherical solid-phase precursor. The precursor was calcined at 700°C under protection of an inert gas for 15 hours, crushed, and then sieved through a 200-mesh sieve to obtain a lithium iron phosphate sample.

[0061] Comparative Example 2:

[0062] In step 1, carbon nanotubes were directly dispersed without adding acetylene black.

[0063] (1) Carbon nanotubes having a length of 10-15 μm and a tube diameter of 50-150 nm were selected as a raw material. 30g of carbon nanotubes and 6g of polyvinylpyrrolidone (PVP) as a dispersing agent were added to 500 ml of deionized water. Ultrasonic dispersion was performed.

[0064] (2) 2 Kg of deionized water were added to a ball-milling tank, 1000g of LiH_2PO_4, 769.2g of Fe_2O_3, and 360g of sucrose were added, and then the mixture from step (1) was added thereto. After wet ball-milling was performed for 24h, a homogeneous suspension fluid slurry was obtained, and was spray-dried to obtain a quasi-spherical solid-phase precursor. The precursor was calcined at 700°C under protection of an inert gas for 15 hours, crushed, and then sieved through a 200-mesh sieve to obtain a carbon nanotube lithium iron phosphate composite sample.

[0065] Comparative Example 3:

[0066] In step 1, acetylene black was directly dispersed without adding carbon nanotubes.

[0067] (1) 30g of acetylene black and 6g of polyvinylpyrrolidone (PVP) as a dispersing agent were added to 500 ml of deionized water, and ultrasonic dispersion was performed.

[0068] (2) 2 Kg of deionized water were added to a ball-milling tank, 1000g of LiH_2PO_4, 769.2g of Fe_2O_3, and 360g of sucrose were added, and then the mixture from step (1) was added thereto. After wet ball-milling was performed for 24h, a homogeneous suspension fluid slurry was obtained, and was spray-dried to obtain a quasi-spherical solid-phase precursor. The precursor was calcined at 700°C under protection of an inert gas for 15 hours, crushed, and then sieved through a 200-mesh sieve to obtain an acetylene black lithium iron phosphate composite sample.

[0069] Comparative Example 4:

[0070] In step 1, carbon nanotubes having a smaller tube diameter and a greater length were used as an added raw material.

[0071] (1) Carbon nanotubes having a length of 30 μm and a tube diameter of 50 nm were selected as a raw material. 10g of carbon nanotubes and 6g of polyvinylpyrrolidone (PVP) as a dispersing agent were added to 500 ml of deionized water. After ultrasonic dispersion, 20g of acetylene black were further added, followed by ultrasonic or high-speed stirring and mixing.

[0072] (2) 2 Kg of deionized water were added to a ball-milling tank, 1000g of LiH_2PO_4, 769.2g of Fe_2O_3, and 360g of sucrose were added, and then the mixture from step (1) was added thereto. After wet ball-milling was performed for 24h, a homogeneous suspension fluid slurry was obtained, and was spray-dried to obtain a quasi-spherical solid-phase precursor. The precursor was calcined at 700°C under protection of an inert gas for 15 hours, crushed, and then sieved through a 200-mesh sieve to obtain an acetylene black lithium iron phosphate composite sample.

[0073] In the present comparative example, since the tube diameter of the carbon nanotubes was too small and the length was greater, mutual entanglement was severe. The carbon nanotubes and the acetylene black were agglomerated, and it was difficult to form an effective conductive network.

[0074] Comparative Example 5:

[0075] In step 1, carbon nanotubes having a larger tube diameter and a smaller length were used as an added raw material.

[0076] (1) Carbon nanotubes having a length less than 10 μm and a tube diameter greater than 200 nm were selected as a raw material. 10g of carbon nanotubes and 6g of polyvinylpyrrolidone (PVP) as a dispersing agent were added to 500 ml of deionized water. After ultrasonic dispersion, 20g of acetylene black were further added, followed by ultrasonic or high-speed stirring and mixing.

[0077] (2) 2 Kg of deionized water were added to a ball-milling tank, 1000g of LiH_2PO_4, 769.2g of Fe_2O_3, and 360g of sucrose were added, and then the mixture from step (1) was added thereto. After wet ball-milling was performed for 24h, a homogeneous suspension fluid slurry was obtained, and was spray-dried to obtain a quasi-spherical solid-phase precursor. The precursor was calcined at 700°C under protection of an inert gas for 15 hours, crushed, and then sieved through a 200-mesh sieve to obtain an acetylene black lithium iron phosphate composite sample.

[0078] In the present comparative example, the tube diameter of the carbon nanotubes was too large and the length was too small, so that although dispersibility was good, it was difficult to form a limited conductive network due to the limited length of the carbon nanotubes.

[0079] Electrochemical Performance Test:

[0080] The negative electrode materials for lithium ion batteries prepared in the above examples and comparative examples, acetylene black, and polyvinidylene fluoride (PVDF) dissolved in N-methylpyrrolidone (NMP) were made into a homogeneous slurry, and the slurry was applied on copper foil. Drying was performed at 110°C in a vacuum for 6 hours to obtain a negative electrode sheet in which the weight ratio of carbon nanotube composite graphite, acetylene black, and polyvinidylene fluoride was 93 : 3 : 4. The negative electrode sheet was punched to obtain a 12 mm-diameter disk, and the 12 mm-diameter disk was assembled into a CR-

2032 button cell in a glovebox having an inert atmosphere. The metallic lithium sheet was a counter electrode. The electrolyte was 1 mol/L of $LiPF_6$/EC + EMC + DMC (a volume ratio of 1 : 1 : 1). The separator was Celegard 2400. The electrochemical performance test was performed by testing battery performance on a Land BT-1 tester of Wuhan Land Electronics Co., Ltd. The charge/discharge voltage was 0V to 2.0V, and the charge/discharge rate was 0.2C. In the present invention, the process of intercalation of lithium ions in graphite in a graphite/lithium half-cell is referred to as charging, and the process of deintercalation of lithium ions in graphite is referred to as discharging. In order to examine the rate characteristics of the carbon nanotube composite graphite material, the button cell was charged at 0.2C to 2V after the button cell underwent one charging and discharging cycle, and was then discharged at 3C to 0V. The rate characteristics of the graphite material were compared according to the ratio C3C/C0.2C of the discharge capacity at 3C to the discharge capacity at 0.2C.

[0081] Table 1 is comparison of the cycle life between Examples 1, 2, 3, 4, and 5 and Comparative Examples 1, 2, and 3, and the charge/discharge rate being 1C.

[0082] Table 1

[0083]

	First Discharge Specific Capacity (mAh/g)	Capacity Retention Ratio (%) after 100 Cycles
Example 1	125.5	100
Example 2	124.5	100
Example 3	122.1	100
Example 4	135.2	100
Example 5	132.1	100
Comparative Example 1	110.5	80
Comparative Example 2	115.6	94
Comparative Example 3	113.9	90

[0084] Table 2 is comparison of the rate discharge performance between Examples 1, 2, 3, 4, and 5 and Comparative Examples 1, 2, and 3.

[0085] Table 2

[0086]

	3C discharge specific capacity (mAh/g)	3C/0.1C (%)
Example 1	120.0	83.6
Example 2	118.4	83.2
Example 3	116.3	82.1
Example 4	128.4	86.2
Example 5	125.5	83.4
Comparative Example 1	104.5	73.1
Comparative Example 2	108.7	75.3
Comparative Example 3	105.3	74.2

Claims

1. A carbon nanotube/lithium iron phosphate composite cathode material, characterized in that carbon nanotubes are uniformly dispersed in a bulk phase and on surfaces of lithium iron phosphate, the carbon nanotubes accounting for 0.5-15% by weight, and lithium iron phosphate accounting for 85-99.5% by weight.

2. An in situ preparation method of the carbon nanotube/lithium iron phosphate composite cathode material according to claim 1, characterized by comprising carbon nanotube dispersion and an in situ solid phase reaction process, a specific preparation process comprising:

(1) carbon nanotube dispersion: weighing carbon nanotubes, acetylene black, and a dispersing agent, ultrasonically dispersing the same in water or an organic solvent to obtain a mixture, a low-concentration mother liquor containing 0.5-8% of carbon nanotubes and acetylene black by weight, the ratio of the weight of carbon to the weight of the dispersing agent being (20 to 5) : 1, the weight of carbon being the sum of the weight of the carbon nanotubes and the weight of the acetylene black, and the weight ratio of the carbon nanotubes to the acetylene black being (0.1 to 10) : 1;

(2) precursor dispersion: mixing a lithium source, an iron source, and a phosphate salt at an atom ratio of Li : Fe : P = 1 : 1 : 1 at one time, and simultaneously adding an organic carbon source and the mixture from step (1), the weight of carbon in the mixture accounting for 0.1-10% of the weight of a final composite electrode material, the organic carbon source accounting for 3-25% of the composite electrode material by weight, adding a mixing and milling medium to perform mixing and ball-milling for 6 to 24 hours, and performing drying at 60°C to 110°C to obtain precursor powder; and

(3) in situ solid phase reaction: after the mixed precursor powder is dried in step (2), calcining the same at 600°C to 850°C in an inert protective atmosphere for 4 to 48 hours, pulverizing the burned material, and then sieving the same through a sieve of 150 to 400 meshes, thereby obtaining the carbon nanotube lithium iron phosphate composite cathode material.

3. The in situ preparation method of the carbon nanotube/lithium iron phosphate composite cathode material according to claim 2, wherein the carbon nanotube has a tube diameter of 10-200 nm and a length of 5-20 μm.

4. The in situ preparation method of the carbon nanotube/lithium iron phosphate composite cathode material according to claim 2, wherein the particle size of the precursor powder is 0.1-20 μm.

5. The in situ preparation method of the carbon nanotube/lithium iron phosphate composite cathode material according to claim 2, wherein the dispersing agent is polyvinylpyrrolidone or polyvinyl alcohol.

6. The in situ preparation method of the carbon nanotube/lithium iron phosphate composite cathode material according to claim 2, wherein the mixing medium is at least one of deionized water, industrial alcohol, or absolute ethyl alcohol.

7. The in situ preparation method of the carbon nanotube/lithium iron phosphate composite cathode material according to claim 2, wherein the organic carbon source comprises sucrose, glucose, or a phenolic resin, the lithium source comprising lithium carbonate, lithium hydroxide, lithium acetate, lithium dihydrogen phosphate, or citric acid, the iron source comprising iron oxalate, iron acetate, ferric citrate, ferric oxide, ferroferric oxide, or ferrous phosphate, and a phosphate radical comprising ammonium dihydrogen phosphate, diammonium hydrogen phosphate, ferrous phosphate, or lithium dihydrogen phosphate.

8. The in situ preparation method of the carbon nanotube/lithium iron phosphate composite cathode material according to claim 2, wherein the carbon nanotube dispersion comprises: adding first the carbon nanotubes and the dispersing agent to water or the organic solvent; after ultrasonic dispersion, adding acetylene black, followed by ultrasonic or high-speed stirring and mixing to obtain a homogeneous mixture of the carbon nanotubes and the acetylene black.

9. The in situ preparation method of the carbon nanotube/lithium iron phosphate composite cathode material according to claim 8, wherein the weight ratio of the water, the carbon nanotubes, and the dispersing agent is 100 : (0.3 to 10) : (0.2 to 1).

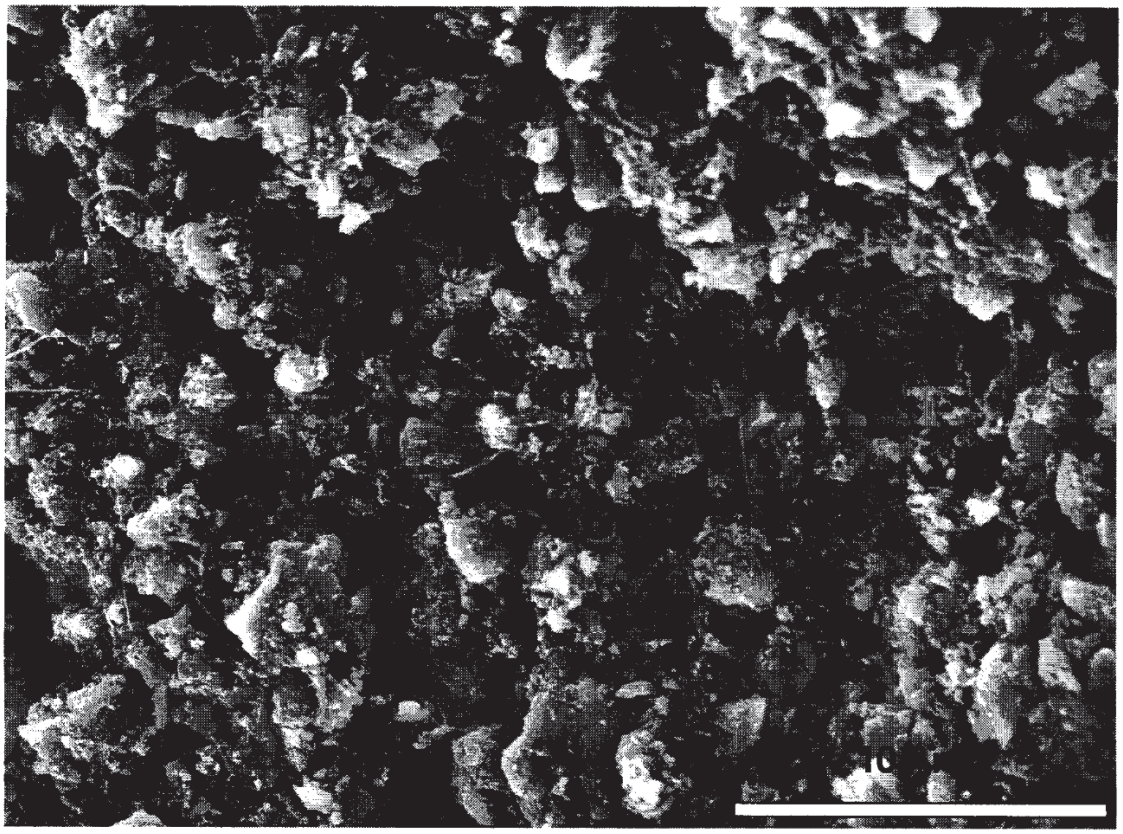

FIG. 1

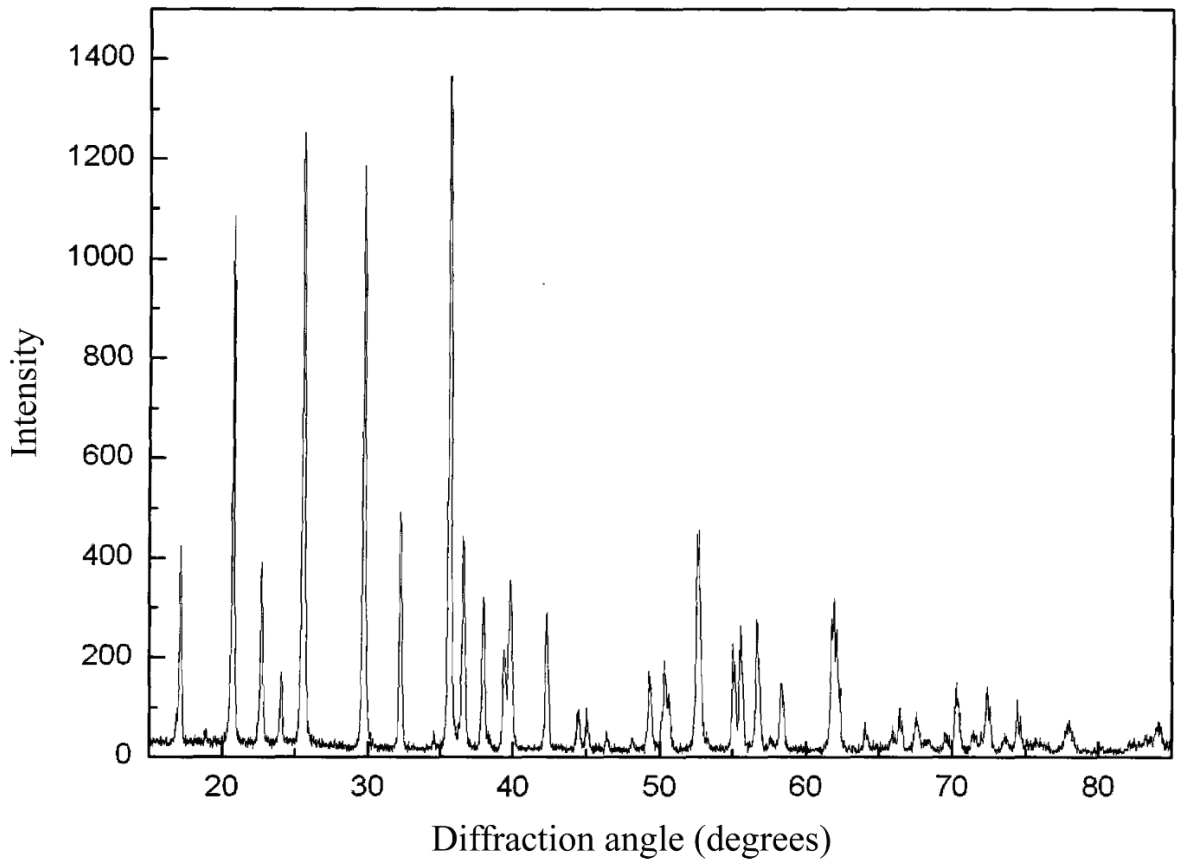
1400
1200
1000
800
600
400
200
0
Intensity
20
30
40
50
60
70
80
Diffraction angle (degrees)

FIG. 2

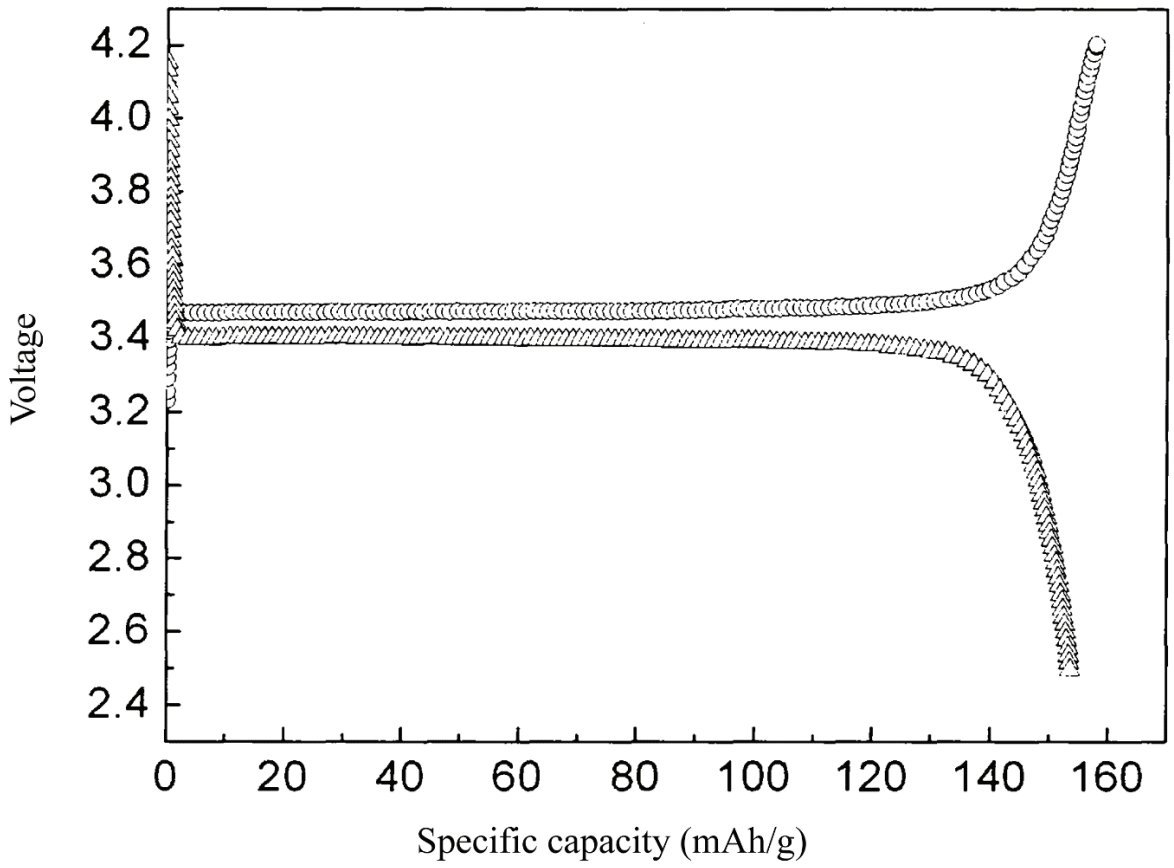
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
Voltage
0
20
40
60
80
100
120
140
160
Specific capacity (mAh/g)

FIG. 3

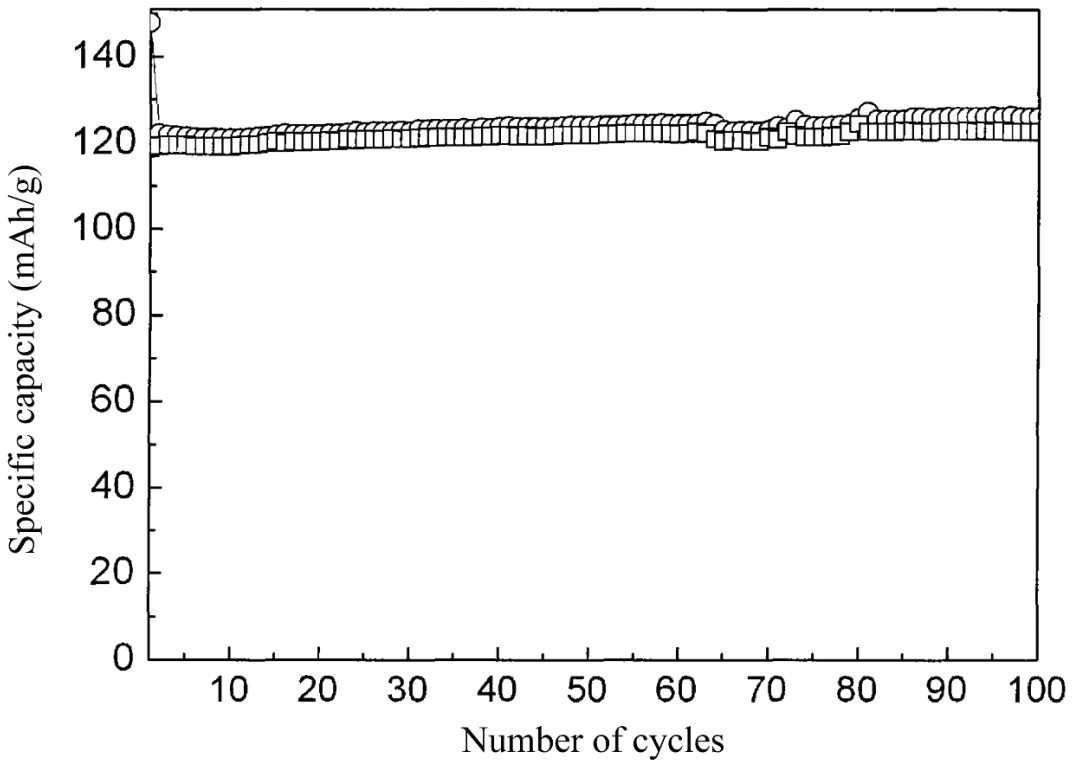
Specific capacity (mAh/g)
140
120
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
100
Number of cycles

FIG. 4

Questel

TRANSLATOR'S CERTIFICATE OF TRANSLATION

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Questel Project Number: FRPC2420011UT-L_Q
Date: May 21, 2024

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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