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[54] Title of Invention

BORON-CONTAINING LITHIUM IRON PHOSPHATE/CARBON COMPOSITE MATERIAL AND PREPARATION METHOD THEREFOR

[57] Abstract

The present invention relates to a positive electrode material for a secondary lithium battery, and in particular to a boron-containing lithium iron phosphate/carbon composite material and a preparation method therefor. The present invention aims mainly to solve the technical problems existing in the prior art that the bonding strength between a coating carbon layer and the surface of lithium iron phosphate is not great enough, the tapped density of the product is low, particle size growth rate is fast and distribution is unevenly concentrated, and the electrical performance of the lithium iron phosphate and the quality consistency of the product are poor. The present invention has the following chemical formula: $Li_{1-x}M_xFe_{1-y}N_yP_{1-z}Si_zO_4 \cdot \xi B_2O_3/C$ or $Li_{1-x}M_xFe_{1-y}N_yP_{1-z}Si_zO_4 \cdot \zeta LiBO_2/C$. Steps are as follows: adding a borate surfactant or/and flux to a ball mill tank loaded with a solvent; stirring the mixture uniformly; then, separately adding an iron source compound, a lithium source compound, a phosphorus source compound, and a carbon-coated carbon source for mixing; evaporating the solvent until dry, and then carrying out sintering of a solid powder under the protection of inert gas; cooling and then taking out; and pulverizing and classifying to obtain a finished product.

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CLAIMS

1. A boron-containing lithium iron phosphate/carbon composite material, characterized by having a chemical formula of: $Li_{1-x}M_xFe_{1-y}N_yP_{1-z}Si_zO_4 \cdot \xi B_2O_3/C$ or $Li_{1-x}M_xFe_{1-y}N_yP_{1-z}Si_zO_4 \cdot \zeta LiBO_2/C$, wherein the metal element M doped at a lithium site in a bulk phase is at least one of Mg, Ca, Zn, Al, Cr, V, Ti, Zr and Nb, and $0 \leq x \leq 0.1$; the metallic element N doped at the iron site in the bulk phase is at least one of Li, Cu, Mg, Ca, Mn, Ni, Co, Zn, Al, Cr, V, Ti, Zr and Nb, and $0 \leq y \leq 0.1$; the silicon element is doped at a phosphorus site in the bulk phase, and $0 \leq z \leq 0.5$; $0.006 \leqq \xi \leqq 0.25$, and $0.01 \leqq \zeta \leqq 0.5$; B_2O_3 or $LiBO_2$ exists in an amorphous state on the surface of lithium iron phosphate and is mixed with a conductive carbon material, and the weight ratio of the carbon material to the boron-containing lithium iron phosphate/carbon composite material is 0.1 to 10%.

2. A method for preparing a boron-containing lithium iron phosphate/carbon composite material, characterized by:

a. adding a borate surfactant or/and flux to a ball mill tank loaded with a solvent, the borate surfactant accounting for 0.05 to 5% of the total mass of solid raw materials; stirring thoroughly and uniformly; and then separately adding an iron source compound, a lithium source compound, a phosphorus source compound and a carbon-coated carbon source at a stoichiometric ratio to perform primary ball milling and mixing; and

b. evaporating the solvent until dry, and sintering by heating the obtained solid powder under the protection of an inert gas; cooling to room temperature, and then taking out; and pulverizing and classifying to obtain the boron-containing lithium iron phosphate/carbon composite material, wherein the weight ratio of carbon-coated carbon to the boron-containing lithium iron phosphate/carbon composite material is 0.1 to 10%.

3. The method for preparing a boron-containing lithium iron phosphate/carbon composite material according to claim 2, characterized in that the aforementioned step b is replaced by step b′:

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b′. evaporating the solvent until dry, and then heating the obtained solid powder under the protection of an inert gas for first sintering; cooling to room temperature and then taking out, and placing into the ball mill tank again; performing secondary ball milling without adding or with adding the borate surfactant or/and flux; evaporating the solvent until dry, and then heating the obtained solid powder under the protection of the inert gas for second sintering; and pulverizing and classifying to obtain the boron-containing lithium iron phosphate/carbon composite material, wherein the weight ratio of carbon-coated carbon to the boron-containing lithium iron phosphate/carbon composite material is 0.1 to 10%.

4. The method for preparing a boron-containing lithium iron phosphate/carbon composite material according to claim 2, characterized in that the borate surfactant added in the step a is at least one of borate monoester, borate diester, borate triester, tetracoordinate spiroborate and derivatives thereof.

5. The method for preparing a boron-containing lithium iron phosphate/carbon composite material according to claim 2 or 3, characterized in that the flux is at least one of a boron compound and an alkali metal fluoride; the boron compound is B_2O_3, H_3BO_3, $LiBO_2$ or a boron-containing compound capable of forming B_2O_3, H_3BO_3, or $LiBO_2$ by decomposition at a high temperature; and the alkali metal fluoride is lithium fluoride.

6. The method for preparing a boron-containing lithium iron phosphate/carbon composite material according to claim 2, characterized in that when the iron source compound, the lithium source compound, the phosphorus source compound and the carbon-coated carbon source are added at the stoichiometric ratio in the aforementioned step (a), a doping element compound is also added at the same time.

7. The method for preparing a boron-containing lithium iron phosphate/carbon composite material according to claim 2, characterized in that the iron source compound is at least one of ferrous oxide, ferric oxide, ferric tetraoxide, ferrous oxalate, ferric oxalate or ferrous phosphate, and ferric phosphate; the lithium source compound is at least one of lithium carbonate, lithium hydroxide, lithium acetate, lithium phosphate and lithium dihydrogen phosphate; the phosphorus

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source compound is at least one of phosphoric acid, lithium phosphate, lithium dihydrogen phosphate, diammonium hydrogen phosphate and ammonium dihydrogen phosphate; and the carbon-coated carbon source is at least one of a polymer compound or a mixture of a polymer compound and a carbon nanotube, acetylene black, or a carbon black conductive additive.

8. The method for preparing a boron-containing lithium iron phosphate/carbon composite material according to claim 2 or 3, characterized in that the inert gas is at least one of nitrogen gas, argon gas, and ammonia gas, or at least one of mixed gases formed by nitrogen gas, argon gas and ammonia gas and hydrogen gas accounting for less than 15% by volume.

9. The method for preparing a boron-containing lithium iron phosphate/carbon composite material according to claim 2, characterized in that the sintering temperature in the aforementioned step b is 550°C to 850°C, and the sintering time is 1 to 30 hours.

10. The method for preparing a boron-containing lithium iron phosphate/carbon composite material according to claim 3, characterized in that the temperature of the first sintering in the aforementioned step b' is 300°C to 550°C, the temperature of the second sintering is 550°C to 850°C, and both the first and the second sintering times are 1 to 30 hours.

BORON-CONTAINING LITHIUM IRON PHOSPHATE/CARBON COMPOSITE MATERIAL AND PREPARATION METHOD THEREFOR

TECHNICAL FIELD

The present invention relates to a positive electrode material for a secondary lithium battery, and in particular to a boron-containing lithium iron phosphate/carbon composite material and a preparation method therefor.

BACKGROUND ART

Since lithium-ion batteries were first launched into the market by Sony Corporation in the early 1990s, lithium-ion batteries have become the first preferred power source for small electronic devices such as mobile communications, notebook computers, and cameras (video cameras) due to their advantages, such as a high operating voltage (3 volts or more relative to metallic lithium), high specific energy, low self-discharge rate, no memory effect, and excellent cycle stability. At present, the application range of the lithium-ion batteries has been expanded to large-capacity and high-power power sources for power tools, mining lamps, electric bicycles, electric vehicles, hybrid electric vehicles, satellites, weapons equipment and the like, and has great market prospects. The key to large-capacity, high-power lithium-ion battery applications is the development of electrode materials that are inexpensive, environmentally friendly and highly safe, and have excellent high-rate characteristics and cycle stability. In 1997, John B. Goodenough et al. of the United States reported a lithium iron phosphate material having an olivine structure based on phosphate polyanions (1. A.K.Padhi, K.S.Nan jundaswamy, and J.B.Goodenough, *Journal of the Electrochemical Society*, vol. 144(4), 1188(1997); 2. US Patent No. 5,910,382). The material has a theoretical discharge capacity of 170 mAh/g and a discharge voltage of about 3.4 V (relative to metallic lithium). Its outstanding advantages are better safety and cycle stability than all currently known positive electrode materials for lithium-ion batteries. Moreover, it is inexpensive, non-polluting and very suitable as positive electrode materials for high-capacity and high-power lithium-ion batteries. However, there is also the obvious disadvantage of low electronic and ionic conductivity (only about 10^{-10} Scm^{-1} at room temperature. See: C.Delacourt, L.Laffond, R.Bouchet, C.Wurm, J-B.Leriche, M.Morcrette, J-M.Tarascon, and C.Masquelier, *Journal of the Electrochemical Society*, vol.152(5)(2005) A913). Therefore, they discharged at a small current

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density of 0.05 mA/cm^2 at that time, and the capacity could only reach about 110 mAh/g. To overcome the above shortcomings, they have found that methods such as carbon coating, doping of iron sites with high-valence metal ions, and partial substitution of phosphate groups with other tetrahedral anions can effectively improve the electronic and ionic conductivity of lithium iron phosphate, thereby greatly improving discharge capacities and rate characteristics (1. N. Ravet, J.B. Goodenough, S. Besner, M. Simoneau, P. Hovington, and M. Armand, in: Proceedings of the 196th ECS Meeting, Honolulu, October 1999; 2. US Patent No.5,910,382, US Patent No.6085015, US Patent No.6391493B1, and US Patent No.6514640B1).

In 2002, Yet-Ming Chiang et al. at the Massachusetts Institute of Technology in the United States found that doping a lithium site with a metal ion having a valence of +2 or more could increase the electronic conductivity by up to eight orders of magnitude, thereby greatly improving the rate charge and discharge characteristics of lithium iron phosphate (1. Sung-Yoon Chung, Jason T. Bloking and Yet-Ming Chiang, Nature Materials, 2002, No.1, pp: 123-128; 2. Yet-Ming Chiang, Sung-Yoon, Jason T. Bloking, and Anna M. Andersson, US Patent Application No. 2004/0005265A1, Jan. 8, 2004). They believe that doping the lithium site with the high-valence metal ion causes the lithium site or the iron site to generate positive ion vacancies, causing Fe^{3+}/Fe^{2+} ions of different valence states to exist in the same phase, and forming a p-type semiconductor. To increase the diffusion rate of lithium ions in the lithium iron phosphate particles, they made the lithium iron phosphate particles doped with lithium sites into nanoscale, which greatly improved the electronic and ionic conductivity, and achieved the high rate characteristics of the lithium iron phosphate material (1. Yet-Ming Chiang, Anthony E.Pullen, and Nonglak Meeting, US 2007/0292747A1; 2. US Patent No. 7338734).

Experimental tests have demonstrated that the electronic/ionic conductivity of lithium iron phosphate is increased by doping by no more than one order of magnitude, while the effect of surface carbon coating on improving the electronic conductivity is much more significant (C. Wang, J. Hong, “Ionic/ Electronic Conducting Characteristics of LiFePO4 Cathode Materials-The Determining Factors for High Rate Performance”, Electrochemical and Solid-State Letters, 10(3) A65-A69 (2007). Therefore, surface coating with a carbon material is currently a commonly used method to improve the electronic conductivity of lithium iron phosphate. Moreover, there are a large number of experiments demonstrating that: the effect of coating lithium iron phosphate with polymer pyrolytic carbon is better than that of the acetylene black carbon material, and the

preparation temperature is also lower. The higher the SP^2 hybridized carbon component in the polymer pyrolytic carbon, the more beneficial it is to improve the electrical performance of lithium iron phosphate. The selection of ferrocene and iron nitrate as catalysts is advantageous for increasing the content of the SP^2 hybridized carbon component in the polymer pyrolytic carbon and decreasing the H/C atomic ratio in the pyrolytic carbon, thereby greatly improving the electronic conductivity of the coated carbon material and the electrical performance of lithium iron phosphate ((1. N. Ravet, M. Gauthier, K. Zaghib, J.B. Goodenough, A.Mauger, F. Gendron, and C.M. Julien, *Chemistry of Materials* 19 (2007) 2595-2602; 2. Marca M.Doeff, James D.Wilcox, Robert Kostecki, and Grace Lau, *Journal of Power Sources* 163 (2006) 180-184; 3. James D. Wilcox, Marca M. Doeff, Marek Marcinek, and Robert Kostecki, *Journal of the Electrochemical Society*, vol. 154(5) (2007) A389-A395.). Adding a small amount of catalyst vanadium oxide to the raw materials can also facilitate the reduction of carbon-containing substances such as polymers on the surface of lithium iron phosphate, produce free carbon and increase the content of SP^2 hybridized carbon components in the coating carbon layer, while facilitating the generation of substances having high electron conductivity such as FeP, Fe_2P and Fe_3P, thereby greatly improving the electrical performance of lithium iron phosphate (US Patent No. 7282301B2).

The above technology lays a theoretical foundation for improving the electronic and ionic conductivity of lithium iron phosphate, but many other technical difficulties need to be broken through in the actual preparation of lithium iron phosphate. These technical difficulties mainly include: 1. Ultra-fine pulverization, uniform dispersion and mixing techniques of raw materials, which are prerequisites to ensure the preparation of pure phase lithium iron phosphate with excellent electrical performance. Compared with existing lithium-ion battery cathode materials such as $LiCoO_2$, $Li(Mn_xNi_yCo_{1-x-y})O_2$ ($0<x$, $y<1$) and intercrystalline $LiMn_2O_4$, the electronic/ionic conductivity of lithium iron phosphate is much lower, and it is necessary to reduce its primary particle size to 3.1 μ m or less in order to ensure good electrical performance (US Patent No. 814764B2). Therefore, the particle size of the raw materials used for the preparation of lithium iron phosphate must be sufficiently fine, which brings new difficulties to the techniques of ultra-fine pulverization, uniform dispersion and mixing of the raw materials. 2. Since the primary particles of lithium iron phosphate have a small particle size, the content of coating carbon on the surface cannot be too high, otherwise the tapped density of the material and the transport speed of lithium ions at the interface between the electrolyte and the lithium iron phosphate particles are

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significantly reduced. The surface carbon content cannot be too low, otherwise it would be difficult to achieve a significant improvement in the electronic conductivity of the lithium iron phosphate material. Furthermore, due to the mismatch between the structure of the coating carbon and the structure of the lithium iron phosphate, it is difficult to achieve uniform coating of the coating carbon having high electronic conductivity on the surface of the lithium iron phosphate, and to ensure sufficient bonding strength between the coating carbon layer and the surface of the lithium iron phosphate. If there is sufficient bonding strength between the coating carbon layer and the surface of the lithium iron phosphate, on the one hand, agglomeration of conductive carbon in the positive electrode sheet during charging and discharging of the battery can be effectively suppressed, which is one of the reasons for many battery electrical performance failures (Marie Kerlau,Marek Marcinek, and Robert Kostecki, "Diagnostic Evaluation of Detrimental Phenomena in ^{13}C-labeled Composite cathodes for Li-ion batteries", Abstract #14 in International Meeting on Lithium Battery 2006 (France)); and on the other hand, it is advantageous to avoid the destruction of the coating carbon layer on the surface of the lithium iron phosphate as much as possible when the material is subjected to the pulverizing and classifying step after being sintered at a high temperature. 3. The selection of the raw material may affect the sintering temperature of the material and the purity of the product phase, and also affect the easiness of industrial implementation. 4. The particle size and the distribution of the raw materials after pulverization are directly related to the reactivity between them, and therefore it is important to select a suitable sintering manner, sintering temperature and sintering time so as to obtain a product in which the particle size and the distribution thereof are suitable and the degree of crystal structure integrity tends to be uniform for improving the overall performance of lithium iron phosphate. 5) Since lithium iron phosphate has a small particle size and the surface is generally coated with a carbon material having a lower density, the tapped or compaction density of the product is low, which affects the manufacturing quality of the electrode sheet of the battery and thus affects the performance of the battery.

SUMMARY OF THE INVENTION

The objective of the present invention is to provide a boron-containing lithium iron phosphate/carbon composite material and a preparation method therefor, which mainly solves technical problems existing in the prior art that there are difficulties in ultra-fine pulverization, uniform dispersion and mixing of raw materials; the bonding strength between a coating carbon

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layer and the surface of lithium iron phosphate is not great enough; pulverization and classification processes may cause damage to the coating carbon layer on the surface of lithium iron phosphate; the tapped density of the product is low; growth speed of the particle size is fast due to the high sintering temperature and distribution is unevenly concentrated; the integrity of the crystal structure of lithium iron phosphate is difficult to make consistent; and the electrical performance of lithium iron phosphate and the quality consistency of the product are poor.

The above technical problems of the present invention are mainly solved by the following technical solutions:

A boron-containing lithium iron phosphate/carbon composite according to the present invention is characterized by having a chemical formula of: $Li_{1-x}M_xFe_{1-y}N_yP_{1-z}Si_zO_4 \cdot \xi B_2O_3/C$ or $Li_{1-x}MxFe_{1-y}N_yP_{1-z}Si_zO_4 \cdot \zeta LiBO_2/C$, wherein the metal element M doped at a lithium site in a bulk phase is at least one of Mg, Ca, Zn, Al, Cr, V, Ti, Zr and Nb, and $0 \leq x \leq 0.1$; the metallic element N doped at the iron site in the bulk phase is at least one of Li, Cu, Mg, Ca, Mn, Ni, Co, Zn, Al, Cr, V, Ti, Zr and Nb, and $0 \leq y \leq 0.1$; the silicon element is doped at a phosphorus site in the bulk phase, and $0 \leq z \leq 0.5$; $0.006 \leqq \xi \leqq 0.25$, and $0.01 \leqq \zeta \leqq 0.5$; B_2O_3 or $LiBO_2$ exists in an amorphous state on the surface of lithium iron phosphate and is mixed with a conductive carbon material, and the weight ratio of the carbon material to the boron-containing lithium iron phosphate/carbon composite material is 0.1 to 10%.

The lithium iron phosphate may be undoped or bulk-doped lithium iron phosphate, and the doping site may be at least one of a lithium site, an iron site, and a phosphorus site. The surface of the lithium iron phosphate material is coated with amorphous B_2O_3 or $LiBO_2$, and molar ratios ξ or ζ thereof to $Li_{1-x}M_xF_{1-y}N_yP_{1-z}Si_zO_4$ are $0.006 \leqq \xi \leqq 0.25$ or $0.01 \leqq \zeta \leqq 0.5$, respectively, preferably $0.03 \leqq \xi \leqq 0.15$ or $0.05 \leqq \zeta \leqq 0.3$. A conductive carbon material is mixed in the amorphous B_2O_3 or $LiBO_2$, and the weight ratio of the carbon material to the boron-containing lithium iron phosphate/carbon composite material is 0.1 to 10%, preferably 0.5 to 5%.

A method for preparing a boron-containing lithium iron phosphate/carbon composite material according to the present invention comprises:

a. adding a borate surfactant or/and flux to a ball mill tank loaded with a solvent, the borate surfactant accounting for 0.05 to 5% of the total mass of solid raw materials; stirring thoroughly and uniformly; and then separately adding an iron source compound, a lithium source

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compound, a phosphorus source compound and a carbon-coated carbon source at a stoichiometric ratio to perform primary ball milling and mixing; and

b. evaporating the solvent until dry, and sintering by heating the obtained solid powder under the protection of an inert gas; cooling to room temperature, and then taking out; and pulverizing and classifying to obtain the boron-containing lithium iron phosphate/carbon composite material, wherein the weight ratio of carbon-coated carbon to the boron-containing lithium iron phosphate/carbon composite material is 0.1 to 10%.

The solvent in step a is an organic solvent, water, or a mixed solvent of an organic solvent and water, preferably an organic solvent. The borate surfactant accounts for 0.05 to 5% of the total mass of solid raw materials, preferably 0.5 to 2.5%. Within the stated addition amount range, the borate surfactant can effectively prevent agglomeration between particles during liquid phase ball milling. Compared with no addition, the beneficial effects of adding the borate surfactant in the ball milling slurry include the following: 1. under the same ball milling conditions, the average particle size of the raw materials can become smaller by milling, the raw materials are dispersed and mixed more uniformly, and necessary conditions are created for preparing the lithium iron phosphate/carbon composite material with fine particle size and further improving the product performance and quality consistency; 2. when the raw materials are ball-milled to the same particle size, the solid content in the slurry can be increased, improving the ball-milling efficiency and saving energy; 3. since the average particle size of the raw materials can become smaller by milling under the same ball milling conditions, the dried powder having a smaller particle size and higher reactivity can be obtained after drying, so that the temperature for preparing the lithium iron phosphate/carbon composite can be lower, and the time can be shorter; and 3. the decomposition products of the borate surfactant under the protection of the high-temperature inert atmosphere are gases such as B_2O_3 and volatile alkane, and the remaining B_2O_3 can be used as a flux component, which is beneficial for lowering the preparation temperature of the lithium iron phosphate/carbon composite material and increasing the tapped density.

Preferably, the step b is replaced by step b′:

b′. evaporating the solvent until dry, and then heating the obtained solid powder under the protection of an inert gas for first sintering; cooling to room temperature and then taking out, and placing into the ball mill tank again; performing secondary ball milling without adding or with

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adding the borate surfactant or/and flux; evaporating the solvent until dry, and then heating the obtained solid powder under the protection of the inert gas for second sintering; and pulverizing and classifying to obtain the boron-containing lithium iron phosphate/carbon composite material, wherein the weight ratio of carbon-coated carbon to the boron-containing lithium iron phosphate/carbon composite material is 0.1 to 10%, preferably 0.5 to 5%.

Preferably, the borate surfactant is at least one of borate monoester, borate diester, borate triester, tetracoordinate spiroborate and derivatives thereof, and the addition amount thereof accounts for 0.05 to 5% of the total mass of solid raw materials, preferably 0.5 to 2.5%. The borate surfactant is more preferably a non-ionic sterically hindered polymeric borate surfactant.

The flux is at least one of a boron compound and an alkali metal fluoride; the boron compound is preferably B_2O_3, H_3BO_3, $LiBO_2$ or a boron-containing compound capable of forming B_2O_3, H_3BO_3, or $LiBO_2$ by decomposition at a high temperature; and the alkali metal fluoride is preferably lithium fluoride. The amount of the flux used depends on the particle size and specific surface area of the prepared boron-containing lithium iron phosphate/carbon composite material. The smaller the particle size, the higher the specific surface area, the higher the amount used. The boron compound flux is added in such an amount that a molar ratio ξ or ζ between a final decomposition or reaction product B_2O_3 or $LiBO_2$ obtained by the high-temperature treatment thereof and lithium iron phosphate is $0.006 \leqq \xi \leqq 0.25$ or $0.01 \leqq \zeta \leqq 0.5$, preferably $0.03 \leqq \xi \leqq 0.15$ or $0.05 \leqq \zeta \leqq 0.3$; and the alkali metal fluoride is added in such an amount that a molar ratio thereof to lithium iron phosphate is 0.015 to 0.5:1, preferably 0.07 to 0.3. Compared with adding no flux, the beneficial effects of adding the flux to the raw materials of the present invention include: 1. lowering the sintering temperature of the material to control the crystal growth rate, so that the boron-containing lithium iron phosphate carbon composite material having a fine particle size is prepared at a lower temperature; 2. reducing the porosity of the material, increasing the uniformity of heating of each part of the raw materials during high-temperature sintering, and effectively avoiding the generation of a heterogeneous phase; 3. increasing the tapped density and improving the processability of the positive electrode sheet; and 4. improving the bonding strength between the lithium iron phosphate and the coating carbon layer, avoiding or reducing the damage of the coating carbon layer on the surface of the lithium iron phosphate in the subsequent pulverization and classification step, and improving the electrical performance of the lithium iron phosphate.

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Preferably, when the iron source compound, the lithium source compound, the phosphorus source compound and the carbon-coated carbon source are added at the stoichiometric ratio in the step (a), a doping element compound is also added at the same time. The dopant element compound is a compound containing a metal element and a silicon element.

Preferably, the iron source compound is at least one of ferrous oxide, ferric oxide, ferric tetraoxide, ferrous oxalate, ferric oxalate or ferrous phosphate, and ferric phosphate; the lithium source compound is at least one of lithium carbonate, lithium hydroxide, lithium acetate, lithium phosphate and lithium dihydrogen phosphate; the phosphorus source compound is at least one of phosphoric acid, lithium phosphate, lithium dihydrogen phosphate, diammonium hydrogen phosphate and ammonium dihydrogen phosphate; and the carbon-coated carbon source is at least one of a polymer compound or a mixture of a polymer compound and a carbon nanotube, acetylene black, or a carbon black conductive additive.

Preferably, the inert gas in steps b and b ′ is at least one of nitrogen gas, argon gas, and ammonia gas, or at least one of mixed gases formed by nitrogen gas, argon gas and ammonia gas and hydrogen gas accounting for less than 15% by volume.

Preferably, the sintering temperature in step b is 550°C to 850°C, and the sintering time is 1 to 30 hours.

Preferably, the temperature of the first sintering in the step b ′ is 300°C to 550°C, the temperature of the second sintering is 550°C to 850°C, and both the first time and the second sintering time are 1 to 30 hours.

According to the present invention, the techniques for ultra-fine pulverization, uniform dispersion and mixing of raw materials are relatively simple and efficient; the bonding strength between the coating carbon layer and the surface of the lithium iron phosphate is higher, and the pulverization and classification processes cause no or little damage to the coating carbon layer on the surface of lithium iron phosphate; and the lithium iron phosphate carbon composite material has the features of small particle size, high tapped density, good overall performance, etc.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Hereinafter, the technical solutions of the present invention will be described in more detail by means of examples.

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Example 1: A boron-containing lithium iron phosphate/carbon composite material of this example has a molecular formula of:

$$LiFePO_4 \cdot 3.769\times10^{-2}B_2O_3/C$$

Steps of a preparation method therefor are:

a. adding 3.540 g of a non-ionic polymeric borate surfactant PBE (average relative molecular weight Mw=28400) to a ball mill tank loaded with 820 g of absolute ethanol, stirring thoroughly and uniformly, and then separately adding 36.945 g of 0.5 mole Li_2CO_3, 179.900 g of 1.0 mole $FeC_2O_4 \cdot 2H_2O$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, 19.500 g of glucose and 2.624 g of B_2O_3 for mixing; adding 5 mm of zirconia balls to the mixed solid powder, the mass ratio of the solid powder to the zirconia balls being 1:8, and stirring and ball-milling the mixture at a speed of 300 rpm for 7 hours;

b′. after evaporating the ethanol until dry, sintering by heating the solid powder produced in step a at 400°C under the protection of a mixed gas of high-purity nitrogen:hydrogen at a volume ratio of 92:8, wherein the heating process is as follows: raising the temperature from room temperature to 400°C for 3 hours, maintaining at 400°C for 4 hours and then cooling to room temperature, then placing the solid powder into 420 g of absolute ethanol, adding 5 mm zirconia balls again, and carrying out secondary ball milling at a speed of 300 rpm for 2 hours, wherein the mass ratio of the solid powder to the zirconia balls is 1:8; after evaporating the solvent until dry, sintering by heating at 620°C under the protection of high-purity nitrogen gas:hydrogen gas at a volume ratio of 92:8, wherein the heating process is as follows: raising the temperature from room temperature to 620°C for 4 hours, maintaining at 620°C for 5 hours and then cooling to room temperature within 2 hours, and after the temperature drops to room temperature, taking out, milling and passing through a 300-mesh sieve to obtain the boron-containing lithium iron phosphate/carbon composite material.

According to a stoichiometric ratio, it was calculated that the obtained boron-containing lithium iron phosphate carbon composite material contains 3.769×10^{-2} moles of B_2O_3, that is, $\xi=3.769\times10^{-2}$.

The carbon content of the boron-containing lithium iron phosphate/carbon composite material was 3.02% as measured by an HCS-140 model high frequency infrared carbon sulfur

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analyzer. The tapped density of the material was 1.22 g/cm ^{3} as measured by a PF-300B tapped density tester. The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.632 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 4.16 μm.

The obtained boron-containing lithium iron phosphate/carbon composite material was mixed with an N-methylpyrrolidone (NMP) solution of polyvinylidene fluoride (PVDF) and acetylene black to prepare a slurry. The slurry was uniformly coated on an Al foil current collector, dried, and rolled to prepare a positive electrode sheet having a thickness of about 100 μm. The mass ratio of lithium iron phosphate: conductive carbon: PVDF is 86:6:8, wherein the conductive carbon includes boron-containing lithium iron phosphate surface-coated carbon and added acetylene black. Then, a 20 mm diameter disc was taken out as a positive electrode of a button-type 2430 battery. A 1 mm thick metal lithium sheet was used as a negative electrode, Celgard2400 was used as a separator, and an electrolyte solution was 1M $LiPF_6$+EC/DMC (at a volume ratio 1:1). After they are assembled into a half battery, the charge/discharge capacity was almost stabilized after being charged and discharged 10 times at a constant current of 0.2 C (30 mA/g) under 2 to 4.2 V (relative to metallic lithium). The discharge capacity at the 10th cycle was used as the discharge capacity at 0.2 C. When the discharge capacity was measured at a rate of 0.2 C or more, the battery was charged to 4.2 V at 0.2 C and then the discharge capacity was measured at that rate. All the specific discharge capacity data did not take into account the mass of the coating carbon and boride flux on the surface of lithium iron phosphate.

Example 2: A boron-containing lithium iron phosphate/carbon composite material of this example has a molecular formula of:

$$LiFePO_4 \cdot 0.070LiBO_2/C$$

Steps of a preparation method therefor are:

a. adding 3.583 g of a non-ionic polymeric borate surfactant PBE (average relative molecular weight Mw=28400) to a ball mill tank loaded with 820 g of absolute ethanol, stirring thoroughly and uniformly, and then separately adding 39.531 g of 0.535 mole Li_2CO_3, 179.900g of 1.0 mole $FeC_2O_4 \cdot 2H_2O$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, 19.500 g of glucose and 4.327 g of 0.070 mole H_3BO_3 for mixing; and

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the remaining steps are the same as in Example 1.

According to a stoichiometric ratio, it was calculated that the obtained boron-containing lithium iron phosphate carbon composite material contains 0.070 moles of $LiBO_2$, that is, ξ=0.070. The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.638 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 4.21 μm. The carbon content of the boron-containing lithium iron phosphate/carbon composite material was 2.97% as measured by an HCS-140 model high frequency infrared carbon sulfur analyzer. The tapped density of the material was 1.25 g/cm^3 as measured by a PF-300B tapped density tester.

Example 3: A boron-containing lithium iron phosphate/carbon composite material of this example has a molecular formula of:

$$LiFePO_4 \cdot 0.25B_2O_3/C$$

Steps of a preparation method therefor are:

a. adding 3.688 g of a non-ionic polymeric borate surfactant PBE (average relative molecular weight Mw=28400) to a ball mill tank loaded with 820 g of absolute ethanol, stirring thoroughly and uniformly, and then separately adding 36.945 g of 0.5 mole Li_2CO_3, 179.900 g of 1.0 mole $FeC_2O_4 \cdot 2H_2O$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, 19.500 g of glucose and 17.405g of B_2O_3 for mixing; and

the remaining steps are the same as in Example 1.

According to a stoichiometric ratio, it was calculated that the obtained boron-containing lithium iron phosphate carbon composite material contains 0.25 moles of B_2O_3, that is, ξ=0.25.

The carbon content of the boron-containing lithium iron phosphate/carbon composite material was 2.92% as measured by an HCS-140 model high frequency infrared carbon sulfur analyzer. The tapped density of the material was 1.47 g/cm^3 as measured by a PF-300B tapped density tester. The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.637 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 4.69 μm.

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Example 4: A boron-containing lithium iron phosphate/carbon composite material of this example has a molecular formula of:

$$LiFePO_4 \cdot 0.5LiBO_2/C$$

Steps of a preparation method therefor are:

a. adding 1.799 g of a non-ionic polymeric borate surfactant PBE (average relative molecular weight Mw=28400) to a ball mill tank loaded with 933 g of absolute ethanol, stirring thoroughly and uniformly, and then separately adding 55.418 g of 0.75 mole Li_2CO_3, 179.900g of 1.0 mole $FeC_2O_4 \cdot 2H_2O$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, 22.700 g of glucose and 30.905 g of 0.5 mole $H_3BO_3$3 for mixing; and

the remaining steps are the same as in Example 1.

According to a stoichiometric ratio, it was calculated that the obtained boron-containing lithium iron phosphate carbon composite material contains 0.5 moles of $LiBO_2$, that is, ξ=0.5. The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.631 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 4.62 μm. The carbon content of the boron-containing lithium iron phosphate/carbon composite material was 3.25% as measured by an HCS-140 model high frequency infrared carbon sulfur analyzer. The tapped density of the material was 1.41 g/cm^3 as measured by a PF-300B tapped density tester.

Example 5: A boron-containing lithium iron phosphate/carbon composite material of this example has a molecular formula of:

$$LiFePO_4 \cdot 3.769\times10^{-2}B_2O_3/C$$

Steps of a preparation method therefor are:

a. adding 1.792 g of a non-ionic polymeric borate surfactant PBE (average relative molecular weight Mw=28400) to a ball mill tank loaded with 933 g of absolute ethanol, stirring thoroughly and uniformly, and then separately adding 36.945 g of 0.5 mole Li_2CO_3, 179.900 g of 1.0 mole $FeC_2O_4 \cdot 2H_2O$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, 65.965 g of glucose and 2.624 g of B_2O_3 for mixing; and

the remaining steps are the same as in Example 1.

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According to a stoichiometric ratio, it was calculated that the obtained boron-containing lithium iron phosphate carbon composite material contains 3.769×10^{-2} moles of B_2O_3, that is, $\xi=3.769\times10^{-2}$.

The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.641 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 3.61 μm. The carbon content of the boron-containing lithium iron phosphate/carbon composite material was 9.96% as measured by an HCS-140 model high frequency infrared carbon sulfur analyzer. The tapped density of the material was 0.90 g/cm^3 as measured by a PF-300B tapped density tester.

Example 6: A boron-containing lithium iron phosphate/carbon composite material of this example has a molecular formula of:

$$LiFePO_4\cdot0.006B_2O_3/C$$

Steps of a preparation method therefor are:

a. adding 3.496 g of a non-ionic polymeric borate surfactant PBE (average relative molecular weight Mw=28400) to a ball mill tank loaded with 820 g of absolute ethanol, stirring thoroughly and uniformly, and then separately adding 29.556 g of 0.4 mole Li_2CO_3, 5.188 g of 0.2 mole LiF, 179.900g of 1.0 mole $FeC_2O_4\cdot2H_2$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, 19.500 g of glucose and 0.418g of mole B_2O_3 for mixing; and

the remaining steps are the same as in Example 1.

According to a stoichiometric ratio, it was calculated that the obtained boron-containing lithium iron phosphate carbon composite material contains 0.006 moles of B_2O_3, that is, $\xi=0.006$. The carbon content of the boron-containing lithium iron phosphate/carbon composite material was 3.10% as measured by an HCS-140 model high frequency infrared carbon sulfur analyzer. The tapped density of the material was 1.31 g/cm^3 as measured by a PF-300B tapped density tester. The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.629 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 3.75 μm.

Example 7: A boron-containing lithium iron phosphate/carbon composite material of this example has a molecular formula of:

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$$LiFePO_4 \cdot 0.006B_2O_3/C$$

Steps of a preparation method therefor are:

a. adding 3.463 g of a non-ionic polymeric borate surfactant PBE (average relative molecular weight Mw=28400) to a ball mill tank loaded with 820 g of absolute ethanol, stirring thoroughly and uniformly, and then separately adding 18.473 g of 0.25 mole Li_2CO_3, 12.971 g of 0.5 mole LiF, 179.900g of 1.0 mole $FeC_2O_4 \cdot 2H_2$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, 19.500 g of glucose and 0.418 g of mole B_2O_3 for mixing; and

the remaining steps are the same as in Example 1.

According to a stoichiometric ratio, it was calculated that the obtained boron-containing lithium iron phosphate carbon composite material contains 0.006 moles of B_2O_3, that is, ξ=0.006. The carbon content of the boron-containing lithium iron phosphate/carbon composite material was 3.06% as measured by an HCS-140 model high frequency infrared carbon sulfur analyzer. The tapped density of the material was 1.34 g/cm^3 as measured by a PF-300B tapped density tester. The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.620 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 3.81 μm.

Example 8: A boron-containing lithium iron phosphate/carbon composite material of this example has a molecular formula of:

$$Li_{0.98}Zr_{0.005}FePO_4 \cdot 3.016\times10^{-2}B_2O_3/C$$

Steps of a preparation method therefor are:

a. adding 3.543 g of a non-ionic polymeric borate surfactant PBE (average relative molecular weight Mw=28400) to a ball mill tank loaded with 818 g of absolute ethanol, stirring thoroughly and uniformly, and then separately adding 36.206 g of 0.49 mole Li_2CO_3, 179.900 g of 1.0 mole $FeC_2O_4 \cdot 2H_2O$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, 19.500 g of glucose, 1.611 g of 0.005 mole $ZrOCl_2 \cdot 8H_2O$, and 2.100 g of B_2O_3 for mixing; adding 5 mm of zirconia balls to the mixed solid powder, the mass ratio of the solid powder to the zirconia balls being 1:8, and stirring and ball-milling the mixture at a speed of 300 rpm for 7 hours;

b′. after evaporating the ethanol until dry, sintering by heating the solid powder produced in step a at 400°C under the protection of a mixed gas of high-purity nitrogen:hydrogen

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at a volume ratio of 92:8, wherein the heating process is as follows: raising the temperature from room temperature to 400°C for 3 hours, maintaining at 400°C for 4 hours and then cooling to room temperature, then placing the solid powder into 420 g of absolute ethanol, adding 5 mm zirconia balls again, and carrying out secondary ball milling at a speed of 300 rpm for 2 hours, wherein the mass ratio of the solid powder to the zirconia balls is 1:8; after evaporating the solvent until dry, sintering by heating at 620°C under the protection of high-purity nitrogen gas:hydrogen gas at a volume ratio of 92:8, wherein the heating process is as follows: raising the temperature from room temperature to 620°C for 4 hours, maintaining at 620°C for 5 hours and then cooling to room temperature within 2 hours, and after the temperature drops to room temperature, taking out, milling and passing through a 300-mesh sieve to obtain the boron-containing $Li_{0.98}Zr_{0.005}FePO_4$/carbon composite material; and

the remaining steps are the same as in Example 1.

According to a stoichiometric ratio, it was calculated that the obtained boron-containing lithium iron phosphate carbon composite material contains 3.016×10^{-2} moles of B_2O_3, that is, $\xi=3.016\times10^{-2}$. The carbon content of the boron-containing lithium iron phosphate/carbon composite material was 2.99% as measured by an HCS-140 model high frequency infrared carbon sulfur analyzer. The tapped density of the material was 1.20 g/cm^3 as measured by a PF-300B tapped density tester. The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.631 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 3.90 μm.

Example 9: A boron-containing lithium iron phosphate/carbon composite material of this example has a molecular formula of:

$$Li_{0.98}Zr_{0.005}FePO_4\cdot0.070LiBO_2/C$$

Steps of a preparation method therefor are:

a. adding 3.557 g of a non-ionic polymeric borate surfactant PBE (average relative molecular weight Mw=28400) to a ball mill tank loaded with 818 g of absolute ethanol, stirring thoroughly and uniformly, and then separately adding 36.206 g of 0.49 mole Li_2CO_3, 179.900 g

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of 1.0 mole $FeC_2O_4 \cdot 2H_2O$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, 19.500 g of glucose, 1.611 g of 0.005 mole $ZrOCl_2 \cdot 8H_2O$, and 3.483 g of $LiBO_2$ for mixing; and

the remaining steps are the same as in Example 8.

According to a stoichiometric ratio, it was calculated that the obtained boron-containing lithium iron phosphate carbon composite material contains 0.070 moles of $LiBO_2$, that is, ξ=0.070. The carbon content of the boron-containing lithium iron phosphate/carbon composite material was 2.95% as measured by an HCS-140 model high frequency infrared carbon sulfur analyzer. The tapped density of the material was 1.25 g/cm^3 as measured by a PF-300B tapped density tester. The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.623 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 3.94 μm.

Example 10: A boron-containing lithium iron phosphate/carbon composite material of this example has a molecular formula of:

$$Li_{0.98}Zr_{0.005}FePO_4 \cdot 0.006B_2O_3/C$$

Steps of a preparation method therefor are:

a. adding 3.504 g of a non-ionic polymeric borate surfactant PBE (average relative molecular weight Mw=28400) to a ball mill tank loaded with 818 g of absolute ethanol, stirring thoroughly and uniformly, and then separately adding 28.817 g of 0.39 mole Li_2CO_3, 5.188 g of 0.2 mole LiF, 179.900 g of 1.0 mole $FeC_2O_4 \cdot 2H_2O$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, 19.500 g of glucose, 1.611 g of 0.005 mole $ZrOCl_2 \cdot 8H_2$, and 0.418g of B_2O_3 for mixing; and

the remaining steps that are the same as in Example 8.

According to a stoichiometric ratio, it was calculated that the obtained boron-containing lithium iron phosphate carbon composite material contains 0.006 moles of B_2O_3, that is, ξ=0.006. The carbon content of the boron-containing lithium iron phosphate/carbon composite material was 2.92% as measured by an HCS-140 model high frequency infrared carbon sulfur analyzer. The tapped density of the material was 1.27 g/cm^3 as measured by a PF-300B tapped density tester. The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.639 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 3.68 μm.

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Example 11: A boron-containing lithium iron phosphate/carbon composite material of this example has a molecular formula of:

$$Li_{0.99}Fe_{0.995}Zr_{0.005}PO_4 \cdot 4.453\times10^{-2}B_2O_3/C$$

Steps of a preparation method therefor are:

a. adding 3.548 g of a non-ionic polymeric borate surfactant PBE (average relative molecular weight Mw=28400) to a ball mill tank loaded with 818 g of absolute ethanol, stirring thoroughly and uniformly, and then separately adding 36.576 g of 0.495 mole Li_2CO_3, 179.900 g of 0.995 mole $FeC_2O_4 \cdot 2H_2O$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, 19.500 g of glucose, 1.611 g of 0.005 mole $ZrOCl_2 \cdot 8H_2O$, and 3.100 g of B_2O_3 for mixing; and

the remaining steps are the same as in Example 8.

According to a stoichiometric ratio, it was calculated that the obtained boron-containing lithium iron phosphate carbon composite material contains 4.453×10^{-2} moles of B_2O_3, that is, $\xi=4.453\times10^{-2}$. The carbon content of the boron-containing lithium iron phosphate/carbon composite material was 3.11% as measured by an HCS-140 model high frequency infrared carbon sulfur analyzer. The tapped density of the material was 1.20 g/cm^3 as measured by a PF-300B tapped density tester. The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.619 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 3.83 μm.

Example 12: A boron-containing lithium iron phosphate/carbon composite material of this example has a molecular formula of:

$$Li_{0.99}Fe_{0.995}Zr_{0.005}PO_4 \cdot 0.070LiBO_2/C$$

Steps of a preparation method therefor are:

a. adding 3.552 g of a non-ionic polymeric borate surfactant PBE (average relative molecular weight Mw=28400) to a ball mill tank loaded with 818 g of absolute ethanol, stirring thoroughly and uniformly, and then separately adding 36.576 g of 0.495 mole Li_2CO_3, 179.900 g of 0.995 mole $FeC_2O_4 \cdot 2H_2O$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, 19.500 g of glucose, 1.611 g of 0.005 mole $ZrOCl_2 \cdot 8H_2O$, and 3.483 g of $LiBO_2$ for mixing; and

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the remaining steps are the same as in Example 8.

According to a stoichiometric ratio, it was calculated that the obtained boron-containing lithium iron phosphate carbon composite material contains 0.07 moles of $LiBO_2$, that is, ξ=0.070. The carbon content of the boron-containing lithium iron phosphate/carbon composite material was 3.00% as measured by an HCS-140 model high frequency infrared carbon sulfur analyzer. The tapped density of the material was 1.23 g/cm^3 as measured by a PF-300B tapped density tester. The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.617 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 3.90 μm.

Example 13: A boron-containing lithium iron phosphate/carbon composite material of this example has a molecular formula of:

$$Li_{0.99}Fe_{0.995}Zr_{0.005}PO_4 \cdot 0.006B_2O_3/C$$

Steps of a preparation method therefor are:

a. adding 3.499 g of a non-ionic polymeric borate surfactant PBE (average relative molecular weight Mw=28400) to a ball mill tank loaded with 818 g of absolute ethanol, stirring thoroughly and uniformly, and then separately adding 29.187 g of 0.395 mole Li_2CO_3, 5.188 g of 0.2 mole LiF, 179.900 g of 0.995 mole $FeC_2O_4 \cdot 2H_2O$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, 19.500 g of glucose, 1.611 g of 0.005 mole $ZrOCl_2 \cdot 8H_2O$, and 0.418 g of B_2O_3 for mixing; and

the remaining steps are the same as in Example 8.

According to a stoichiometric ratio, it was calculated that the obtained boron-containing lithium iron phosphate carbon composite material contains 0.006 moles of B_2O_3, that is, ξ=0.006. The carbon content of the boron-containing lithium iron phosphate/carbon composite material was 2.91% as measured by an HCS-140 model high frequency infrared carbon sulfur analyzer. The tapped density of the material was 1.24 g/cm^3 as measured by a PF-300B tapped density tester. The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.630 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 3.62 μm.

Comparative Example 1' Preparation of boron-free lithium iron phosphate/carbon composite material that is beyond the present invention

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a. separately adding 36.945 g of 0.5 mole Li_2CO_3, 179.900 g of 1.0 mole $FeC_2O_4 \cdot 2H_2O$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, and 19.500 g of glucose to a ball mill tank loaded with 820 g of absolute ethanol for mixing;

b. adding 5 mm of zirconia balls to the mixed solid powder, the mass ratio of the solid powder to the zirconia balls being 1:8, and stirring and ball-milling the mixture at a speed of 300 rpm for 7 hours;

c. after evaporating the ethanol until dry, sintering by heating the solid powder produced in step b at 400°C under the protection of a mixed gas of high-purity nitrogen:hydrogen at a volume ratio of 92:8, wherein the heating process is as follows: raising the temperature from room temperature to 400°C for 3 hours, maintaining at 400°C for 4 hours and then cooling to room temperature, then placing the solid powder into 420 g of absolute ethanol, adding 5 mm zirconia balls again, and carrying out secondary ball milling at a speed of 300 rpm for 2 hours, wherein the mass ratio of the solid powder to the zirconia balls is 1:8;

d. after evaporating the solvent until dry, sintering by heating at 700°C under the protection of high-purity nitrogen gas:hydrogen gas at a volume ratio of 92:8, wherein the heating process is as follows: raising the temperature from room temperature to 700°C for 4 hours, maintaining at 700°C for 5 hours and then cooling to room temperature within 2 hours, and after the temperature drops to room temperature, taking out, milling and passing through a 300-mesh sieve to obtain the boron-containing lithium iron phosphate/carbon composite material.

The carbon content of the boron-containing lithium iron phosphate/carbon composite material was 2.96% as measured by an HCS-140 model high frequency infrared carbon sulfur analyzer. The tapped density of the material was 1.08 g/cm^3 as measured by a PF-300B tapped density tester. The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.865 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 4.66 μm.

Comparative Example 2' Preparation of boron-free lithium iron phosphate/carbon composite material that is beyond the present invention

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a. separately adding 36.945 g of 0.5 mole Li_2CO_3, 179.900 g of 1.0 mole $FeC_2O_4 \cdot 2H_2O$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, and 19.500 g of glucose to a ball mill tank loaded with 820 g of absolute ethanol for mixing; and

the remaining steps are the same as in Example 1.

The carbon content of the boron-free lithium iron phosphate/carbon composite material was 3.10% as measured by an HCS-140 model high frequency infrared carbon sulfur analyzer. The tapped density of the material was 1.02 g/cm^3 as measured by a PF-300B tapped density tester. The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.879 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 4.41 μm.

Comparative Example 3' Preparation of boron-free lithium iron phosphate/carbon composite material that is beyond the present invention

a. separately adding 36.945 g of 0.5 mole Li_2CO_3, 179.900 g of 1.0 mole $FeC_2O_4 \cdot 2H_2O$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, and 65.965 g of glucose to a ball mill tank loaded with 820 g of absolute ethanol for mixing; and

he remaining steps are the same as in Example 1.

The carbon content of the boron-free lithium iron phosphate/carbon composite material was 9.98% as measured by an HCS-140 model high frequency infrared carbon sulfur analyzer. The tapped density of the material was 0.79 g/cm^3 as measured by a PF-300B tapped density tester. The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.871 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 4.35 μm. Comparative Example 4' Preparation of boron-free $Li_{0.98}Zr_{0.005}FePO_4$/carbon composite material that is beyond the present invention

a. separately adding 36.206 g of 0.49 mole Li_2CO_3, 179.900 g of 1.0 mole $FeC_2O_4 \cdot 2H_2O$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, 19.500 g of glucose and 1.611 g of 0.005 mole $ZrOCl_2 \cdot 8H_2O$ to a ball mill tank loaded with 818 g of absolute ethanol for mixing; and

the remaining steps are the same as in Example 1.

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The carbon content of the boron-free lithium iron phosphate/carbon composite material was 3.14% as measured by an HCS-140 model high frequency infrared carbon sulfur analyzer. The tapped density of the material was 1.00 g/cm^3 as measured by a PF-300B tapped density tester. The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.859 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 4.39 μm.

Comparative Example 5' Preparation of boron-free $Li_{0.99}Fe_{0.995}Zr_{0.005}PO_4$/carbon composite material that is beyond the present invention

a. separately adding 36.576 g of 0.495 mole Li_2CO_3, 179.900 g of 0.995 mole $FeC_2O_4 \cdot 2H_2O$, 115.000 g of 1.0 mole $NH_4H_2PO_4$, 19.500 g of glucose and 1.611 g of 0.005 mole $ZrOCl_2 \cdot 8H_2O$ to a ball mill tank loaded with 818 g of absolute ethanol for mixing; and

the remaining steps are the same as in Example 1.

The carbon content of the boron-free lithium iron phosphate/carbon composite material was 3.16% as measured by an HCS-140 model high frequency infrared carbon sulfur analyzer. The tapped density of the material was 0.98 g/cm^3 as measured by a PF-300B tapped density tester. The average particle size of solid particles in the slurry after 7 hours of ball milling in step b was 0.863 μm as measured by a laser particle size analyzer. The average particle size of the boron-containing lithium iron phosphate carbon composite material obtained in step d was 4.33 μm.

Table 1 shows the average particle sizes of the raw materials after 7 hours of ball milling and the average particle sizes of the composite material products obtained by high-temperature sintering in various examples and comparative examples. As can be seen, when the solid content of the slurry is substantially maintained at about 30% and the added borate surfactant accounts for 1.00% of the mass of the solid raw materials, the average particle size of the particles after ball milling did not change very much, and was between 0.61 μm and 0.65 μm, with an average of 0.630 μm. In the comparative examples, no borate surfactant was added, and the average particle size of the particles after ball milling was also relatively uniform, but the average particle size increased significantly compared with that when the surfactant was added, reaching 0.867 μm, with an increase of about 37.7%, indicating that the addition of the borate surfactant significantly improved the efficiency of liquid phase ball milling. Comparing the examples of the present invention with the comparative examples that are beyond the present invention, after the borate

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surfactant and the flux were added, the average particle sizes of the products prepared at the same sintering temperature and time were also finer than those without the addition.

Table 1 Effect of borate surfactant on material particle size

Example	Slurry solid content (wt%)	Ball milling time (h)	Borate weight percentage of solid raw materials (wt%)	Average particle size after ball milling for 7 hours (μm)	Average particle size of composite material (μm)
1	30.6	7	1.00	0.632	4.16
2	30.31	7	1.00	0.638	4.21
3	30.92	7	1.00	0.637	4.69
4	30.30	7	1.00	0.631	4.62
5	29.99	7	1.00	0.641	3.61
6	29.80	7	1.00	0.629	3.75
7	29.60	7	1.00	0.620	3.81
8	30.13	7	1.00	0.631	3.90
9	30.21	7	1.00	0.623	3.94
10	29.90	7	1.00	0.639	3.68
11	30.16	7	1.00	0.619	3.83
12	30.18	7	1.00	0.617	3.90
13	29.87	7	1.00	0.630	3.62
1'	0	7	0	0.865	5.76
2'	0	7	0	0.879	5.15
3'	0	7	0	0.871	4.72
4'	0	7	0	0.859	5.39
5'	0	7	0	0.863	5.33

Table 2 shows the preparation conditions, tapped density, and average particle sizes of the boron-containing lithium iron phosphate/carbon composite materials in various examples of the present invention, and for comparison, the corresponding conditions in various comparative examples that are beyond the present invention are also shown. It can be seen from Comparative Examples 1 to 7 and Comparative Examples 1’ to 3’: 1) For the material in which the coating

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carbon accounts for about 3% of the composite material, even though the preparation temperature is as low as 80°C, the tapped density of the composite material of the present invention is increased by at least 11.11% and at most about 36.11%, and at the same temperature, the tapped density is increased by at least 17.64%. For composite materials with the same carbon content of about 10% (Example 5 and Comparative Example 3'), the tapped density of the composite material of the present invention is increased by about 13.92%. 2) When the preparation temperature, carbon content and flux content are substantially the same, the average particle size of the composite material of the present invention is generally smaller by 1 μm or more. For lithium iron phosphate doped at lithium or iron sites ($Li_{0.98}Zr_{0.005}FePO_4$ and $Li_{0.99}Fe_{0.995}Zr_{0.005}PO_4$), the changing trends of tapped density and average particle size are similar to those without doping. Therefore, the boron-containing lithium iron phosphate carbon composite material prepared by the present invention has the characteristics of high tapped density and small particle size. This shows that the addition of sintering agents is beneficial to the preparation of fine and dense lithium iron phosphate/carbon composite material particles at lower temperatures.

Table 2 Effect of preparation temperature and sintering agent on tapped density of lithium iron phosphate/carbon composite material

Example	Molecular formula of lithium iron phosphate	Sintering temperature (°C)	Carbon weight percentage of composite material (%)	Boron compound flux type and molar ratio thereof to lithium iron phosphate	Molar ratio of lithium fluoride to lithium iron phosphate	Tapped density (g/cm^3)	Average particle size of composite material (μm)
1	$LiFePO_4$	620°C	3.02	B_2O_3,ξ=3.769*10^{-2}	0	1.22	4.16
2	$LiFePO_4$	620°C	2.97	H_3BO_3,ζ=0.07	0	1.25	4.21
3	$LiFePO_4$	620°C	2.92	B_2O_3,ξ=0.25	0	1.47	4.69
4	$LiFePO_4$	620°C	3.25	H_3BO_3,ζ=0.5	0	1.41	4.62
5	$LiFePO_4$	620°C	9.96	B_2O_3,ξ=3.769*10^{-2}	0	0.90	3.61
6	$LiFePO_4$	620°C	3.10	B_2O_3,ξ=0.006	0.20	1.31	3.75
7	$LiFePO_4$	620°C	3.06	B_2O_3,ξ=0.006	0.50	1.34	3.81
8	$Li_{0.98}Zr_{0.005}FePO_4$	620°C	2.99	B_2O_3,ξ=3.016*10^{-2}	0	1.20	3.90
9	$Li_{0.98}Zr_{0.005}FePO_4$	620°C	2.95	$LiBO_2$,ζ=0.07	0	1.25	3.94
10	$Li_{0.98}Zr_{0.005}FePO_4$	620°C	2.92	B_2O_3,ξ=0.006	0.20	1.27	3.68
11	$Li_{0.99}Fe_{0.995}Zr_{0.005}PO_4$	620°C	3.11	B_2O_3,ξ=4.453*10^{-2}	0	1.20	3.83

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12	$Li_{0.99}Fe_{0.995}Zr_{0.005}PO_4$	620°C	3.00	$LiBO_2$,ζ=0.07	0	1.23	3.90
13	$Li_{0.99}Fe_{0.995}Zr_{0.005}PO_4$	620°C	2.91	B_2O_3,ξ=0.006	0.20	1.24	3.62
1'	$LiFePO_4$	700°C	2.96	0	0	1.08	5.76
2'	$LiFePO_4$	620°C	3.10	0	0	1.02	5.15
3'	$LiFePO_4$	620°C	10.00	0	0	0.79	4.72
4'	$Li_{0.98}Zr_{0.005}FePO_4$	620°C	3.14	0	0	1.00	5.39
5'	$Li_{0.99}Fe_{0.995}Zr_{0.005}PO_4$	620°C	3.16	0	0	0.98	5.33

The boron-containing lithium iron phosphate/carbon composite materials prepared in various examples and comparative examples was combined with a lithium metal sheet to form 2430 button-type batteries, and the results of rate charging and discharging are shown in Table 3. As can be seen, for undoped lithium iron phosphate, and lithium iron phosphate doped at lithium or iron sites, when the coating carbon content is equivalent, the discharge capacity of the composite material of the present invention at different rates is generally higher than that of the composite material that is beyond the present invention. One the one hand, this is because the average particle size of the composite material particles is small, which accelerates the diffusion rate of lithium ions therein. On the other hand, this is because the bonding strength between the carbon material and the surface of lithium iron phosphate is increased due to the “adhesive” effect of the flux, thereby increasing the electronic conductivity of the composite material. Therefore, the composite material of the present invention has advantages such as low preparation temperature, small average particle size, high tapped density, and good rate charge and discharge characteristics.

Table 3 Discharge capacity of button-type 2430 half-battery at different charge and discharge rates

Example	C_d/mAh/g (0.2 C)	C_d/mAh/g (1.0 C)	C_d/mAh/g (3.0 C)	C_d/mAh/g (5.0 C)	C_d/mAh/g (8.0 C)
1	160	135	119	102	98
2	149	132	112	100	94
3	145	129	108	96	89
4	142	124	102	93	85
5	158	149	138	127	120
6	152	139	123	118	109
7	149	138	121	115	105

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8	150	133	118	101	98
9	147	133	115	96	90
10	152	141	125	107	102
11	154	143	133	120	113
12	157	145	130	119	110
13	157	146	136	124	117
1'	155	114	95	86	77
2 ′	150	119	100	91	80
3 ′	153	134	113	105	97
4 ′	145	126	105	92	81
5 ′	151	129	109	96	84

Questel

TRANSLATOR'S CERTIFICATE OF TRANSLATION

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