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METHOD FOR DESIGNING HIGH-CAPACITY ELECTRODE MATERIAL BY PARTICLE SURFACE RECONSTRUCTION.

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The invention provides a method for designing high-capacity electrode material by particle surface reconstruction. The invention provides a simple and accurate strategy for surface reconstruction and modification of high-capacity anode materials, which adopts easily-obtained metal soluble salts to accurately replace metal atoms on the surface of common metal oxyacid salts (oxalate, carbonate, hydroxide) lithium ion battery anode material particles at room temperature, so as to realize external reconstruction interface modification of single or multi-component crystal structures with inconsistent looseness. This method can effectively retain the original micro-nano structure of lithium-ion battery materials, and has strong adaptability to raw materials. It also makes use of the high catalytic activity of newly introduced metal atoms, material defects and the influence of atomic size on the looseness of crystal surface to realize interface reconstruction and modification of common high-capacity anode materials, which can effectively improve the electrochemical performance of materials.

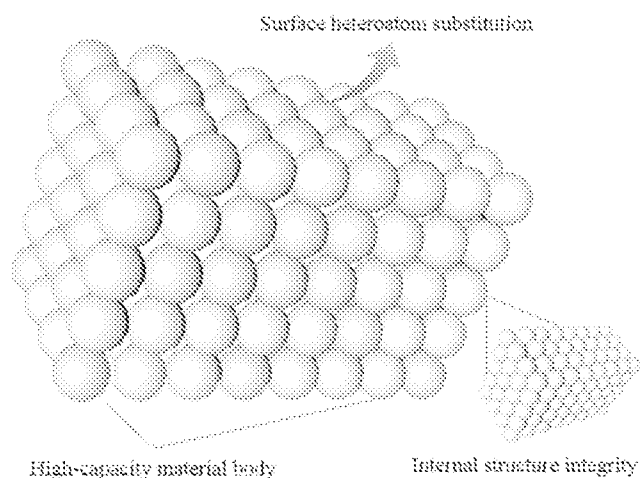


FIG. 1

METHOD FOR DESIGNING HIGH-CAPACITY ELECTRODE MATERIAL BY PARTICLE SURFACE RECONSTRUCTION

TECHNICAL FIELD

The invention relates to a method for designing a high-capacity electrode material by particle surface reconstruction, and belongs to the technical field of anode materials of lithium-ion batteries.

BACKGROUND

Since Sony Corporation of Japan introduced the graphite anode for commercial lithium-ion batteries, lithium-ion batteries with graphite anode have been widely used in watches, mobile phones, notebooks and electric vehicles. However, with the upgrading of electronic equipment, the capacity of traditional lithium-ion battery is difficult to meet the increasingly high energy density requirements of electronic equipment. Therefore, developing lithium-ion batteries with high energy density will be an important direction for the development of lithium-ion batteries.

The design and manufacture of high-energy lithium-ion batteries are inseparable from the selection of electrode materials. At present, the anode materials of high energy density lithium-ion batteries mainly include ultra-high-capacity alloy anodes such as Li, Sn, Ge, Si and P, and metal oxides, sulfides, fluorides and metal oxyacids. Among them, compared with other high-capacity negative electrodes, metal oxyacid salts show excellent energy storage potential because of their short preparation process and energy-saving advantages. Tirado's research group first reported and revealed the application prospect of oxalate metalates in lithium-ion batteries. Subsequently, the research groups at home and abroad studied the lithium storage properties of metal oxalate metalates respectively. They found that although the metal oxalate metalate showed high capacity

and stable cycling performance during lithium storage, it faced low and poor lithium-ion conductivity in the first cycle of coulombic efficiency in the early stage of energy storage. In order to overcome these shortcomings, the researchers put forward some measures, such as morphology control, transition metal ion doping and carbon coating on the particle surface. The appearance of these measures greatly improved the electrochemical properties of metal oxyacid salts, but the materials still showed unsatisfactory electrochemical properties under these modification measures.

SUMMARY

The purpose of the invention is to provide a high-capacity metal oxalate metalate anode material for particle surface reconstruction design. The invention is realized by the following technical scheme:

S1, dispersing a metal oxysalt high-capacity negative electrode material in a mixed solution of an organic solvent and deionized water to obtain a uniformly dispersed mixed solution, wherein the mass-volume ratio of the metal oxysalt to the mixed solution is 0.1-1 g:50-200 ml;

S2, adding soluble metal salt into the mixed solution obtained in S1, reacting at 0-200°C for 5-72 h, filtering, washing and drying to obtain the surface reconstructed material containing the crystal water;

S3, sintering the surface reconstructed material containing the crystal water obtained in S3 at 200-350°C for 4-10 h under vacuum or inert atmosphere to obtain the surface reconstructed high-capacity lithium-ion battery anode material.

The organic solvent in S1 comprises one or more of absolute ethanol, ethylene glycol, CTAB, NMP, DMA, DMSO and DMF.

The mixed solution in S1 further comprises one or more of PDDA, Pss, sulfuric acid and hydrochloric acid.

The soluble metal salts in S2 include one or more of nitrates, sulfates and acetates of transition metal.

The molar ratio of soluble metal salt to metal oxyacid salt in S2 is 0.01-1:1-0.01.

Compared with the prior art, the invention has the beneficial effects that:

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Precise surface reconstruction of high-capacity metal oxysalt anode material can be achieved through a simple technological process. This method not only highlights the advantages of existing modification methods, but also introduces metal heteroatoms with different degrees of looseness and high conductivity and catalytic activity to reconstruct the surface of metal oxysalt anode materials. The in-situ reconstructed interface contains different atomic components from the original body, which can give full play to the performance of the original high-capacity anode material and make full use of the reconstructed interface metal heteroatoms to further improve the electrochemical performance of the material.

BRIEF DESCRIPTION OF THE FIGURES

Fig. 1 is a schematic diagram of material surface reconstruction related to the present invention;

Fig. 2 shows the scanning electron microscope pattern and the EDS pattern of Fe, Cu and O elements in the same area of the reconstructed interface of iron (II) oxalate prepared in Example 1 of the present invention;

Fig. 3 is a cyclic stability curve of iron (II) oxalate reconstructed interface material prepared in Example 2 of the present invention.

DESCRIPTION OF THE INVENTION

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The invention will be further explained with the attached drawings and specific embodiments.

Example 1

A copper atom surface reconstruction strategy for preparing high-capacity iron (II) oxalate material comprises the following specific steps:

S1, dispersing iron (II) oxalate high-capacity anode material in a mixed solution consisting of 80 ml absolute ethanol and 10 ml deionized water to obtain a uniformly dispersed mixed solution; among them, the ratio of metal oxysalt to mixed solution is 1 g: 90 ml;

S2, adding 0.14 g of copper sulfate pentahydrate into the mixed solution obtained in S1, reacting at 50°C for 6 h, filtering, washing and drying to obtain the surface reconstructed material containing crystal water;

S3, sintering the surface reconstructed material containing crystal water obtained in S3 at 270°C for 4 h in vacuum or inert atmosphere to obtain the high-capacity lithium-ion battery anode material with surface reconstructed copper atoms.

The scanning electron microscope pattern of the surface reconstruction interface of the copper atom prepared in this example is shown in Fig. 2.

Example 2

A copper atom surface reconstruction strategy for preparing a high-capacity iron (II) oxalate lithium-ion battery anode material comprises the following specific steps:

S1, dispersing iron (II) oxalate high-capacity material in a mixed solution consisting of 80 ml absolute ethanol and 10ml deionized water to obtain a uniformly dispersed mixed solution; among them, the ratio of metal oxyacid salt to mixed solution is 1 g: 90 ml;

S2, adding 0.14 g of copper sulfate pentahydrate into the mixed solution obtained in S1, and reacting at 50°C for 6 h; filtering, washing and drying after the reaction is finished to obtain the surface reconstructed material containing crystal water;

and S3, sintering the surface reconstructed material containing crystal water obtained in S3 at 270°C for 4 h in an inert atmosphere to obtain the anode material of the iron (II) oxalate lithium-ion battery with surface reconstructed copper atoms.

Weigh 0.1 g of iron (II) oxalate prepared in this example, 0.01 g of acetylene black, 0.02 g of carbon nanotubes and 0.01 g of polyvinylidene fluoride (PVDF), put them into a mortar, add 1.8 ml of N-methyl-2-pyrrolidone solution, grind and stir for 40 min, evenly spread the slurry on copper foil, dry it in hot air at 60°C for 30min, then transfer it to a vacuum oven at 60°C for continuous drying for 12 h, and then cut the pole pieces with a diameter of 13.5 mm.

In a glove box filled with argon gas, the electrode plate can be assembled into a battery with the existing commercially available diaphragm, lithium sheet, battery case and nickel mesh by using general conventional methods. The cyclic stability curve of iron (II) oxalate anode material reconstructed by copper atoms can be obtained through the Sunway battery test cabinet, as shown in Fig. 3.

Example 3

A method for preparing a high-capacity iron (II) oxalate material by a nickel and cobalt atom combined surface reconstruction strategy comprises the following specific steps:

S1, dispersing iron (II) oxalate high-capacity material in a mixed solution consisting of 80 ml absolute ethanol, 10 ml NMP and 10 ml deionized water to obtain a uniformly dispersed mixed solution; among them, the ratio of metal oxyacid salt to mixed solution is 1 g:100 ml;

S2, adding 0.01 g of nickel sulfate hexahydrate and 0.01 g of cobalt sulfate heptahydrate into the mixed solution obtained in S1, and reacting at 50°C for 6 h; filtering, washing and drying after the reaction, and obtaining the iron (II) oxalate material containing crystal water with nickel and cobalt atoms combined surface reconstruction;

S3, sintering the surface reconstructed material containing crystal water obtained in S3 at 300°C for 4 h in an inert atmosphere to obtain the high-capacity lithium-ion battery anode material with nickel and cobalt atoms combined surface reconstructed.

Example 4

A cobalt atom surface reconstruction strategy for preparing high-capacity copper hydroxide material comprises the following specific steps:

S1, dispersing a high-capacity anode material of copper hydroxide in a mixed solution consisting of 80 ml absolute ethanol, 10 ml deionized water, 0.5 g CTAB and 2 ml concentrated hydrochloric acid to obtain a uniformly dispersed mixed solution; Among them, the ratio of metal oxyacid salt to mixed solution is 1 g: 90 ml;

S2, adding 6.3 g of cobalt nitrate hexahydrate into the mixed solution obtained in S1, and reacting at 80°C for 24 h; filtering, washing and drying after the reaction is finished to obtain the material with surface reconstruction containing crystal water;

And S3, sintering the material with the surface reconstruction of crystal water obtained in S3 at 300°C for 4 h in an inert atmosphere to obtain the high-capacity lithium-ion battery anode material with the surface reconstruction of cobalt atoms.

Example 5

A manganese atom surface reconstruction strategy for preparing a high-capacity iron (II) carbonate material comprises the following specific steps:

S1, dispersing iron (II) carbonate high-capacity material in a mixed solution consisting of 30 ml absolute ethanol, 60 ml deionized water, 1 ml concentrated hydrochloric acid, 0.5 g Pss and 2.5 g ascorbic acid to obtain a uniformly dispersed mixed solution; among them, the ratio of metal oxyacid salt to mixed solution is 1 g:90 ml;

S2, adding 5.5 g of ferrous sulfate heptahydrate into the mixed solution obtained in S1, and reacting at 80°C for 24 h; filtering, washing and drying after the reaction is finished to obtain the material with surface reconstruction containing crystal water;

And S3, sintering the material with the surface reconstruction of crystal water obtained in S3 at 300°C for 4 h in an inert atmosphere to obtain the high-capacity lithium-ion battery anode material with the surface reconstruction of manganese atoms.

1. A method for designing a high-capacity electrode material by particle surface reconstruction, comprising:

s1, dispersing a metal oxysalt high-capacity negative electrode material in a mixed solution of an organic solvent and deionized water to obtain a uniformly dispersed mixed solution, wherein the mass-volume ratio of the metal oxysalt to the mixed solution is 0.1-1 g:50-200 ml;

s2, adding soluble metal salt into the mixed solution obtained in s1, reacting at 0-200°C for 5-72 h, filtering, washing and drying to obtain the surface reconstructed material containing the crystal water;

s3, sintering the surface reconstructed material containing the crystal water obtained in s3 at 200-350°C for 4-10 h under vacuum or inert atmosphere to obtain the surface reconstructed high-capacity lithium-ion battery anode material.

2. The method for designing a high-capacity electrode material by particle surface reconstruction according to claim 1, characterized in that the organic solvent in s1 comprises one or more of absolute ethanol, ethylene glycol, CTAB, NMP, DMA, DMSO and DMF.

3. The method for designing a high-capacity electrode material by particle surface reconstruction according to claim 1, characterized in that the mixed solution in s1 further comprises one or more of PDDA, Pss, sulfuric acid and hydrochloric acid.

4. The method for designing a high-capacity electrode material by particle surface reconstruction according to claim 1, characterized in that the soluble metal salts in s2 include one or more of nitrates, sulfates and acetates of transition metal.

5. The method for designing a high-capacity electrode material by particle surface reconstruction according to claim 1, characterized in that the molar ratio of soluble metal salt to metal oxyacid salt in s2 is 0.01-1:1-0.01.

1. Ein Verfahren zum Entwerfen eines Elektrodenmaterials mit hoher Kapazität durch Rekonstruktion der Teilchenoberfläche, umfassend:

S1, Dispergieren eines Metalloxysalz-Negativelektrodenmaterials mit hoher Kapazität in einer gemischten Lösung aus einem organischen Lösungsmittel und entionisiertem Wasser, um eine gleichmäßig dispergierte gemischte Lösung zu erhalten, wobei das Massen-Volumen-Verhältnis des Metalloxysalzes zur gemischten Lösung 0,1-1 g:50-200 ml beträgt;

S2, Zugabe von löslichem Metallsalz in die in S1 erhaltene gemischte Lösung, Reaktion bei 0-200°C für 5-72 h, Filtrieren, Waschen und Trocknen, um das oberflächenrekonstruierte Material zu erhalten, enthaltend das Kristallwasser;

S3, Sintern des oberflächenrekonstruierten Materials, enthaltend das in S3 erhaltene Kristallwasser, bei 200-350°C für 4-10 h unter Vakuum oder inerter Atmosphäre, um das oberflächenrekonstruierte Lithium-Ionen-Batterie-Anodenmaterial mit hoher Kapazität zu erhalten.

2. Das Verfahren zum Entwerfen eines Elektrodenmaterials mit hoher Kapazität durch Rekonstruktion der Teilchenoberfläche gemäß Anspruch 1, dadurch gekennzeichnet, dass das organische Lösungsmittel in S1 eines oder mehrere von absolutem Ethanol, Ethylenglykol, CTAB, NMP, DMA, DMSO und DMF umfasst.

3. Das Verfahren zum Entwerfen eines Elektrodenmaterials mit hoher Kapazität durch Rekonstruktion der Teilchenoberfläche gemäß Anspruch 1, dadurch gekennzeichnet, dass die gemischte Lösung in S1 weiterhin eines oder mehrere von PDDA, Pss, Schwefelsäure und Salzsäure umfasst.

4. Das Verfahren zum Entwerfen eines Elektrodenmaterials mit hoher Kapazität durch Rekonstruktion der Teilchenoberfläche gemäß Anspruch 1, dadurch gekennzeichnet, dass die löslichen Metallsalze in S2 eines oder mehrere von Nitraten, Sulfaten und Acetaten von Übergangsmetall umfassen.

5. Das Verfahren zum Entwerfen eines Elektrodenmaterials mit hoher Kapazität durch Rekonstruktion der Teilchenoberfläche gemäß Anspruch 1, dadurch gekennzeichnet, dass das molare Verhältnis von löslichem Metallsalz zu Metalloxysäuresalz in S2 0,01-1:1-0,01 beträgt.

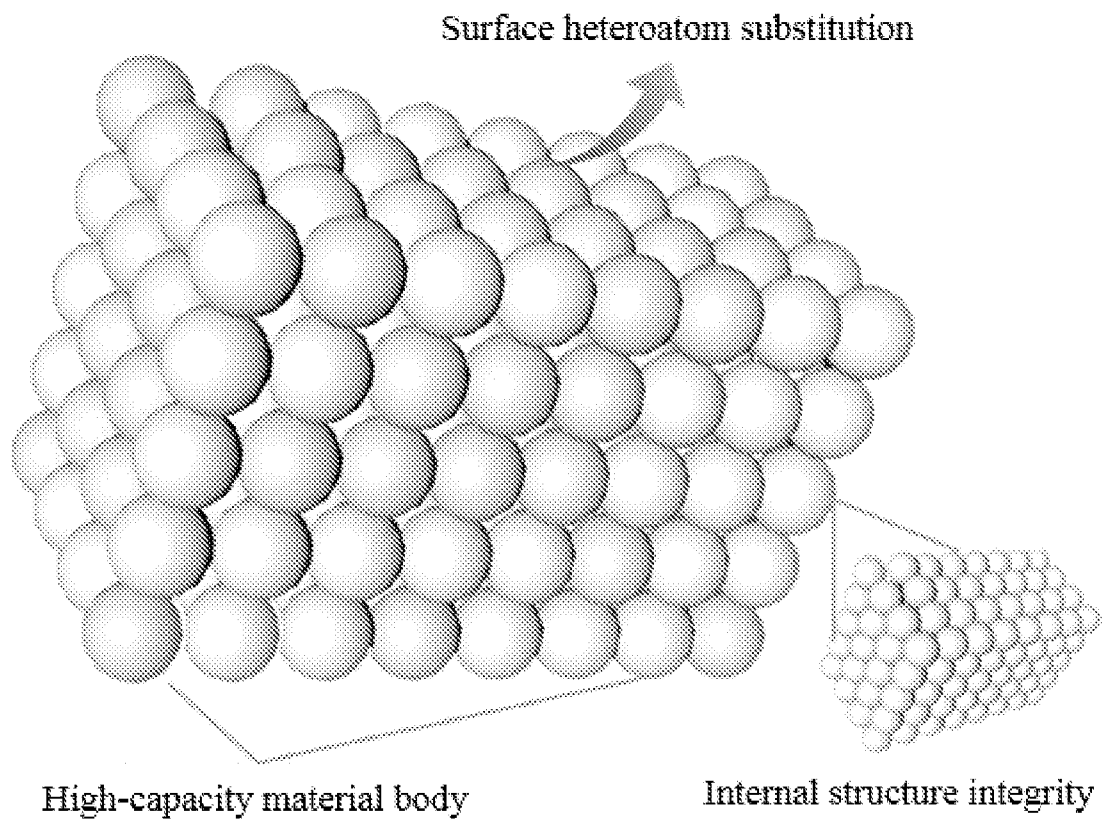


FIG. 1

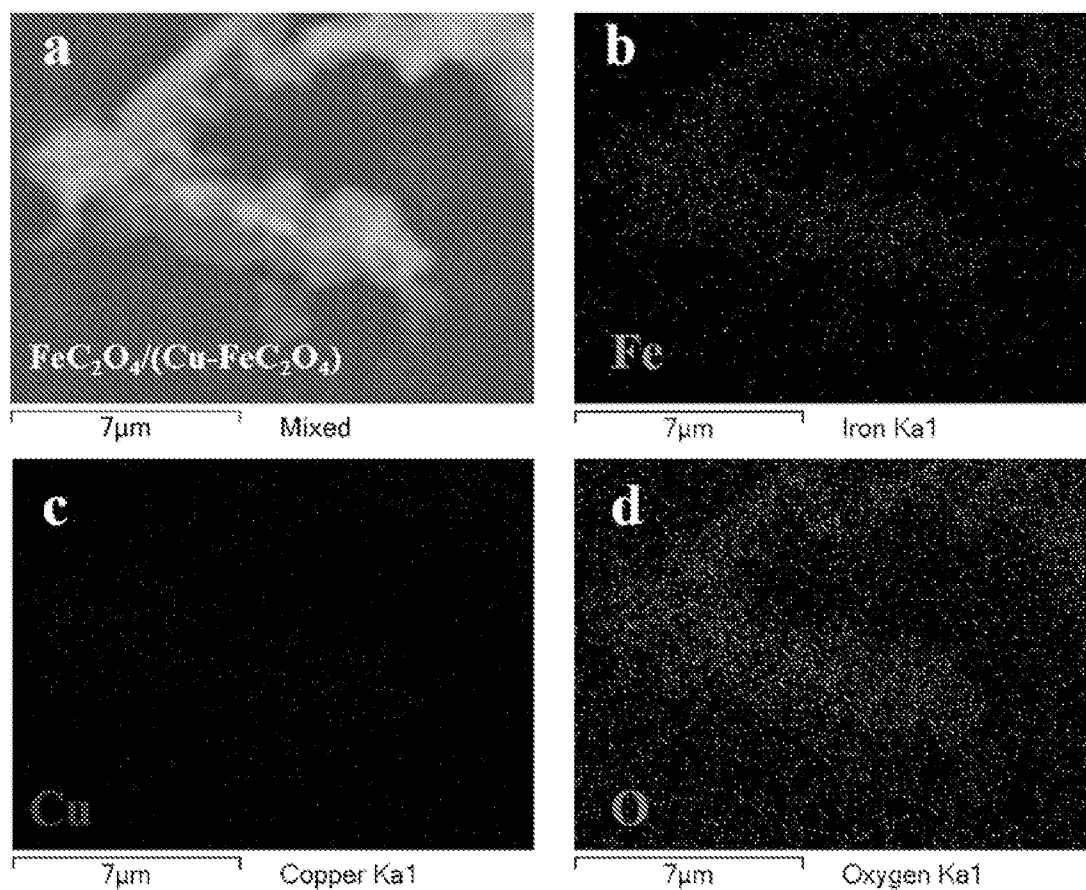


FIG. 2

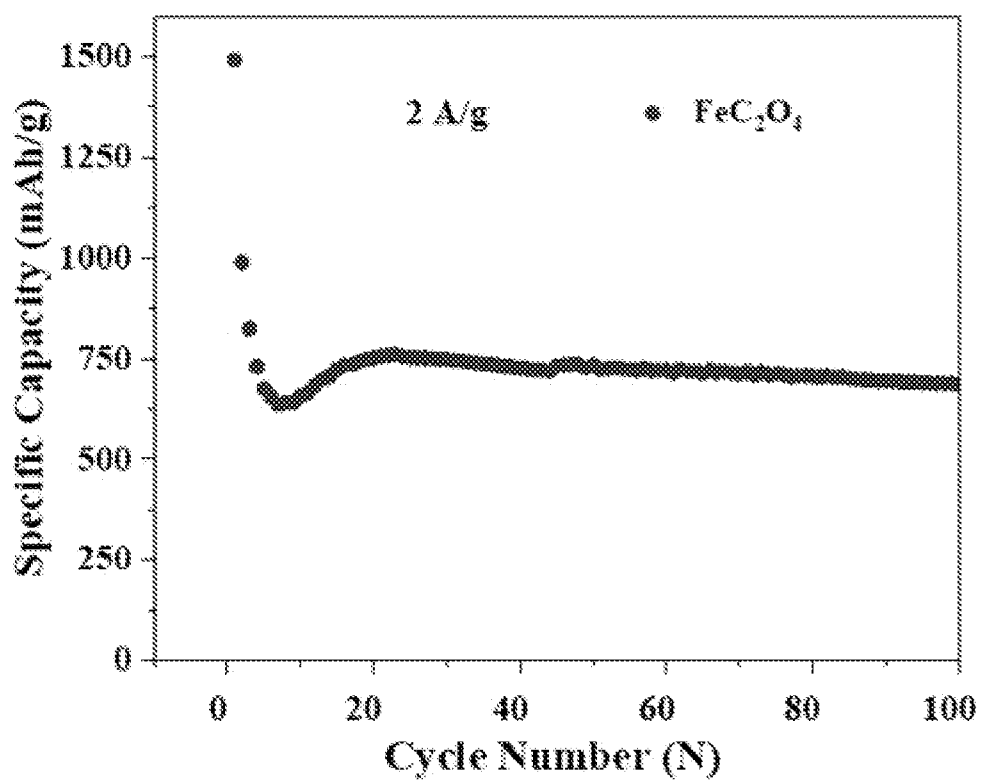


FIG. 3