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(54) **High-performance Sodium Ion Battery Anode Material And Its Preparation Method.**

(57) The invention discloses a high-performance sodium ion battery anode material and its preparation method, and it belongs to the technical field of electrochemistry. The present invention dissolves CoCl2·6H2O, NiCl2·6H2O and urotropine in deionized water, performs hydrothermal reaction under the nitrogen environment, and then performs the suction filtration, washing and drying treatment to obtain NiCo2(OH)6 powders; mixes the NiCo2(OH)6 powders with the sulfur powders, and then performs vulcanization reaction to obtain the NiCo2S4 nanometer hexagonal sheet, namely the high-performance sodium ion battery anode material; under the current density of 1000mA/g, the first reversible specific capacity of the anode material of high-performance sodium ion battery can reach 528mAh/g, the reversible specific capacity can reach 442mAh/g after 100 cycles and 402mAh/g after 500 cycles. The anode material has high specific capacity, good cycle performance and excellent electrochemical performance.

## Description



# High-performance Sodium Ion Battery Anode Material And Its Preparation Method

## TECHNICAL FIELD

The invention relates to the technical field of electrochemistry, and in particular to a high-performance sodium ion battery anode material and a preparation method thereof.

## BACKGROUND

The lithium ion battery system has been widely used owing to the advantages of the high discharge voltage, the large energy density, the low self-discharge, the long cycle life, and the environmental protection. However, due to the shortage of lithium resources, it is urgent to develop the next generation energy storage battery system with excellent comprehensive performance. However, the difficulties in the study of sodium ion batteries lie in the fact that the larger radius of the sodium ion makes the ion deintercalation more difficult in the electrochemical reaction process and the structure of the electrode material more unstable, which makes the overall electrochemical performance of sodium ion batteries worse than that of lithium ion batteries. Therefore, how to prepare the anode material for sodium ion battery with high specific capacity and good cycle performance is an urgent technical problem to be solved.

## SUMMARY

The main purpose of the present invention is to provide a high-performance sodium ion battery anode material and its preparation method, so as to solve the problems of the unstable electrode material structure and the poor electrochemical performance of sodium ion battery in the prior art. Under the current density of 1000mA/g, the first reversible specific capacity of the anode material of high-performance sodium ion battery can reach 528mAh/g, the reversible specific capacity can reach 442mAh/g after 100 cycles and 402mAh/g after 500 cycles. The anode material has high specific capacity, good cycle performance and excellent electrochemical performance.

In order to achieve the above purpose, the invention provides the following scheme:

One of the purposes of the present invention is to provide a preparation method of the high-performance sodium ion battery anode material, comprising the following steps: Dissolving $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and urotropine in the deionized water, performing hydrothermal

reaction under the nitrogen environment, and then performing the suction filtration, washing and drying treatment to obtain $NiCo_2(OH)_6$ powders; mixing the $NiCo_2(OH)_6$ powders with the sulfur powders, and then performing the vulcanization reaction to obtain the $NiCo_2S_4$ nanometer hexagonal sheets, namely the high-performance sodium ion battery anode material;

The molar ratio of the $CoCl_2 \cdot 6H_2O$, the $NiCl_2 \cdot 6H_2O$ and urotropine is (1-2):(3-5): (15-18);

The mass ratio of the $NiCo_2(OH)_6$ powders to the sulfur powders is (3-4):(2-3).

Further, the molar volume ratio of $CoCl_2 \cdot 6H_2O$ to the deionized water is 1mmol:400mL.

Further, the hydrothermal reaction is performed under the magnetic stirring at 120℃, for 6 hours.

Further, the washing means washing twice with deionized water and then twice with the ethanol; the drying means drying in an oven at 80℃ for 8 hours.

Further, the vulcanization reaction is carried out in a mixture of hydrogen and argon at 280℃ for 2 hours.

Further, the volume ratio of hydrogen to argon in the hydrogen-argon mixed gas is 10:90.

The second object of the invention is to provide a preparation method of high-performance sodium ion battery anode material.

The third object of the invention is to provide an application of the high-performance sodium ion battery anode material in the preparation of the sodium ion battery.

The invention discloses the following technical effects:

Under the current density of 1000mA/g, the first reversible specific capacity of the high-performance sodium ion battery anode material in the invention can reach 528mAh/g, the reversible specific capacity can reach 442mAh/g after 100 cycles and 402mAh/g after 500 cycles. The anode material has high specific capacity, good cycle performance and excellent electrochemical performance.;

**DESCRIPTION OF THE INVENTION**

Various exemplary embodiments of the present invention will now be described in detail, which should not be regarded as a limitation of the present invention, but rather as a more detailed description of certain aspects, characteristics and embodiments of the present invention.

It should be understood that the terms described in the present invention are only for describing specific embodiments, and are not intended to limit the present invention. In addition, the numerical range in the present invention should be understood as every intermediate value

between the upper limit and the lower limit of the range is also specifically disclosed. Intermediate values within any stated value or stated range and every smaller range between any other stated value or intermediate values within the stated range are also included in the present invention. The upper and lower limits of these smaller ranges can be independently included in or excluded from the range.

Without departing from the scope or spirit of the invention, it is obvious to those skilled in this field that many modifications and changes can be made to the specific embodiments of the specification of the invention. Other embodiments derived from the description of the present invention will be apparent to the skilled person. The specification and examples of this application are only exemplary.

As used herein, the terms "including", "comprising", "having", "containing", etc. are all open terms, which means including but not limited to.

Embodiment 1

$CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and urotropine are dissolved in deionized water. The molar ratio of $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and urotropine is 1.5:3:17, and the molar volume ratio of $CoCl_2 \cdot 6H_2O$ to deionized water is 1mmol:400mL, the hydrothermal reaction is carried out under nitrogen and magnetic stirring conditions. The temperature of the hydrothermal reaction is 120℃ and the time is 6 hours; then, the precipitate is obtained by extraction and filtration; the precipitate is washed twice with deionized water and twice with ethanol, and dried for 8 hours in an oven at 80℃ to obtain $NiCo_2(OH)_6$ powders; and then mixed it with the sulfur powders, the mass ratio of $NiCo_2(OH)_6$ powders to sulfur powders is 3.5:3; and the mixed powder is vulcanized for 2 hours at 280℃ in a mixture of hydrogen and argon (the volume ratio of hydrogen to argon is 10:90), to obtain the high-performance sodium ion battery anode material.

Embodiment 2

$CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and urotropine are dissolved in deionized water. The molar ratio of $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and urotropine is 1:3:15, and the molar volume ratio of $CoCl_2 \cdot 6H_2O$ to deionized water is 1mmol:400mL, the hydrothermal reaction is carried out under nitrogen and magnetic stirring conditions. The temperature of the hydrothermal reaction is 120℃ and the time is 6 hours; then, the precipitate is obtained by extraction and filtration; the precipitate is washed twice with deionized water and twice with ethanol, and dried for 8 hours in an oven at 80℃ to obtain $NiCo_2(OH)_6$ powders, and then mixed it with the sulfur powders, the

mass ratio of $NiCo_2(OH)_6$ powders to sulfur powders is 3:2; and the mixed powder is vulcanized for 2 hours at 280℃ in a mixture of hydrogen and argon (the volume ratio of hydrogen to argon is 10:90), to obtain the high-performance sodium ion battery anode material.

Embodiment 3

$CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and urotropine are dissolved in deionized water. The molar ratio of $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and urotropine is 2:5:18, and the molar volume ratio of $CoCl_2 \cdot 6H_2O$ to deionized water is 1mmol:400mL, the hydrothermal reaction is carried out under nitrogen and magnetic stirring conditions. The temperature of the hydrothermal reaction is 120℃ and the time is 6 hours; then, the precipitate is obtained by extraction and filtration; the precipitate is washed twice with deionized water and twice with ethanol, and dried for 8 hours in an oven at 80°C to obtain $NiCo_2(OH)_6$ powders, and then mixed it with the sulfur powders, the mass ratio of $NiCo_2(OH)_6$ powders to sulfur powders is 4:3; and the mixed powder is vulcanized for 2 hours at 280°C in a mixture of hydrogen and argon (the volume ratio of hydrogen to argon is 10:90), to obtain the high-performance sodium ion battery anode material.

Comparative example 1

$CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and urotropine are dissolved in deionized water. The molar ratio of $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and urotropine is 1.5:3:17, and the molar volume ratio of $CoCl_2 \cdot 6H_2O$ to deionized water is 1mmol:400mL, the hydrothermal reaction is carried out under nitrogen and magnetic stirring conditions. The temperature of the hydrothermal reaction is 120°C and the time is 6 hours; then, the precipitate is obtained by extraction and filtration; the precipitate is washed twice with deionized water and twice with ethanol, and dried for 8 hours in an oven at 80℃ to obtain $NiCo_2(OH)_6$ powders; the sodium ion battery anode material is obtained without vulcanization reaction.

Comparative example 2

$CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and urotropine are dissolved in deionized water. The molar ratio of $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and urotropine is 2:1:18, and the molar volume ratio of $CoCl_2 \cdot 6H_2O$ to deionized water is 1mmol:400mL, the hydrothermal reaction is carried out under nitrogen and magnetic stirring conditions. The temperature of the hydrothermal reaction is 120℃ and the time is 6 hours; then, the precipitate is obtained by extraction and filtration; the precipitate is washed twice with deionized water and twice with ethanol, and dried for 8 hours in an oven at 80℃ to obtain $NiCo_2(OH)_6$ powders, and then mixed it with the sulfur powders, the

mass ratio of $NiCo_2(OH)_6$ powders to sulfur powders is 3.5:3; and the mixed powder is vulcanized for 2 hours at 280℃ in a mixture of hydrogen and argon (the volume ratio of hydrogen to argon is 10:90), to obtain the high-performance sodium ion battery anode material.

Comparative example 3

$CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and urotropine are dissolved in deionized water. The molar ratio of $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and urotropine is 1.5:3:17, and the molar volume ratio of $CoCl_2 \cdot 6H_2O$ to deionized water is 1mmol:400mL, the hydrothermal reaction is carried out under nitrogen and magnetic stirring conditions. The temperature of the hydrothermal reaction is 120℃ and the time is 6 hours; then, the precipitate is obtained by extraction and filtration; the precipitate is washed twice with deionized water and twice with ethanol, and dried for 8 hours in an oven at 80℃ to obtain $NiCo_2(OH)_6$ powders, and then mixed it with the sulfur powders, the mass ratio of $NiCo_2(OH)_6$ powders to sulfur powders is 1:1.2; and the mixed powder is vulcanized for 2 hours at 280℃ in a mixture of hydrogen and argon (the volume ratio of hydrogen to argon is 10:90), to obtain the high-performance sodium ion battery anode material.

Effect verification example

The 2032 type button cell is assembled by using the materials prepared in each example and comparative example as the anodes, the graphene as a conductive additive, the polyvinylidene fluoride as a binder ( The mass ratio of anode material, graphene and polyvinylidene fluoride is 70:15:15), sodium metal as a counter electrode, polypropylene microporous membrane as a separator, and 1mol/L of $NaSO_3CF_3$/ diethylene glycol dimethyl ether as an electrolyte. The whole battery assembly process is completed in the glove box with water/oxygen content below 0.15mg/m$^3$. The constant current charge-discharge test of the battery is performed at room temperature by the LANDCT2001A battery test system with a test voltage range of 0.01-2.80V and a current density of 1000 mA/g. The cyclic voltametric test is carried out on CHI 660e electrochemical work station, and the specific results are shown in table 1.

Table 1

| Projects | The first reversible specific capacity (mAh/g) | The reversible specific capacity of 100 cycles (mAh/g) | The reversible specific capacity of 500 cycles (mAh/g) |
|---|---|---|---|
| Embodiment 1 | 528 | 442 | 402 |
| Embodiment 2 | 516 | 437 | 395 |
| Embodiment 2 | 525 | 435 | 387 |
| Comparative example 1 | 436 | 364 | 348 |
| Comparative example 2 | 482 | 385 | 326 |
| Comparative example 3 | 475 | 364 | 339 |

As shown in table 1, under the current density of 1000mA/g, the first reversible specific capacity of the high-performance sodium ion battery anode material can reach 528mAh/g, the reversible specific capacity can reach 442mAh/g after 100 cycles, and 402mAh/g after 500 cycles, which indicates that the anode material has high specific capacity, good cycle performance and excellent electrochemical performance.

The above-mentioned embodiments only describe the preferred mode of the present invention, and do not limit the scope of the present invention. Without departing from the design spirit of the present invention, variations and improvements made by general technicians in this field should fall within the protection scope determined by the claims of the present invention.

## CLAIMS

1. A preparation method of a high-performance sodium ion battery anode material, which is characterized by comprising the following steps: dissolving $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and urotropine in deionized water, performing hydrothermal reaction under the nitrogen environment, and then performing the suction filtration, washing and drying treatment to obtain $NiCo_2(OH)_6$ powders; mixing the $NiCo_2(OH)_6$ powders with sulfur powders, and then performing the vulcanization reaction to obtain the high-performance sodium ion battery anode material; the molar ratio of the $CoCl_2 \cdot 6H_2O$, the $NiCl_2 \cdot 6H_2O$ and the urotropine is (1-2):(3-5):(15-18); the mass ratio of the $NiCo_2(OH)_6$ powders to the sulfur powders is (3-4):(2-3).

2. According to the preparation method of claim 1, which is characterized in that the molar volume ratio of $CoCl_2 \cdot 6H_2O$ to deionized water is 1mmol:400mL.

3. According to the preparation method of claim 1, which is characterized in that the hydrothermal reaction is carried out with the magnetic stirring, the temperature of the hydrothermal reaction is 120°C, and the duration is 6 hours.

4. According to the preparation method of claim 1, which is characterized in washing twice with deionized water and twice with ethanol and drying in an oven at 80°C for 8 hours.

5. According to the preparation method of claim 1, which is characterized in that the vulcanization reaction is carried out in a mixture of hydrogen and argon at 280°C for 2 hours.

6. According to the preparation method of claim 5, which is characterized in that the volume ratio of hydrogen to argon in the hydrogen-argon mixed gas is 10:90.

7. A high-performance sodium ion battery anode material is prepared by the preparation method of any one of claims 1 to 6.

8. An application of the high-performance sodium ion battery anode material according to claim 7 is included in the preparation of the sodium ion battery.

## Revendications

1. Un procédé de préparation d'un matériau d'électrode négative haute-performance pour une batterie à ions sodium, caractérisé en ce qu'il comprend les étapes suivantes: $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ et d'Urotropine sont dissous dans de l'eau désionisée et soumis à une réaction hydrothermique dans des conditions d'azote, le procédé consiste ensuite à filtrer, laver et sécher pour obtenir la poudre de $NiCo_2(OH)_6$; ensuite, la poudre de $NiCo_2(OH)_6$ est mélangée avec la poudre de soufre pour subir une réaction de vulcanisation afin d'obtenir le matériau d'électrode négative haute-performance pour une batterie à ions sodium;
le rapport molaire entre $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ et l'Urotropine est (1-2):(3-5):(15-18);
le rapport massique de la poudre de $NiCo_2(OH)_6$ à la poudre de soufre est (3-4): (2-3).

2. Le procédé de préparation selon la revendication 1, caractérésé en ce que ledit rapport molaire de $CoCl_2$:$6H_2O$ et l'Urotropine est 1mmol:400mL.

3. Le procédé de préparation selon la revendication 1, caractérésé en ce que ladite réaction hydrothermique est effectuée sous l'effet d'une force magnétique agitée avec une température de 120°Cet une durée de 6 heures.

4. Le procédé de préparation selon la revendication 1, caractérésé en ce que ledit lavage est effectué deux fois avec de l'eau désionisée et deux fois avec de l'éthanol; le séchage est effectué de 8 heures dans un four à 80°C.

5. Le procédé de préparation selon la revendication 1, caractérésé en ce que ladite réaction de vulcanisation est une réaction de deux heures dans un mélange d'hydrogène-argon à 280°C.

6. Le procédé de préparation selon la revendication 5, caractérésé en ce que ledit rapport volumétrique de l'hydrogène par rapport à l'argon dans le mélange d'hydrogène-argon est de 10:90.

7. Le matériau d'électrode négative haute-performance pour une batterie à ions sodium est préparé par le procédé de préparation selon l'une quelconque des revendications 1 à 6.

8. Une application du matériau d'électrode négative haute-performance pour une batterie à ions sodium selon la revendication 7 est inclusée dans la préparation de la batterie à ions sodium.