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HIGH-NICKEL TERNARY CATHODE MATERIAL SYNTHESIZED USING LITHIUM CARBONATE AS MAIN LITHIUM SOURCE AND PREPARATION METHOD THEREOF.

(57)

The present invention discloses a high-nickel ternary cathode material synthesized using lithium carbonate as a main lithium source and a preparation method thereof, and belongs to the technical field of high-nickel ternary cathode materials. The preparation method includes: using lithium carbonate and lithium hydroxide as a lithium source, and mixing a high-nickel ternary cathode material precursor, the lithium carbonate and a metal oxide additive, wherein a molar ratio of a lithium element in the lithium carbonate to nickel, cobalt and manganese elements in the high-nickel ternary cathode material precursor is 0.70–0.90, an added amount of the metal oxide additive accounts for 0.1–0.5 wt% of the mass of the high-nickel ternary cathode material precursor, and the high-nickel ternary cathode material is prepared using high- temperature gradient sintering technology and crystal growth control technology through three times of sintering. Beneficial effect: when used as the lithium source, the dosage of the lithium carbonate per unit is reduced by about 10%, so the high-nickel ternary cathode material has a distinct cost advantage compared with existing products in the industry; and primary particles grow radially from a center point, and the high-nickel ternary cathode material has an obvious advantage in cycle performance and rate performance compared with the existing products and is high in gram capacity.

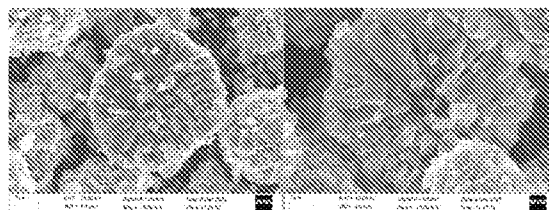


FIG. 1

HIGH-NICKEL TERNARY CATHODE MATERIAL SYNTHESIZED USING LITHIUM CARBONATE AS MAIN LITHIUM SOURCE AND PREPARATION METHOD THEREOF

5 TECHNICAL FIELD

[0001] The present invention belongs to the technical field of high-nickel ternary cathode materials and specifically discloses a high-nickel ternary cathode material synthesized using lithium carbonate as a main lithium source and a preparation method thereof.

10 BACKGROUND

[0002] In recent years, with the high-speed development of the new energy automobile industry, demands for lithium-ion batteries have grown rapidly. People's demand for driving ranges of new energy automobiles has been on the rise. As the quantity demanded for high-energy-density lithium-ion batteries grows rapidly, the demand for high-nickel cathode materials grows at a high speed. High-nickel ternary materials have the characteristic of high capacity and also have disadvantages. Because of high nickel content, incomplete oxidation of bivalent nickel leads to serious $\text{Li}^{1+}/\text{Ni}^{2+}$ mixing. To control the size of primary particles, the sintering temperature of the high-nickel ternary materials is generally low. The melting point of lithium carbonate is obviously higher than that of lithium hydroxide, so it is quite difficult to synthesize high-nickel ternary materials using lithium carbonate. There is currently no successful experience in the industry.

[0003] At present, a high-nickel ternary cathode material is prepared mainly using a secondary sintering process which comprises the following steps: evenly mixing a precursor, lithium hydroxide and an additive, carrying out primary high-temperature sintering in a kiln, carrying out crushing, washing, drying and surface coating, and then carrying out secondary sintering, but the problems of high preparation cost and low gram capacity of the material remain.

[0004] The Chinese patent application document with the publication number CN111517377A discloses a high-nickel ternary cathode material precursor, a high-nickel ternary cathode material and a preparation method thereof. The preparation method of the high-nickel ternary cathode material precursor includes: (1) adding a nickel-cobalt salt solution, a first precipitant and a second precipitant to a first reaction base solution to carry out a first synthesis reaction to obtain a nickel-cobalt binary precursor; (2) adding the nickel-cobalt binary precursor to a second reaction base solution, introducing compressed air into a reaction system to carry out pre-oxidation treatment, and after the pre-oxidation treatment is completed, adding

a manganese salt solution and the second precipitant to the reaction system to carry out a second synthesis reaction to obtain a manganese salt coated high-nickel ternary cathode material precursor. By the method, the high-nickel ternary cathode material precursor is prepared through two-stage synthesis reactions without a protective atmosphere in the whole process, and thus the method is simple and low in processing cost. However, the lithium source used in the patent is still lithium hydroxide, costs are high, cycle performance and rate performance of the material are poor, and therefore, the patent should be further improved.

SUMMARY

[0005] The technical issues that the present invention is to solve are how to prepare a high-nickel ternary cathode material using lithium carbonate as a main lithium source, how to control primary particles to grow radially from a center point and how to prepare a high-nickel cathode material with a high gram capacity.

[0006] The present invention solves the technical issues by the following technological means:

[0007] A first aspect of the present invention provides a preparation method of a high-nickel ternary cathode material synthesized using lithium carbonate as a main lithium source, comprising the following steps:

[0008] (1) mixing a high-nickel ternary cathode material precursor, lithium carbonate and a metal oxide additive; where a molar ratio of a lithium element in the lithium carbonate to nickel, cobalt and manganese elements in the high-nickel ternary cathode material precursor is 0.70–0.90, and an added amount of the metal oxide additive accounts for 0.1–0.5 wt% of the mass of the high-nickel ternary cathode material precursor;

[0009] (2) carrying out sintering on the materials mixed in step (1), and carrying out natural cooling after the sintering;

[0010] (3) grinding and sieving the materials cooled in step (2) to obtain a primary intermediate product;

[0011] (4) mixing the primary intermediate product obtained in step (3) with the lithium hydroxide in a certain ratio, where a molar ratio of the lithium element to the nickel, cobalt and manganese elements in the high-nickel ternary cathode material precursor is 1.02-1.10 after the mixing;

[0012] (5) carrying out sintering on the materials mixed in step (4), and carrying out natural cooling after the sintering;

[0013] (6) grinding and sieving the materials cooled in step (5) to obtain a secondary intermediate product;

[0014] (7) washing, filtering and drying the secondary intermediate product obtained in step (6);

[0015] Note: the purpose of washing, filtering and drying is to remove the lithium hydroxide and the lithium carbonate left on the surface.

5 **[0016]** (8) evenly mixing the material in step (7) with boron oxide and titanium oxide in a certain ratio; and

[0017] (9) carrying out sintering on the materials evenly mixed in step (8), and carrying out natural cooling after the sintering to obtain the high-nickel ternary cathode material.

10 **[0018]** Beneficial effect: in the present invention, by using the lithium carbonate and the lithium hydroxide as the lithium source and using high-temperature gradient sintering technology and crystal growth control technology, the high-nickel ternary material with primary particles growing radially from a center point can be obtained through three times of sintering, which is high in gram capacity and has a distinct cost advantage.

15 **[0019]** Preferably, in step (1), the high-nickel ternary cathode material precursor is represented by a chemical formula $\text{Ni}_x\text{Co}_y\text{Mn}_z(\text{OH})_2$, where $0.70 \leq x \leq 0.90$, $0.03 \leq y \leq 0.15$, $0.03 \leq z \leq 0.15$, and $x + y + z = 1.00$.

[0020] Preferably, in step (1), the particle size D50 of the high-nickel ternary cathode material precursor is 3–15 μm .

20 **[0021]** Preferably, in step (1), the metal oxide additive is a combination of one or more of zirconia, tungsten oxide, titanium oxide and strontium oxide.

[0022] Preferably, the sintering in steps (2), (5) and (9) is each carried out in the oxygen atmosphere furnace, and a volume content of oxygen is $\geq 90\%$.

25 **[0023]** Preferably, the sintering in step (2) is a gradient sintering: low-temperature sintering followed by high-temperature sintering; a temperature of the low-temperature sintering is $\leq 770^\circ\text{C}$, and a temperature of the high-temperature sintering is $820\text{--}950^\circ\text{C}$.

[0024] Preferably, in step (4), a molar ratio of the lithium element to the nickel, cobalt and manganese elements in the high-nickel ternary cathode material precursor is 1.05.

[0025] Preferably, in step (5), the sintering temperature is $740\text{--}830^\circ\text{C}$.

30 **[0026]** Preferably, in step (8), an added amount of the boron oxide and an added amount of the titanium oxide account for 0.2% and 0.1% of the mass of the material in step (7) respectively.

[0027] A second aspect of the present invention provides a high-nickel ternary cathode material prepared by the above preparation method.

[0028] The present invention has the following advantages:

[0029] 1. In this solution, the lithium carbonate is mainly used as the main lithium source to synthesize the high-nickel ternary material, the lithium content of the lithium carbonate is 18.7%, the lithium content of the lithium hydroxide is 16.5%, and prices of both the lithium carbonate and the lithium hydroxide are consistent; when used as the lithium source, the dosage of the lithium carbonate per unit is reduced by about 10%, so the high-nickel ternary material has a distinct cost advantage compared with existing products in the industry; and the primary particles grow radially from the center point, and the high-nickel ternary material has an obvious advantage in cycle performance and rate performance compared with the existing products.

[0030] 2. By using the lithium carbonate to partially substitute the lithium hydroxide, the high-nickel ternary material has an obvious cost advantage.

[0031] 3. Compared with existing technical solutions, the high-nickel ternary material has obvious advantages, the temperature of primary sintering can be 100–250 °C higher than the temperature in a solution using lithium hydroxide, the high-nickel ternary material that grows radially from the center point can be prepared, thereby being high in gram capacity.

BRIEF DESCRIPTION OF THE DRAWINGS

[0032] FIG. 1 is an electron micrograph of a material prepared according to Embodiment 1 of the present invention;

[0033] FIG. 2 is a chart of the electrical performance of the material prepared according to Embodiment 1 of the present invention;

[0034] FIG. 3 is an electron micrograph of a material prepared according to Embodiment 2 of the present invention;

[0035] FIG. 4 is a chart of the electrical performance of the material prepared according to Embodiment 2 of the present invention;

[0036] FIG. 5 is an electron micrograph of a material prepared according to Embodiment 3 of the present invention;

[0037] FIG. 6 is a chart of the electrical performance of the material prepared according to Embodiment 3 of the present invention.

DESCRIPTION OF EMBODIMENTS

[0038] In order to make the objects, technical solutions and advantages of the embodiments of the present invention clearer, the technical solutions of the present invention will be described clearly and completely as follows in conjunction with the embodiments of the present invention. It is evident that the described embodiments are a part of the embodiments of the present invention rather than all the embodiments. Based on the embodiments of the present invention, all the other embodiments obtained by those ordinarily skilled in the art without making an inventive effort all belong to the protection scope of the present invention.

[0039] Embodiment 1:

[0040] A preparation method of a high-nickel ternary cathode material synthesized using lithium carbonate as a main lithium source, including the following steps:

[0041] (1) mixing a high-nickel ternary cathode material precursor, lithium carbonate, strontium oxide and a titanium oxide additive; where the high-nickel ternary cathode material precursor is $\text{Ni}_{0.83}\text{Co}_{0.12}\text{Mn}_{0.05}(\text{OH})_2$, the particle size D50 of the high-nickel ternary cathode material precursor is 3–15 μm , a molar ratio of a lithium element in the lithium carbonate to nickel, cobalt and manganese elements in the high-nickel ternary cathode material precursor is 0.70, the strontium oxide accounts for 0.15% of the mass of the high-nickel ternary cathode material precursor, and the titanium oxide accounts for 0.15% of the mass of the high-nickel ternary cathode material precursor; and weighing the above materials according to a ratio and feeding the materials into a 10L high-speed mixer to carry out mixing for 60 min;

[0042] (2) loading the materials mixed in step (1) into a saggar, feeding the saggar into an atmosphere furnace to carry out sintering, heating up to 750 °C at a rate of 2 °C/min, and keeping the temperature at 750 °C for 4 h; heating up to 850 °C at a rate of 1.0 °C/min, and keeping the temperature at 850 °C for 10 h; carrying out natural cooling; and introducing pure oxygen in the whole process, and keeping a volume content of oxygen in the atmosphere furnace above 90%;

[0043] (3) grinding and sieving the materials cooled in step (2) to obtain a primary intermediate product;

[0044] (4) weighing the primary intermediate product obtained in step (3) with lithium hydroxide in a certain ratio, feeding the materials into the mixer to carry out mixing; where, a molar ratio of the lithium element to the nickel, cobalt and manganese elements in the high-nickel ternary cathode material precursor is 1.05 after the mixing;

[0045] (5) loading the materials mixed in step (4) into the saggar, feeding the saggar into the atmosphere furnace to carry out sintering again, heating up to 770 °C at a rate of 2 °C/min, and keeping the temperature at 770 °C for 12 h; carrying out natural cooling; and introducing pure oxygen in the whole process, and keeping a volume content of the oxygen in the atmosphere

furnace above 90%;

[0046] (6) grinding and sieving the materials cooled in step (5) to obtain a secondary intermediate product;

5 **[0047]** (7) feeding the material (namely the secondary intermediate product) in step (6) into a washing, filtering and drying integrated device to carry out washing, filtering and drying, and removing the lithium hydroxide and the lithium carbonate left on the surface; where a ratio of the material to water is 1:1.5, and the drying temperature is 120 °C;

10 **[0048]** (8) evenly mixing the material in step (7) with the boron oxide and the titanium oxide in a certain ratio, where an added amount of the boron oxide and an added amount of the titanium oxide account for 0.2% and 0.1% of the mass of the material in step (7) respectively, and weighing the above materials according to a ratio and feeding the materials into the 10L high-speed mixer to carry out mixing for 60 min; and

15 **[0049]** (9) loading the materials mixed in step (8) into the saggar, feeding the saggar into the atmosphere furnace to carry out sintering again, heating up to 500 °C at a rate of 2 °C/min, and keeping the temperature at 500 °C for 10 h; carrying out natural cooling; introducing pure oxygen in the whole process, and keeping a volume content of the oxygen in the atmosphere furnace above 90%; and grinding and sieving the materials to obtain the high-nickel ternary cathode material for lithium-ion batteries.

20 **[0050]** The morphology and electrical performance of the material prepared according to this embodiment are tested;

[0051] The material obtained according to this embodiment is shown in the electron micrograph of FIG. 1. and can be seen from the picture to grow radially from the center point;

25 **[0052]** the electrical performance of the material obtained according to this embodiment is shown in FIG. 2, and it can be seen from the picture that the discharge gram capacity of the prepared cathode material reaches up to 212.2 mAh/g, shown in Table 1.

[0053] Embodiment 2:

[0054] A preparation method of a high-nickel ternary cathode material synthesized using lithium carbonate as a main lithium source, including the following steps:

30 **[0055]** (1) mixing a high-nickel ternary cathode material precursor, lithium carbonate, strontium oxide and a titanium oxide additive; where the high-nickel ternary cathode material precursor is $\text{Ni}_{0.83}\text{Co}_{0.12}\text{Mn}_{0.05}(\text{OH})_2$, the particle size D50 of the high-nickel ternary cathode material precursor is 3–15 μm , a molar ratio of a lithium element in the lithium carbonate to nickel, cobalt and manganese elements in the high-nickel ternary cathode material precursor is 0.80, the strontium oxide accounts for 0.15% of the mass of the high-nickel ternary cathode

material precursor, and the titanium oxide accounts for 0.15% of the mass of the high-nickel ternary cathode material precursor; and weighing the above materials according to a ratio and feeding the materials into a 10L high-speed mixer to carry out mixing for 60 min;

[0056] (2) loading the materials mixed in step (1) into a saggar, feeding the saggar into an atmosphere furnace to carry out sintering, heating up to 750 °C at a rate of 2 °C/min, and keeping the temperature at 750 °C for 4 h; heating up to 850 °C at a rate of 1.0 °C/min, and keeping the temperature at 850 °C for 10 h; carrying out natural cooling; and introducing pure oxygen in the whole process, and keeping a volume content of oxygen in the atmosphere furnace above 90%;

[0057] (3) grinding and sieving the materials cooled in step (2) to obtain an intermediate product;

[0058] (4) weighing the materials ground in step (3) with lithium hydroxide in a certain ratio, feeding the materials into the mixer to carry out mixing; where, a molar ratio of the lithium element to the nickel, cobalt and manganese elements in the high-nickel ternary cathode material precursor is 1.05 after the mixing;

[0059] (5) loading the materials mixed in step (4) into the saggar, feeding the saggar into the atmosphere furnace to carry out sintering again, heating up to 770 °C at a rate of 2 °C/min, and keeping the temperature at 770 °C for 12 h; carrying out natural cooling; and introducing pure oxygen in the whole process, and keeping a volume content of the oxygen in the atmosphere furnace above 90%;

[0060] (6) grinding and sieving the materials cooled in step (5) to obtain a secondary intermediate product;

[0061] (7) feeding the material (namely the secondary intermediate product) in step (6) into a washing, filtering and drying integrated device to carry out washing, filtering and drying, and removing the lithium hydroxide and the lithium carbonate left on the surface;

[0062] where, a ratio of the material to water is 1:1.5, and the drying temperature is 120 °C.

[0063] (8) evenly mixing the material in step (7) with boron oxide and titanium oxide in a certain ratio;

[0064] where an added amount of the boron oxide and an added amount of the titanium oxide account for 0.2% and 0.1% of the mass of the material in step (7) respectively, and weighing the above materials according to a ratio and feeding the materials into the 10L high-speed mixer to carry out mixing for 60 min; and

[0065] (9) loading the materials mixed in step (8) into the saggar, feeding the saggar into the atmosphere furnace to carry out sintering again, heating up to 500 °C at a rate of 2 °C/min, and

keeping the temperature at 500 °C for 10 h; carrying out natural cooling; introducing pure oxygen in the whole process, and keeping a volume content of the oxygen in the atmosphere furnace above 90%; and grinding and sieving the materials to obtain the high-nickel ternary cathode material for lithium-ion batteries.

5 **[0066]** The morphology and electrical performance of the material prepared according to this embodiment are tested;

[0067] The material obtained according to this embodiment is shown in the electron micrograph of FIG. 3. and can be seen from the picture to grow radially from the center point;

10 **[0068]** the electrical performance of the material obtained according to this embodiment is shown in FIG. 4, and it can be seen from the picture that the discharge gram capacity of the prepared cathode material reaches up to 210.5 mAh/g, shown in Table 1.

[0069] Embodiment 3:

[0070] A preparation method of a high-nickel ternary cathode material synthesized using lithium carbonate as a main lithium source, including the following steps:

15 **[0071]** (1) mixing a high-nickel ternary cathode material precursor, lithium carbonate, strontium oxide and a titanium oxide additive; where the high-nickel ternary cathode material precursor is $\text{Ni}_{0.83}\text{Co}_{0.12}\text{Mn}_{0.05}(\text{OH})_2$, the particle size D50 of the high-nickel ternary cathode material precursor is 3–15 μm , a molar ratio of a lithium element in the lithium carbonate to nickel, cobalt and manganese elements in the high-nickel ternary cathode material precursor is
20 0.90, the strontium oxide accounts for 0.15% of the mass of the high-nickel ternary cathode material precursor, and the titanium oxide accounts for 0.15% of the mass of the high-nickel ternary cathode material precursor; and weighing the above materials according to a ratio and feeding the materials into a 10L high-speed mixer to carry out mixing for 60 min;

25 **[0072]** (2) loading the materials mixed in step (1) into a saggar, feeding the saggar into an atmosphere furnace to carry out sintering, heating up to 750 °C at a rate of 2 °C/min, and keeping the temperature at 750 °C for 4 h; heating up to 850 °C at a rate of 1.0 °C/min, and keeping the temperature at 850 °C for 10 h; carrying out natural cooling; and introducing pure oxygen in the whole process, and keeping a volume content of oxygen in the atmosphere furnace above 90%;

30 **[0073]** (3) grinding and sieving the materials cooled in step (2) to obtain a primary intermediate product;

[0074] (4) weighing the primary intermediate product obtained in step (3) with lithium hydroxide in a certain ratio, feeding the materials into the mixer to carry out mixing; where, a molar ratio of the lithium element to the nickel, cobalt and manganese elements in the high-

nickel ternary cathode material precursor is 1.05 after the mixing;

[0075] (5) loading the materials mixed in step (4) into the saggur, feeding the saggur into the atmosphere furnace to carry out sintering again, heating up to 770 °C at a rate of 2 °C/min, and keeping the temperature at 770 °C for 12 h; carrying out natural cooling; and introducing pure oxygen in the whole process, and keeping a volume content of the oxygen in the atmosphere furnace above 90%;

[0076] (6) grinding and sieving the materials cooled in step (5) to obtain a secondary intermediate product;

[0077] (7) feeding the material (namely the secondary intermediate product) in step (6) into a washing, filtering and drying integrated device to carry out washing, filtering and drying, and removing the lithium hydroxide and the lithium carbonate left on the surface; where, a ratio of the material to water is 1:1.5, and the drying temperature is 120 °C;

[0078] (8) evenly mixing the material in step (7) with boron oxide and titanium oxide in a certain ratio;

[0079] where an added amount of the boron oxide and an added amount of the titanium oxide account for 0.2% and 0.1% of the mass of the material in step (7) respectively; and weighing the above materials according to a ratio and feeding the materials into the 10L high-speed mixer to carry out mixing for 60 min; and

[0080] (9) loading the materials mixed in step (8) into the saggur, feeding the saggur into the atmosphere furnace to carry out sintering again, heating up to 500 °C at a rate of 2 °C/min, and keeping the temperature at 500 °C for 10 h; carrying out natural cooling; introducing pure oxygen in the whole process, and keeping a volume content of the oxygen in the atmosphere furnace above 90%; and grinding and sieving the materials to obtain the high-nickel ternary cathode material for lithium-ion batteries.

[0081] The morphology and electrical performance of the material prepared according to this embodiment are tested;

[0082] The material obtained according to this embodiment is shown in the electron micrograph of FIG. 5. and can be seen from the picture to grow radially from the center point;

[0083] The electrical performance of the material obtained according to this embodiment is shown in FIG. 6, and it can be seen from the picture that the discharge gram capacity of the prepared cathode material reaches up to 209.3 mAh/g, shown in Table 1.

[0084] Embodiment 4:

[0085] A difference between this embodiment and Embodiment 1 is that a sintering temperature “850 °C” in step (2) is changed to “900 °C”, and other steps are the same as those

in Embodiment 1.

[0086] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0087] Embodiment 5:

- 5 **[0088]** A difference between this embodiment and Embodiment 1 is that a sintering temperature “850 °C” in step (2) is changed to “950 °C”, and other steps are the same as those in Embodiment 1.

[0089] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

10 **[0090] Embodiment 6:**

[0091] A difference between this embodiment and Embodiment 2 is that a sintering temperature “850 °C” in step (2) is changed to “900 °C”, and other steps are the same as those in Embodiment 2.

- 15 **[0092]** The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0093] Embodiment 7:

[0094] A difference between this embodiment and Embodiment 2 is that a sintering temperature “850 °C” in step (2) is changed to “950 °C”, and other steps are the same as those in Embodiment 2.

- 20 **[0095]** The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0096] Embodiment 8:

- 25 **[0097]** A difference between this embodiment and Embodiment 3 is that a sintering temperature “850 °C” in step (2) is changed to “900 °C”, and other steps are the same as those in Embodiment 3.

[0098] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0099] Embodiment 9:

- 30 **[0100]** A difference between this embodiment and Embodiment 3 is that a sintering temperature “850 °C” in step (2) is changed to “950 °C”, and other steps are the same as those in Embodiment 3.

[0101] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0102] Embodiment 10:

[0103] A difference between this embodiment and Embodiment 1 is that in step (4), a molar ratio of a lithium element to nickel, cobalt and manganese elements is 1.02, and other steps are the same as those in Embodiment 1.

[0104] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0105] Embodiment 11:

[0106] A difference between this embodiment and Embodiment 1 is that in step (4), a molar ratio of a lithium element to nickel, cobalt and manganese elements is 1.08, and other steps are the same as those in Embodiment 1.

[0107] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0108] Embodiment 12:

[0109] A difference between this embodiment and Embodiment 2 is that in step (4), a molar ratio of a lithium element to nickel, cobalt and manganese elements is 1.02, and other steps are the same as those in Embodiment 2.

[0110] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0111] Embodiment 13:

[0112] A difference between this embodiment and Embodiment 2 is that in step (4), a molar ratio of a lithium element to nickel, cobalt and manganese elements is 1.08, and other steps are the same as those in Embodiment 2.

[0113] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0114] Embodiment 14:

[0115] A difference between this embodiment and Embodiment 3 is that in step (4), a molar ratio of a lithium element to nickel, cobalt and manganese elements is 1.02, and other steps are the same as those in Embodiment 3.

[0116] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0117] Embodiment 15:

[0118] A difference between this embodiment and Embodiment 3 is that in step (4), a molar ratio of a lithium element to nickel, cobalt and manganese elements is 1.08, and other steps are the same as those in Embodiment 3.

5 **[0119]** The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0120] Embodiment 16:

10 **[0121]** Differences between this embodiment and Embodiment 1 are that in step (1), a precursor is $\text{Ni}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}(\text{OH})_2$; and in step (5), a sintering temperature is 740 °C, and other steps are the same as those in Embodiment 1.

[0122] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0123] Embodiment 17:

15 **[0124]** Differences between this embodiment and Embodiment 2 are that in step (1), a precursor is $\text{Ni}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}(\text{OH})_2$; and in step (5), a sintering temperature is 740 °C, and other steps are the same as those in Embodiment 2.

[0125] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0126] Embodiment 18:

20 **[0127]** Differences between this embodiment and Embodiment 1 are that in step (1), a precursor is $\text{Ni}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}(\text{OH})_2$; and in step (2), a sintering temperature “850 °C” is changed to “900 °C”; and in step (5), a sintering temperature is 740 °C, and other steps are the same as those in Embodiment 1.

25 **[0128]** The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0129] Embodiment 19:

30 **[0130]** Differences between this embodiment and Embodiment 2 are that in step (1), a precursor is $\text{Ni}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}(\text{OH})_2$; in step (2), a sintering temperature “850 °C” is changed to “900 °C”; and in step (5), a sintering temperature is 740 °C, and other steps are the same as those in Embodiment 2.

[0131] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0132] Embodiment 20:

[0133] Differences between this embodiment and Embodiment 1 are that in step (1), a precursor is $\text{Ni}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}(\text{OH})_2$; in step (4), a molar ratio of a lithium element to nickel, cobalt and manganese elements is 1.02; and in step (5), a sintering temperature is 740 °C, and other steps are the same as those in Embodiment 1.

[0134] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0135] Embodiment 21:

[0136] Differences between this embodiment and Embodiment 1 are that in step (1), a precursor is $\text{Ni}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}(\text{OH})_2$; in step (4), a molar ratio of a lithium element to nickel, cobalt and manganese elements is 1.08; and in step (5), a sintering temperature is 740 °C, and other steps are the same as those in Embodiment 1.

[0137] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0138] Embodiment 22:

[0139] Differences between this embodiment and Embodiment 2 are that in step (1), a precursor is $\text{Ni}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}(\text{OH})_2$; in step (2), a sintering temperature “850 °C” is changed to “900 °C”; in step (4), a molar ratio of a lithium element to nickel, cobalt and manganese elements is 1.02; and in step (5), a sintering temperature is 740 °C, and other steps are the same as those in Embodiment 2.

[0140] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0141] Embodiment 23:

[0142] Differences between this embodiment and Embodiment 2 are that in step (1), a precursor is $\text{Ni}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}(\text{OH})_2$; in step (2), a sintering temperature “850 °C” is changed to “900 °C”; in step (4), a molar ratio of a lithium element to nickel, cobalt and manganese elements is 1.08; and in step (5), a sintering temperature is 740 °C, and other steps are the same as those in Embodiment 2.

[0143] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0144] Embodiment 24:

[0145] Differences between this embodiment and Embodiment 2 are that in step (1), a precursor is $\text{Ni}_{0.75}\text{Co}_{0.15}\text{Mn}_{0.10}(\text{OH})_2$; and in step (5), a sintering temperature is 830 °C, and

other steps are the same as those in Embodiment 2.

[0146] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0147] Embodiment 25:

- 5 **[0148]** Differences between this embodiment and Embodiment 3 are that in step (1), a precursor is $\text{Ni}_{0.75}\text{Co}_{0.15}\text{Mn}_{0.10}(\text{OH})_2$; and in step (5), a sintering temperature is 830 °C, and other steps are the same as those in Embodiment 3.

[0149] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

10 **[0150] Embodiment 26:**

[0151] Differences between this embodiment and Embodiment 2 are that in step (1), a precursor is $\text{Ni}_{0.75}\text{Co}_{0.15}\text{Mn}_{0.10}(\text{OH})_2$; in step (2), a sintering temperature “850 °C” is changed to “900 °C”; and in step (5), a sintering temperature is 830 °C, and other steps are the same as those in Embodiment 2.

- 15 **[0152]** The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0153] Embodiment 27:

- [0154]** Differences between this embodiment and Embodiment 3 are that in step (1), a precursor is $\text{Ni}_{0.75}\text{Co}_{0.15}\text{Mn}_{0.10}(\text{OH})_2$; in step (2), a sintering temperature “850 °C” is changed to “900 °C”; and in step (5), a sintering temperature is 830 °C, and other steps are the same as those in Embodiment 3.

[0155] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0156] Embodiment 28:

- 25 **[0157]** Differences between this embodiment and Embodiment 2 are that in step (1), a precursor is $\text{Ni}_{0.75}\text{Co}_{0.15}\text{Mn}_{0.10}(\text{OH})_2$; in step (2), a sintering temperature “850 °C” is changed to “900 °C”; in step (4), a molar ratio of a lithium element to nickel, cobalt and manganese elements is 1.02; and in step (5), a sintering temperature is 830 °C, and other steps are the same as those in Embodiment 2.

- 30 **[0158]** The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0159] Embodiment 29:

[0160] Differences between this embodiment and Embodiment 3 are that in step (1), a precursor is $\text{Ni}_{0.75}\text{Co}_{0.15}\text{Mn}_{0.10}(\text{OH})_2$; in step (2), a sintering temperature “850 °C” is changed to “900 °C”; in step (4), a molar ratio of a lithium element to nickel, cobalt and manganese elements is 1.02; and in step (5), a sintering temperature is 830 °C, and other steps are the same as those in Embodiment 3.

[0161] Embodiment 30:

[0162] Differences between this embodiment and Embodiment 2 are that in step (1), a precursor is $\text{Ni}_{0.75}\text{Co}_{0.15}\text{Mn}_{0.10}(\text{OH})_2$; in step (2), a sintering temperature “850 °C” is changed to “950 °C”; in step (4), a molar ratio of a lithium element to nickel, cobalt and manganese elements is 1.08; and in step (5), a sintering temperature is 830 °C, and other steps are the same as those in Embodiment 2.

[0163] The electrical performance of a material prepared according to this embodiment is tested, and test results are shown in Table 1.

[0164] Embodiment 31:

[0165] Differences between this embodiment and Embodiment 3 are that in step (1), a precursor is $\text{Ni}_{0.75}\text{Co}_{0.15}\text{Mn}_{0.10}(\text{OH})_2$; in step (2), a sintering temperature “850 °C” is changed to “950 °C”; in step (4), a molar ratio of a lithium element to nickel, cobalt and manganese elements is 1.08; and in step (5), a sintering temperature is 830 °C, and other steps are the same as those in Embodiment 3.

[0166] Table 1 is shown as follows:

Cases Electrical performance	Initial charge gram capacity (mAh/g) at 0.1C	Initial discharge gram capacity (mAh/g) at 0.1C	Initial efficiency at 0.1C (%)
Embodiment 1	231.8	212.2	91.5
Embodiment 2	232.8	210.5	90.4
Embodiment 3	233.0	209.3	89.8
Embodiment 4	233.2	211.8	90.8
Embodiment 5	231.2	205.6	88.9
Embodiment 6	233.3	209.6	89.8
Embodiment 7	230.8	202.8	87.9
Embodiment 8	231.4	204.3	88.3
Embodiment 9	230.8	200.8	87.0
Embodiment 10	233.4	206.6	88.5
Embodiment 11	232.9	211.9	91.0
Embodiment 12	231.7	204.6	88.3
Embodiment 13	232.4	210.1	90.4
Embodiment 14	232.5	202.3	87.0

Embodiment 15	232.3	208.6	89.8	LU506345
Embodiment 16	242.8	218.3	89.9	
Embodiment 17	241.7	215.2	89.0	
Embodiment 18	242.1	214.8	88.7	
Embodiment 19	240.9	212.2	88.1	
Embodiment 20	240.7	211.8	88.0	
Embodiment 21	242.1	218.6	90.3	
Embodiment 22	238.9	205.6	86.4	
Embodiment 23	242.1	212.7	87.9	
Embodiment 24	216.2	195.6	90.5	
Embodiment 25	215.9	195.3	90.5	
Embodiment 26	216.8	194.7	89.8	
Embodiment 27	216.4	194.2	89.7	
Embodiment 28	215.4	188.6	87.6	
Embodiment 29	214.8	195.5	91.0	
Embodiment 30	215.7	187.2	86.8	
Embodiment 31	215.0	195.1	90.7	

[0167] From the data listed in Table 1:

[0168] It can be seen by comparing Embodiments 1/2/3 that the initial discharge gram capacity at 0.1C and the initial efficiency at 0.1C decline as the dosage of lithium carbonate increases, which may be caused by the reasons: a decomposition temperature of lithium carbonate is too high, with an increase in dosage, lithium ions cannot intercalate into the inside of a structure, and there is too much lithium carbonate with residual alkali on the surface;

[0169] It can be seen by comparing Embodiments 1/4/5 that as a primary sintering temperature rises, the gram capacity at 0.1C and the initial efficiency at 0.1C decline; and when the temperature reaches up to a particular temperature and then drops suddenly, N^{3+} is unstable perhaps due to the too high primary sintering temperature and undergoes a disproportionation reaction to break down into N^{2+} and N^4 again, leading to a low gram capacity and a low initial efficiency;

[0170] It can be seen by comparing two groups of data from Embodiments 2/6/7 and Embodiments 3/8/9 that either a too-large dosage of lithium carbonate or a too-high sintering temperature can cause a decline in gram capacity and initial efficiency;

[0171] It can be seen by comparing three groups of data from Embodiments 1/10/11, Embodiments 2/12/13 and Embodiments 3/14/15 that in step (4), a too-low molar ratio of lithium to nickel, cobalt and manganese can lead to a low gram capacity at 0.1C and a low initial efficiency at 0.1C; when the molar ratio reaches a certain ratio, if the gram capacity at 0.1C and the initial efficiency at 0.1C cannot be improved by increasing the molar ratio, it is

possibly because a too low molar ratio of lithium to nickel, cobalt and manganese and an incomplete internal structure lead to lithium-nickel mixing; and when the molar ratio reaches a certain ratio, the structure is complete, the lithium-nickel mixing has been effectively controlled, and the lithium-nickel mixing cannot be reduced by continuously increasing the molar ratio;

[0172] It can be seen by comparing three groups of data from Embodiments 24/26, Embodiments 2/6/8 and Embodiments 17/19 that as the nickel content increases, the higher the nickel content is, the larger the effect of the primary sintering temperature is, a Ni75 ternary material is least sensitive to the sintering temperature, a Ni90 ternary material is most sensitive to the sintering temperature, and it is possibly because the nickel content is higher, trivalent nickel undergoes a disproportionation reaction more easily;

[0173] It can be seen by comparing three groups of data from Embodiments 24/25, Embodiments 4/6/8 and Embodiments 18/19 that as the nickel content increases, the larger the dosage of the initially dosed lithium carbonate on the gram capacity of the material is, the higher the nickel content is, and the less the dosage of lithium carbonate is, which are caused by the reasons: the decomposition temperature of the lithium carbonate is higher, the higher the nickel content is, the larger the difficulty of lithium ions diffused to the inside of the structure is.

[0174] The above embodiments are only used to illustrate the technical solutions of the present invention, not to limit the present invention; although the present invention has been illustrated in detail by referring to the aforementioned embodiments, those of ordinary skill in the art should understand that: they can still make modifications to the technical solution recorded in each aforementioned embodiment, or make equivalent replacements to part of technical features thereof, but these modifications or replacements do not make the nature of the corresponding technical solution departing from the spirit and scope of the technical solution of each embodiment of the present application.

CLAIMS

1. A preparation method of a high-nickel ternary cathode material synthesized using lithium carbonate as a main lithium source, comprising the following steps:

5 (1) mixing a high-nickel ternary cathode material precursor, lithium carbonate and a metal oxide additive, wherein a molar ratio of a lithium element in the lithium carbonate to nickel, cobalt and manganese elements in the high-nickel ternary cathode material precursor is 0.70–0.90; and an added amount of the metal oxide additive accounts for 0.1–0.5 wt% of the mass of the high-nickel ternary cathode material precursor;

10 (2) carrying out sintering on the materials mixed in step (1), and carrying out natural cooling after the sintering;

(3) grinding and sieving the materials cooled in step (2) to obtain a primary intermediate product;

15 (4) mixing the primary intermediate product obtained in step (3) with lithium hydroxide in a certain ratio, wherein a molar ratio of the lithium element to the nickel, cobalt and manganese elements in the high-nickel ternary cathode material precursor is 1.02–1.10 after the mixing;

(5) carrying out sintering on the materials mixed in step (4), and carrying out natural cooling after the sintering;

20 (6) grinding and sieving the materials cooled in step (5) to obtain a secondary intermediate product;

(7) washing, filtering and drying the secondary intermediate product obtained in step (6);

(8) evenly mixing the material in step (7) with boron oxide and titanium oxide in a certain ratio; and

25 (9) carrying out sintering on the materials evenly mixed in step (8), and carrying out natural cooling after the sintering to obtain the high-nickel ternary cathode material.

2. The preparation method according to claim 1, wherein in step (1), the high-nickel ternary cathode material precursor is represented by a chemical formula of $\text{Ni}_x\text{Co}_y\text{Mn}_z(\text{OH})_2$, wherein $0.70 \leq x \leq 0.90$, $0.03 \leq y \leq 0.15$, $0.03 \leq z \leq 0.15$, and $x + y + z = 1.00$.

30 3. The preparation method according to claim 1 or claim 2, wherein the high-nickel ternary cathode material precursor in step (1) has a particle size D50 of 3–15 μm .

4. The preparation method according to claim 3, wherein in step (1), the metal oxide

additive is a combination of one or more of zirconia, tungsten oxide, titanium oxide and strontium oxide.

5 5. The preparation method according to claim 4, wherein in steps (2), (5) and (9), the sintering is carried out in an oxygen atmosphere furnace, and a volume content of oxygen is $\geq 90\%$.

6. The preparation method according to claim 1, wherein the sintering in step (2) is a gradient sintering: low-temperature sintering followed by high-temperature sintering; a temperature of the low-temperature sintering is $\leq 770\text{ }^{\circ}\text{C}$, and a temperature of the high-temperature sintering is $820\text{--}950\text{ }^{\circ}\text{C}$.

10 7. The preparation method according to claim 1, wherein in step (4), a molar ratio of the lithium element to the nickel, cobalt and manganese elements in the high-nickel ternary cathode material precursor is 1.05.

8. The preparation method according to claim 1, wherein in step (5), the sintering temperature is $740\text{--}830\text{ }^{\circ}\text{C}$.

15 9. The preparation method according to claim 1, wherein in step (8), an added amount of boron oxide and an added amount of titanium oxide account for 0.2% and 0.1% of the mass of the material in step (7) respectively.

10. A high-nickel ternary cathode material prepared by the preparation method according to any one of claims 1 to 9.

Ansprüche

1. Verfahren zur Herstellung eines ternären Kathodenmaterials mit hohem Nickelgehalt, das unter Verwendung von Lithiumcarbonat als Hauptlithiumquelle synthetisiert wird, dadurch gekennzeichnet, dass es folgende Schritte umfasst:

(1) Mischen eines ternären Kathodenmaterialvorläufers mit hohem Nickelgehalt, von Lithiumcarbonat und eines Metalloxidadditivs, wobei das Molverhältnis des Lithiumelements in dem Lithiumcarbonat zu dem Nickel-Kobalt-Manganelement in dem ternären Kathodenmaterialvorläufer mit hohem Nickelgehalt 0,70 bis 0,90 beträgt; und die zugegebene Menge des Metalloxidadditivs 0,1 bis 0,5 Gew.-% der Masse des ternären Kathodenmaterialvorläufers mit hohem Nickelgehalt ausmacht;

(2) Sintern des in Schritt (1) gemischten Materials und natürliches Abkühlen nach dem Sintern;

(3) Mahlen und Sieben des in Schritt (2) abgekühlten Materials, um ein primäres Zwischenprodukt zu erhalten;

(4) Mischen des in Schritt (3) erhaltenen primären Zwischenprodukts mit Lithiumhydroxid in einem bestimmten Verhältnis, wobei nach dem Mischen das Molverhältnis des Lithiumelements zu dem Nickel-Kobalt-Manganelement in dem ternären Kathodenmaterialvorläufer mit hohem Nickelgehalt 1,02 bis 1,10 beträgt;

(5) Sintern des in Schritt (4) gemischten Materials und natürliches Abkühlen nach dem Sintern;

(6) Mahlen und Sieben des in Schritt (5) abgekühlten Materials, um ein sekundäres Zwischenprodukt zu erhalten;

(7) Waschen, Filtern und Trocknen des in Schritt (6) erhaltenen sekundären Zwischenprodukts;

(8) Mischen des Materials aus Schritt (7) mit Boroxid und Titanoxid in einem bestimmten Verhältnis gut;

(9) Sintern des in Schritt (8) gut gemischten Materials und natürliches Abkühlen nach dem Sintern, um das ternäre Kathodenmaterial mit Nickelgehalt zu erhalten.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die chemische Formel des ternären Kathodenmaterialvorläufers mit hohem Nickelgehalt in Schritt (1) $\text{Ni}_x\text{Co}_y\text{Mn}_z(\text{OH})_2$ ist, wobei $0,70 \leq x \leq 0,90$, $0,03 \leq y \leq 0,15$, $0,03 \leq z \leq 0,15$ und $x + y + z = 1,00$.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, dass die Teilchengröße D50 des ternären Kathodenmaterialvorläufers mit hohem Nickelgehalt in Schritt (1) 3 bis 15 μm beträgt.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, dass das Metalloxidadditiv in Schritt (1) eines oder eine Kombination von mehreren von Zirkoniumoxid, Wolframoxid, Titanoxid und

Strontiumoxid ist.

5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, dass das Sintern in den Schritten (2), (5) und (9) in einem Ofen mit Sauerstoffatmosphäre mit einem Volumengehalt an Sauerstoff von $\geq 90\%$ durchgeführt wird.

5 6. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass das Sintern in Schritt (2) ein Gradientensintern ist, wobei das Sintern zuerst bei einer niedrigen Temperatur und dann bei einer hohen Temperatur durchgeführt wird, wobei die niedrige Temperatur $\leq 770^\circ\text{C}$ beträgt, und die hohe Temperatur 820 bis 950°C beträgt.

10 7. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass das Molverhältnis des Lithiumelements zu dem Nickel-Kobalt-Manganelement in dem ternären Kathodenmaterialvorläufer mit hohem Nickelgehalt in Schritt (4) 1,05 beträgt.

8. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Temperatur des Sinterns in Schritt (5) 740 bis 830°C beträgt.

15 9. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die zugegebenen Mengen von Boroxid und Titanoxid in Schritt (8) 0,2 bzw. 0,1 Gew.-% der Masse des Materials aus Schritt (7) ausmachen.

10. Ternäres Kathodenmaterial mit hohem Nickelgehalt, das nach dem Verfahren gemäß einem der Ansprüche 1 bis 9 hergestellt ist.

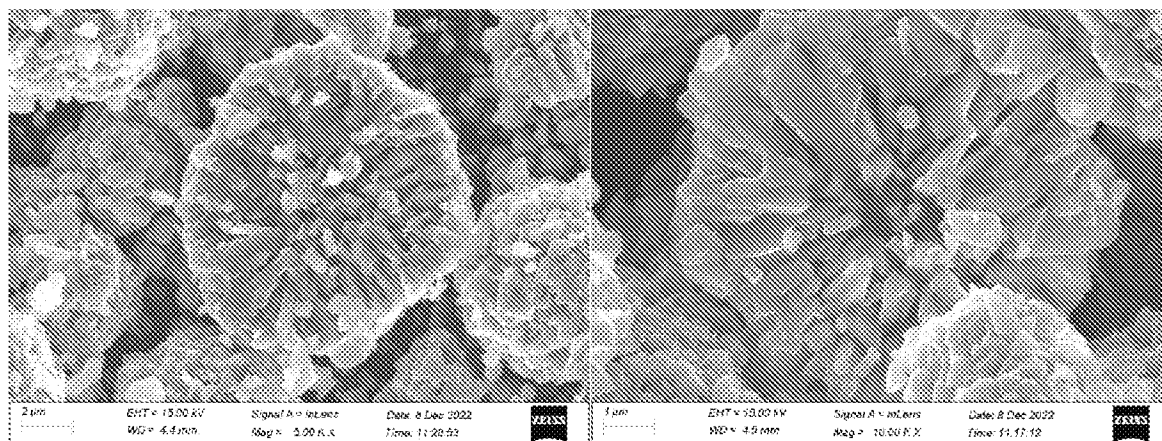


FIG. 1

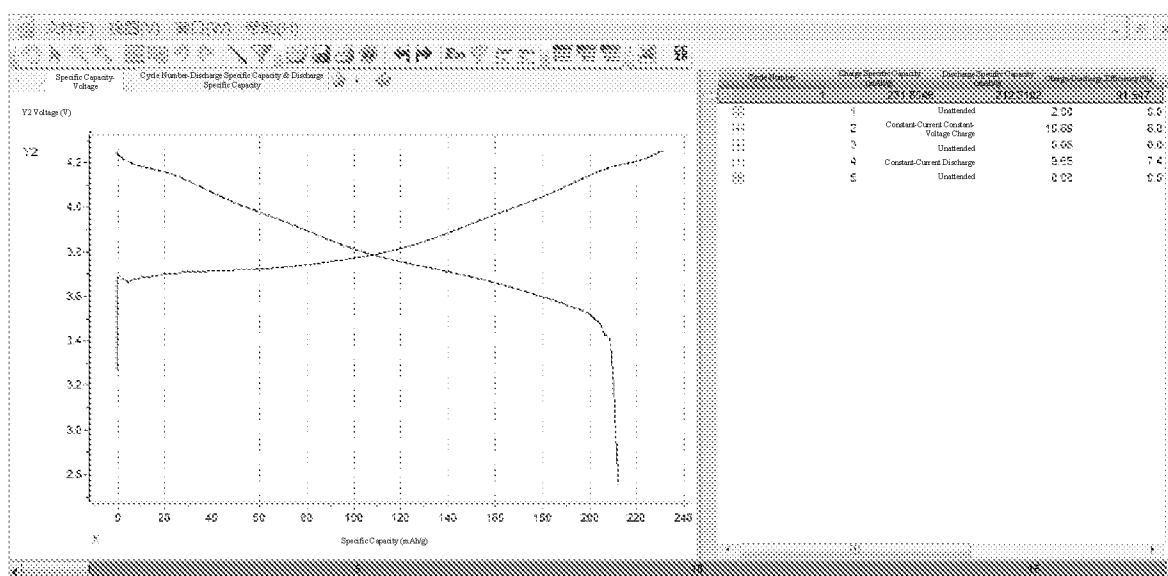


FIG. 2

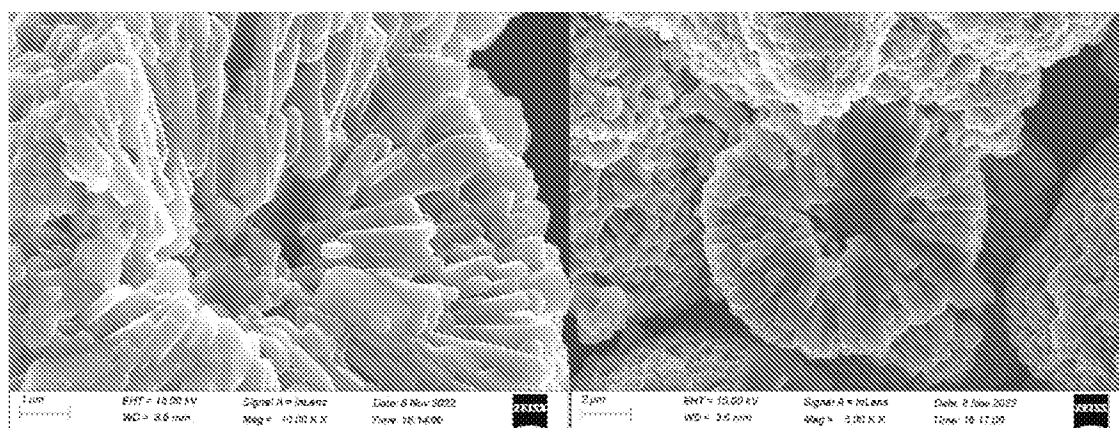


FIG. 3

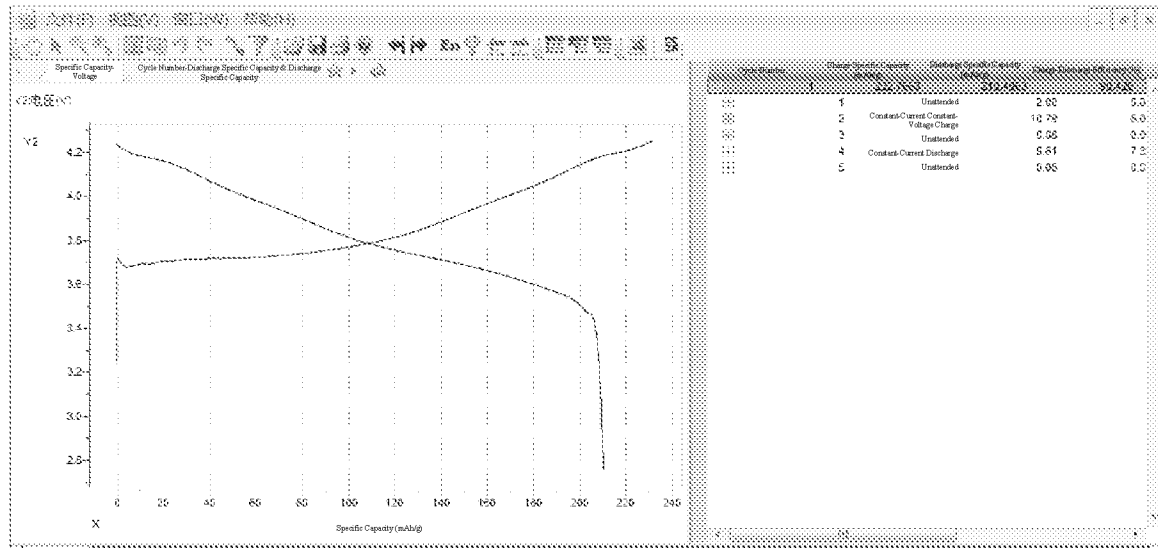


FIG. 4

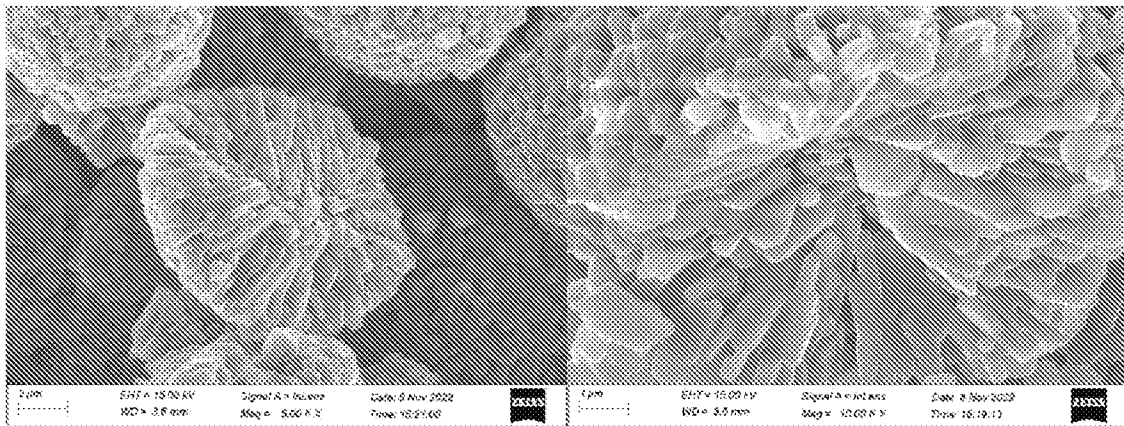


FIG. 5

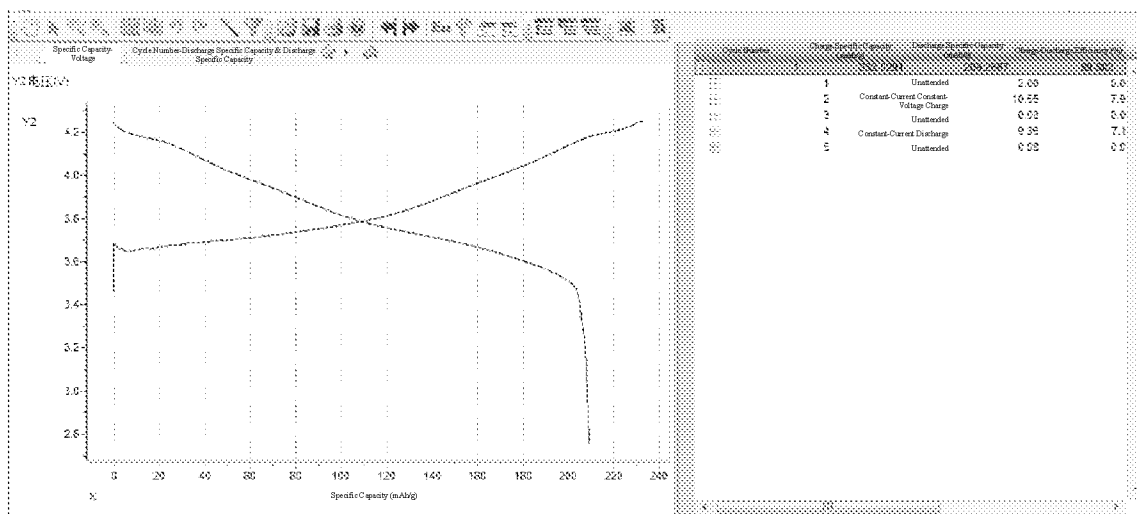


FIG. 6