(19) LE GOUVERNEMENT DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie

(11) N° de publication : **LU101837**

(12) **BREVET D'INVENTION** **B1**

(21) N° de dépôt: LU101837

(22) Date de dépôt: 05/06/2020

(51) Int. Cl.:
C01G 53/00, H01M 4/1391, H01M 4/36, H01M 4/525, H01M 4/62

(30) Priorité:
06/06/2019 CN CN201910490578.2

(43) Date de mise à disposition du public: 07/12/2020

(47) Date de délivrance: 18/02/2021

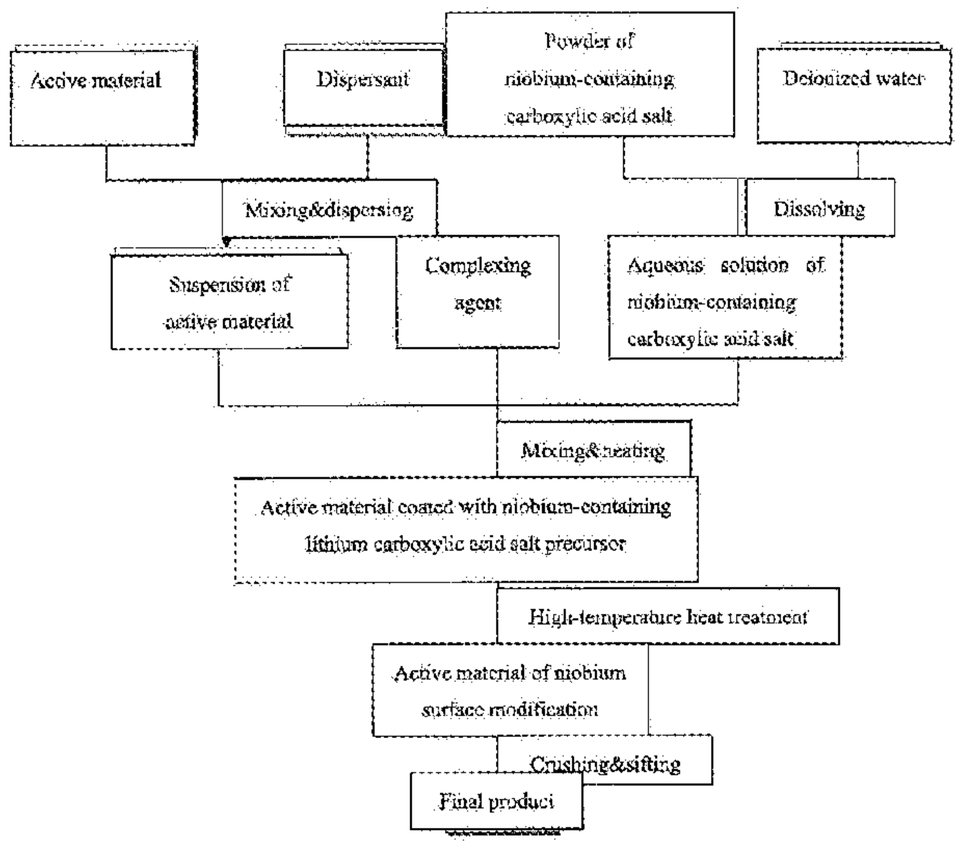
(73) Titulaire(s):
ENERGY RESEARCH INSTITUTE OF SHANDONG ACADEMY OF SCIENCES – 250014 Jinan, Shandong Province (Chine)

(72) Inventeur(s):
WANG Bo – 250014 Jinan, Shandong Province (Chine), CAI Feipeng – 250014 Jinan, Shandong Province (Chine), QIN Xianzhong – 250014 Jinan, Shandong Province (Chine), JIANG Bo – 250014 Jinan, Shandong Province (Chine), JIANG Guilin – 250014 Jinan, Shandong Province (Chine)

(74) Mandataire(s):
GIERLICH & PISCHITZIS Partnerschaft mbB – 60594 Frankfurt am Main (Allemagne)

(54) **Method for Modifying High-nickel Positive Electrode Material.**

(57) A method for modifying a high-nickel positive electrode material, wherein a high-nickel laminated positive electrode material is processed by using a carboxylic acid derivative of niobium such that lithium residue on the surface of the material reacts with the carboxylic acid derivative of niobium and generates Li(NbO(C2O4)2)nH2O, and then different surface reconstruction layers are formed on the surface of the material after high temperature heat treatment, as a result, the cycling performance and discharge performance of the material are significantly improved.



Specification

Method for Modifying High-nickel Positive Electrode Material

Technical Field

The invention relates to a method for performing surface coating for a high-nickel positive electrode material and an electrode prepared by using the method, belonging to the technical field of lithium batteries.

Background

During the preparation of high-nickel electrode materials, excessive lithium is usually required for suppressing cation mixing and lithium volatilization. However, the addition of excessive lithium causes the following problems: 1) after the product is sintered, excessive lithium remains on the surface, and can easily react with H_2O and CO_2 in the air, forming LiOH and Li_2CO_3 residues; 2) in the mixing process of preparing the electrode, Lithium residue reacts with the adhesive solvent N-methyl pyrrolidone, which causes "gel" phenomenon and makes mixing difficult; 3) when the battery is operated for a long period of time, the lithium residue can react with the organic electrolyte, which generates CO_2, N_2, O_2 and other gases and causes "flatulence" of batteries; and 4) LiOH and Li_2CO_3 are electrochemically inert materials with very low ion conductivity, which hinders the transmission of ions and electrons and affects the ratio performance of the materials. Therefore, when preparing high-nickel laminated materials, measures need to be taken to reduce the amount of residual lithium on the surface. "Water washing--secondary heating" is a common method for removing lithium residues in the prior art. However, when being washed by a large amount of water, the surface structure of the material will be damaged, which reduces capacity and cycling stability.

On the other hand, since Ni^{4+} in high-nickel electrode materials is very unstable, $Ni^{4+} \rightarrow Ni^{2+}$ reaction may easily occur between the high-nickel electrode material and the organic electrolyte at high temperature and high voltage; moreover, Ni^{2+} and Li^{+} have similar ionic radius, so the migration from the transition metal status to Li status may easily occur, which results in "cation mixing". In order to suppress the reaction between active materials and the organic electrolyte, the method of coating with inert materials, such as Al_2O_3, MgO, AlF_3, etc., is usually adopted, but the ion conductivities of these materials

are very low, which affects the ratio performance of the materials. Another treatment is to coat with lithium conductive materials, such as Li_3PO4, Li_2TiO_3, Li_3VO_4, etc. This method can isolate the organic electrolyte from the active surface, but requires the addition of a lithium source, which cannot reduce the content of residual lithium on the surface.

Therefore, the high-nickel positive electrode material needs to reduce the residual lithium content and provide a physical protective layer; meanwhile, the surface layer has a high ion conductivity.

CN102244231A provides a method for cladding surfaces of an anode active material and/or the anode and methods for manufacturing the anode and a battery, wherein gas-phase precursors are used to pass into a reactor alternately, and, via chemical adsorption and chemical reaction, a deposited film is formed on the substrate, which is to be deposited and located in the reactor, as a result, the cycling performance and specific capacity of the lithium-ion battery are significantly improved, and electrode materials are more stable.

CN103339062A relates to a lithium spinel-type lithium manganese-based composite oxide (LMO) used as a positive electrode active material for lithium batteries, wherein the crystallite size of LMO is 250~350nm, the distortion is at most 0.085, and the specific surface area growth rate is at most 10.0% when it is placed in water with a temperature of 25°C and a pH value of 7 to go through an ultrasonic dispersion with an ultrasonic intensity of 40W for 600 seconds, as a result, LMO is capable of preventing output power decrease following repeated charging and discharging at high temperature.

Summary of the Invention

The present invention provides a surface modification method, which uses a carboxylic acid derivative of niobium as a reactant so as to convert and utilize the surface lithium residue, to regulate the reaction heat treatment temperature, and to generate a surface reconstruction layer on the surface of the high-nickel laminated material, thereby reducing the content of lithium residue and enhancing the ratio and cycling stability of the material.

In the present invention, a carboxylic acid derivative of niobium is used for treating the high-nickel laminated positive electrode material so that the lithium residue on the material surface reacts with the carboxylic acid derivative of niobium, and then forms a surface reconstruction layer on the material surface after high temperature heat treatment, thereby improving the performance of the material. It is found by the inventor that, when the heat treatment temperature is 500-750°C, the structure of the surface

reconstruction layer changes with the temperature and physical protective layers with different phases are generated. Therefore, heat treatment temperature may be appropriately chosen according to the performance necessities.

The present invention provides a method of preparing a high-nickel positive electrode material, including the following steps of:

(1) mixing a high-nickel laminated material with a dispersant, and stirring intensely to prepare a suspension of the high-nickel laminated material;

(2) dissolving a carboxylic acid derivative of niobium into deionized water so as to prepare an aqueous solution of carboxylic acid derivative of niobium;

(3) mixing the suspension of the high-nickel laminated material with the aqueous solution of carboxylic acid derivative of niobium, and adding a complexing agent, wherein the mass ratio between the high-nickel laminated material and the carboxylic acid derivative of niobium is 20-100; a ratio of the amount of the substance between the complexing agent and the carboxylic acid derivative of niobium is 1-5;

(4) heating and vigorously stirring the mixture obtained in Step (3) at 90-150°C till the solvent is completely volatilized so as to obtain a solid powder of a high-nickel laminated material coated with a carboxylic acid lithium niobium precursor;

(5) performing a heat treatment for the solid powder of high-nickel laminated material coated with carboxylic acid lithium niobium in an oxidizing atmosphere so as to obtain a surface-modified high-nickel laminated material; and

(6) crushing and sifting the surface-modified material so as to obtain the high-nickel positive electrode material.

The molecular formula of said high-nickel laminated material is $LiNi_{1-x}M_x$, wherein M is one of Co, Mn and Al, and x is 0.01-0.4, preferably x is 0.1-0.4.

The carboxylic acid derivative of niobium is a carboxylic acid salt of niobium with a small carbon atom number, preferably a monobasic or dibasic carboxylic acid niobium salt having 1-5 carbon atoms, and more preferably niobium oxalate or ammonium niobium oxalate.

The dispersant is one or more of water, ethanol, ethylene glycol, propylene glycol, propanol, and butanol.

The complexing agent is one or more of citric acid, tartaric acid, EDTA and ammonia water.

The mixing method may be one of the following: directly mixing the active material suspension and the carboxylic acid derivative of niobium, slowly adding the active material suspension to the solution of the carboxylic acid derivative of niobium by means of a metering pump, and slowly adding the solution of the carboxylic acid derivative of niobium to the active material suspension by means of a metering pump.

In Step (1), a mass ratio of the high-nickel laminated material to the dispersant is 0.01-0.5, preferably 0.1-0.3.

In Step (2), a mass ratio of the carboxylic acid derivative of niobium to the deionized water is 0.01-0.3, preferably 0.05-0.2.

Step (4) is carried out at 0.01-0.5MPa, preferably 0.5-0.3MPa.

In Step (5), the oxidizing atmosphere is an oxygen or air atmosphere, the heat treatment temperature is 450-900°C, and the heat treatment time is 1-12h; the preferable heat treatment temperature is 500-800°C, and the treatment time is 4-8h.

The other aspect of the present invention also discloses a high-nickel positive electrode material prepared by said method and its application to batteries.

Beneficial Effects of the Invention:

According to the present invention, a high-nickel laminated positive electrode material is processed by using the carboxylic acid derivative of niobium such that lithium residue on the surface of the material reacts with the carboxylic acid derivative of niobium, and then different surface reconstruction layers are formed on the surface of the material after high temperature heat treatment, as a result, the cycling performance and discharge performance of the material are significantly improved.

Description of the Drawing

Fig. 1 is a schematic diagram showing the preparation process of the electrode material.

Embodiments

With reference to the drawing of the description and the Examples, the present invention will be further limited as follows.

Example 1

Mix 10g of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM-1) with a certain amount of absolute ethanol to prepare slurry of active material. Dissolve 0.1g of niobium oxalate (NO) in 10mL of deionized water to prepare an aqueous solution of niobium oxalate. Slowly and dropwise add the aqueous solution of niobium oxalate to the slurry of NCM-1, and add a small amount of citric acid, and then continuously stir and heat the mixture and keep the temperature of the slurry at 60°C. After adding the solution of niobium oxalate dropwise, raise the temperature to 80°C, and continue stirring the mixture till the solvent is completely volatilized. After volatilization of the solvent, dry the obtained powder at 100°C for 4h, and then perform heat treatment at 500°C for 5h in an oxygen atmosphere so as to obtain the final product NCM-NO-1. The residual lithium contents of unmodified product and NO modified products are shown in Table 1; the contrast of ratio performances of the products before and after modification are shown in Table 2; and the contrast of cycling performances of the products before and after modification are shown in Table 3.

Table 1

	LiOH, ppm	Li_2CO_3, ppm	Total alkali content, ppm
NCM	2452	2958	1275
NCM-NO-1	1424	2540	896

Table 2

	0.1C, $mAh \cdot g^{-1}$	1C, $mAh \cdot g^{-1}$	2C, $mAh \cdot g^{-1}$	5C, $mAh \cdot g^{-1}$	10C, $mAh \cdot g^{-1}$
NCM	190.2	169.5	**155.3**	125.3	102.3
NCM-NO-1	195.4	175.3	164.9	145.2	130.8

Table 3

	Specific discharge capacity of the first cycle $mAh \cdot g^{-1}$	Specific discharge capacity of 100 cycles, $mAh \cdot g^{-1}$	Capacity retention ratio of 100 cycles, %
NCM-1	169.5	136.7	80.6
NCM-NO-1	175.3	151.3	86.3

Example 2

Mix 10g of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM-1) with a certain amount of absolute ethanol to prepare slurry. Dissolve 0.2g of ammonium niobium oxalate (ANO) in 15mL of deionized water to prepare an aqueous solution of ammonium niobium oxalate. Slowly and dropwise add the ANO aqueous solution to the slurry of NCM-1, and add a certain amount of EDTA, and then continuously stir and heat the mixture and keep the reaction temperature of the slurry at 60°C. After adding the solution of ammonium niobium oxalate (ANO) dropwise, raise the temperature to 80°C, and continue stirring the mixture till the solvent is completely volatilized. Dry the powder at 100°C for 4h, and then perform heat treatment at 700°C for 5h in an oxygen atmosphere so as to obtain the final product NCM-ANO-2. The residual lithium contents of unmodified product and ANO modified products are shown in Table 4, and the contrast of electrical properties of the products before and after modification are shown in Tables 5 and 6..

Table 4

	LiOH, ppm	Li_2CO_3, ppm	Total alkali content, ppm
NCM-1	2452	2958	1275
NCM-ANO-2	952	1864	630

Table 5

	0.1C, $mAh \cdot g^{-1}$	1C, $mAh \cdot g^{-1}$	2C, $mAh \cdot g^{-1}$	5C, $mAh \cdot g^{-1}$	10C, $mAh \cdot g^{-1}$
NCM-1	190.2	169.5	155.3	125.3	102.3
NCM-ANO-2	193.2	176.1	167.2	155.2	140.2

Table 6

	Specific capacity of the first cycle, $mAh \cdot g^{-1}$	Specific capacity of 100 cycles, $mAh \cdot g^{-1}$	Specific capacity retention ratio, %
NCM-1	169.5	136.7	80.6
NCM-ANO-2	176.3	155.8	88.4

Example 3

Mix 10g of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$(NCM-2) with a certain amount of absolute ethanol to prepare slurry. Dissolve 0.2g of niobium oxalate (NO) in 10mL of deionized water to prepare an NO aqueous solution.

Slowly and dropwise add an NO aqueous solution to the slurry of NCM-2, and add a small amount of citric acid, and then continuously stir and heat the mixture and keep the temperature of the slurry at 60°C. After adding the NO solution dropwise, maintain the temperature at 60°C, and continue stirring the mixture till the solvent is completely volatilized. Perform vacuum drying for the powder at 120°C for 4h in a vacuum drying oven, and then perform heat treatment at 700°C for 5h in an oxygen atmosphere so as to obtain the final product NCM-NO-3. The residual lithium contents of unmodified product and NO modified products, as well as the contrast of their electrical properties are shown in Tables 7-9.

Table 7

	LiOH, ppm	Li_2CO_3, ppm	Total alkali content, ppm
NCM-2	4532	5486	2360
NCM-NO-3	1751	2824	1045

Table 8

	0.1C, $mAh \cdot g^{-1}$	1C, $mAh \cdot g^{-1}$	2C, $mAh \cdot g^{-1}$	5C, $mAh \cdot g^{-1}$	10C, $mAh \cdot g^{-1}$
NCM-2	192.3	168.2	152.1	145.8	128.3
NCM-NO-3	193.8	172.1	165.2	155.7	143.2

Table 9

	Specific capacity of the first cycle, $mAh \cdot g^{-1}$	Specific capacity of 100 cycles, $mAh \cdot g^{-1}$	Capacity retention ratio of 100 cycles, %
NCM-2	168.5	136.8	81.2
NCM-NO-3	173.1	154.9	89.5

Example 4

Dissolve 10g of ammonium niobium oxalate (ANO) in 10mL of water and heat the solution to 60°C. Slowly pour 10g of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCM-3) powder into the ANO solution, add a small amount of EDTA, continuously stir for 30min, and then intensely stir at 80°C till the solvent is completely volatilized. After volatilization of the solvent, transfer the powder into a vacuum drying oven to dry it at 120°C for 4h, and then perform high-temperature heat treatment at 750°C for 6h in an oxygen atmosphere

so as to obtain the final product NCM-ANO-4. The residual lithium contents of unmodified product and ANO modified products, as well as the contrast of their electrical properties are shown in Tables 10-12.

Table 10

	0.1C, $mAh \cdot g^{-1}$	1C, $mAh \cdot g^{-1}$	2C, $mAh \cdot g^{-1}$	5C, $mAh \cdot g^{-1}$	10C, $mAh \cdot g^{-1}$
NCM-3	190.5	170.2	158.1	146.8	137.8
NCM-ANO-4	191.8	172.1	165.2	158.7	143.2

Table 11

	Specific capacity of the first cycle, $mAh \cdot g^{-1}$	Specific capacity of 100 cycles, $mAh \cdot g^{-1}$	Capacity retention ratio of 100 cycles, %
NCM-3	168.5	135.3	80.3
NCA-ANO-4	173.1	154.9	89.5

Table 12

	LiOH, ppm	Li_2CO_3, ppm	Total alkali content, ppm
NCM-3	3414	4843	1275
NCA-ANO-4	1249	2657	867

The above examples exemplarily illustrate the technical effects and the implementation process of the present invention only. However, one skilled in the art should understand that any changes in form and details, which are made on such a basis and do not exceed the scope of protection of the claims, belong to the scope of protection of the present invention.

Comparative Example 1

Mix LiNi0.6Co0.2Mn0.2O2 (NCM-1) with 1wt% of Al_2O_3 through ball mill, and perform heat treatment at 750°C under O_2 atmosphere for 6h, thereby obtaining Al_2O_3-modified high-nickel ternary NCM-1 material (NCM-1-Al).

Table 13

	LiOH, ppm	Li_2CO_3, ppm	Total alkali content, ppm
NCM-1	2452	2958	1275

NCM-1-Al	1424	2540	896

Table 14

	0.1C, $mAh \cdot g^{-1}$	1C, $mAh \cdot g^{-1}$	2C, $mAh \cdot g^{-1}$	5C, $mAh \cdot g^{-1}$	10C, $mAh \cdot g^{-1}$
NCM-1	169.4	153.5	137.4	110.3	95.2
NCM-1-Al	167.8	152.2	140.5	122.5	113.1

Table 15

	1C Capacity of the first cycle, $mAh \cdot g^{-1}$	1C Capacity after 100 cycles, $mAh \cdot g^{-1}$	1C Capacity retention ratio after 100 cycles, %
NCM-1	168.2	131.5	78.1
NCM-1-Al	166.5	143.2	86.0

Comparative Example 2

Mix 10g of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM-1) with a certain amount of absolute ethanol to prepare slurry of active material. Dissolve 0.1g of niobium oxalate (NO) in 10mL of deionized water to prepare an aqueous solution of niobium oxalate. Slowly and dropwise add the NO aqueous solution to the slurry of NCM-1, and add a small amount of citric acid, and then continuously stir and heat the mixture and keep the temperature of the slurry at 60°C. After adding the NO solution dropwise, raise the temperature to 80°C, and continue stirring the mixture till the solvent is completely volatilized. After volatilization of the solvent, dry the obtained powder at 100°C for 4h, and then perform heat treatment at 400°C for 5h in an oxygen atmosphere so as to obtain the final product NCM-NO-1-400. The residual lithium contents of unmodified product and NO modified products, as well as the contrast of their electrical properties are shown in Tables 16-18.

Table 16

	LiOH, ppm	Li_2CO_3, ppm	Total alkali content, ppm
NCM-1	2452	2958	1275
NCM-ANO-1-400	1850	2750	1060

Table 17

	1C Capacity of the first cycle $mAh \cdot g^{-1}$	1C Capacity of 100 cycles $mAh \cdot g^{-1}$	1C Cycling retention ratio of 100 cycles, %
NCM-1	168.2	131.5	78.1
NCM-ANO-1-400	165.5	128.2	77.5

Table 18

	0.1C, $mAh \cdot g^{-1}$	1C, $mAh \cdot g^{-1}$	2C, $mAh \cdot g^{-1}$	5C, $mAh \cdot g^{-1}$	10C, $mAh \cdot g^{-1}$
NCM-1	190.2	169.5	155.3	125.3	102.3
NCM-NO-1-400	189.5	166.1	157.7	129.4	110.8

Comparative Example 3

Mix 10g of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM-1) with a certain amount of absolute ethanol to prepare slurry of active material. Dissolve 0.1g of niobium oxalate (NO) in 10mL of deionized water to prepare an aqueous solution of niobium oxalate. Slowly and dropwise add the NO aqueous solution to the slurry of NCM622, and add a small amount of citric acid, and then continuously stir and heat the mixture and keep the temperature of the slurry at 60°C. After adding the NO solution dropwise, raise the temperature to 80°C, and continue stirring the mixture till the solvent is completely volatilized. After volatilization of the solvent, dry the obtained powder at 100°C for 4h, and then perform heat treatment at 900°C for 5h in an oxygen atmosphere so as to obtain the final product NCM-NO-1-900. The residual lithium contents of unmodified product and NO modified products, as well as the contrast of their electrical properties are shown in Tables 19-21.

Table 19

	LiOH, ppm	Li_2CO_3, ppm	Total alkali content, ppm
NCM-1	2452	2958	1275
NCM-ANO-1-900	1253	1630	673

Table 20

	1C Capacity of the	1C Capacity of 100	1C Capacity retention

	first cycle, $Ah \cdot g^{-1}$	cycles, $Ah \cdot g^{-1}$	ratio of 100 cycles, %
NCM-1	168.2	131.5	78.1
NCM-ANO-1-900	170.5	145.9	85.6

Table 21

	0.1C, $mAh \cdot g^{-1}$	1C, $mAh \cdot g^{-1}$	2C, $mAh \cdot g^{-1}$	5C, $mAh \cdot g^{-1}$	10C, $mAh \cdot g^{-1}$
NCM-1	190.2	169.5	155.3	125.3	102.3
NCM622-1-900	189.5	172.1	158.7	135.4	125.8

Comparative Example 1 shows that the ratio performance and cycling stability, especially the ratio performance, of NO modified products are better than those of Al_2O_3 modified products; baased on the contrast between Example 1 and Comparative Examples 2 and 3, NCM-1, which is modified by 1wt% of NO, has better lithium residue removal and electrochemical performance when the treatment temperature ia 500°C, because, when the heat treatment temperature is low, the formed Li-Nb oxide precursor cannot be completely decomposed, and, when the heat treatment temperature is high, the thickness of the surface Li_3NbO_3 phase is large, which can effectively remove lithium residue and significantly improve cycling stability but has little effect on ratio performance enhancement.

Claims

1.A method of preparing a high-nickel positive electrode material, including the following steps of:

(1) mixing a high-nickel laminated material with a dispersant, and stirring intensely to prepare a suspension of the high-nickel laminated material;

(2) dissolving a carboxylic acid derivative of niobium into deionized water so as to prepare an aqueous solution of carboxylic acid derivative of niobium;

(3) mixing the suspension of the high-nickel laminated material with the aqueous solution of carboxylic acid derivative of niobium, and adding a complexing agent, wherein the mass ratio between the high-nickel laminated material and the carboxylic acid derivative of niobium is 20-100; a ratio of the amount of the substance between the complexing agent and the carboxylic acid derivative of niobium is 1-5;

(4) heating and vigorously stirring the mixture obtained in Step (3) at 90-150°C till the solvent is completely volatilized so as to obtain a solid powder of a high-nickel laminated material coated with a carboxylic acid lithium niobium precursor;

(5) performing a heat treatment for the solid powder of high-nickel laminated material coated with carboxylic acid lithium niobium in an oxidizing atmosphere so as to obtain a surface-modified high-nickel laminated material; and

(6) crushing and sifting the surface-modified material so as to obtain the high-nickel positive electrode material.

2. The method according to claim 1, wherein the molecular formula of said high-nickel laminated material in step 1) is $LiNi_{1-x}M_x$, wherein M is one of Co, Mn and Al, and x is 0.01-0.4, preferably x is 0.1-0.3.

3. The method according to claim 1, wherein the dispersant is one or more of water, ethanol, ethylene glycol, propylene glycol, propanol, and butanol; the complexing agent is one or more of citric acid, tartaric acid, EDTA and ammonia water.

4. The method according to claim 1, wherein the carboxylic acid derivative of niobium is a carboxylic acid salt of niobium with a small carbon atom number, preferably a monobasic or dibasic carboxylic acid niobium salt having 1-5 carbon atoms, and more preferably niobium oxalate or ammonium niobium oxalate.

5. The method according to claim 1, wherein the mixing method may be one of the following: directly mixing the active material suspension and the carboxylic acid derivative of niobium, slowly adding the active material suspension to the solution of the carboxylic acid derivative of niobium by means of a metering pump, and slowly adding the solution of the carboxylic acid derivative of niobium to the active material suspension by means of a metering pump.

6. The method according to claim 1, wherein in Step (1), a mass ratio of the high-nickel laminated material to the dispersant is 0.01-0.5, preferably 0.1-0.3.

7. The method according to claim 1, wherein in Step (2), a mass ratio of the carboxylic acid derivative of niobium to the deionized water is 0.01-0.3, preferably 0.05-0.2.

8. The method according to claim 1, wherein Step (4) is carried out at 0.01-0.1MPa, preferably 0.05-0.1MPa.

9. The method according to claim 1, wherein in Step (5), the oxidizing atmosphere is an oxygen or air atmosphere, the heat treatment temperature is 450-900°C, and the heat treatment time is 1-12h; the preferable heat treatment temperature is 500-800°C, and the treatment time is 4-8h.

10 A high-nickel positive electrode material prepared by the method according any of the claims 1-9.

1. Ein Verfahren zur Herstellung eines positiven Elektrodenmaterials mit hohem Nickelgehalt, einschließlich der folgenden Schritte:

(1) Mischen eines laminierten Materials mit hohem Nickelgehalt mit einem Dispergiermittel und intensives Rühren, um eine Suspension des laminierten Materials mit hohem Nickelgehalt herzustellen;

(2) Auflösen eines Carbonsäurederivats von Niob in entionisiertem Wasser, um eine wässrige Lösung des Carbonsäurederivats von Niob herzustellen;

(3) Mischen der Suspension des laminierten Materials mit hohem Nickelgehalt mit der wässrigen Lösung des Carbonsäurederivats von Niob und Hinzufügen eines Komplexbildners, wobei das Massenverhältnis zwischen dem laminierten Material mit hohem Nickelgehalt und dem Carbonsäurederivat von Niob 20 -100 beträgt; wobei ein Verhältnis der Substanzmenge zwischen dem Komplexbildner und dem Carbonsäurederivat von Niob 1-5 beträgt;

(4) Erhitzen und kräftiges Rühren der in Schritt (3) erhaltenen Mischung bei 90-150°C, bis das Lösungsmittel vollständig verflüchtigt ist, um ein festes Pulver eines laminierten Materials mit hohem Nickelgehalt, das mit einem Carbonsäure-Lithium-Niob-Precursor beschichteten ist, zu erhalten;

(5) Durchführen einer Wärmebehandlung für das feste Pulver des laminierten Materials mit hohem Nickelgehalt, das mit dem Carbonsäure-Lithium-Niob-Precursor beschichteten ist, in einer oxidierenden Atmosphäre, um ein oberflächenmodifiziertes laminiertes Material mit hohem Nickelgehalt zu erhalten; und

(6) Zerkleinern und Sieben des oberflächenmodifizierten Materials, um das positive Elektrodenmaterial mit hohem Nickelgehalt zu erhalten.

2. Verfahren nach Anspruch 1, wobei die Molekülformel des laminierten Materials mit hohem Nickelgehalt in Schritt 1) $LiNi_{1-x}M_x$ ist, wobei M eines von Co, Mn und wobei Al ist und x 0,01 bis 0,4, wobei vorzugsweise ist x 0,1-0,3.

3. Verfahren nach Anspruch 1, wobei das Dispergiermittel eines oder mehrere von Wasser, Ethanol, Ethylenglykol, Propylenglykol, Propanol und Butanol ist; Der Komplexbildner ist eine oder mehrere von Zitronensäure, Weinsäure, EDTA und Ammoniakwasser.

4. Verfahren nach Anspruch 1, wobei das Carbonsäurederivat von Niob ein Carbonsäuresalz von Niob mit einer kleinen Kohlenstoffatomzahl ist, vorzugsweise ein einbasiges oder zweibasisches Carbonsäure-Niob-Salz mit 1-5 Kohlenstoffatomen und bevorzugter Nioboxalat oder Ammoniumniobiumoxalat.

5. Verfahren nach Anspruch 1, wobei das Mischverfahren eines der folgenden sein kann: direktes Mischen der Suspension des aktiven Materials und des Carbonsäurederivats von Niob , langsames Hinzufügen der Suspension des aktiven Materials zu der Lösung des Carbonsäurederivats von Niob mittels einer Dosierpumpe und langsame Zugabe der Lösung des Carbonsäurederivats von Niob zu der Suspension des aktiven Materials mittels einer Dosierpumpe.

6. Verfahren nach Anspruch 1, wobei in Schritt (1) ein Massenverhältnis des laminierten Materials mit hohem Nickelgehaltzum Dispergiermittel 0,01 bis 0,5, vorzugsweise 0,1 bis 0,3 beträgt.

7. Verfahren nach Anspruch 1, wobei in Schritt (2) ein Massenverhältnis des Carbonsäurederivats von Niob zu dem entionisierten Wasser 0,01 bis 0,3, vorzugsweise 0,05 bis 0,2 beträgt.

8. Verfahren nach Anspruch 1, wobei Schritt (4) bei 0,01-0,1 MPa durchgeführt wird , vorzugsweise 0,05 bis 0,1 MPa.

9. Verfahren nach Anspruch 1, wobei in Schritt (5) die oxidierende Atmosphäre eine Sauerstoff- oder Luftatmosphäre ist, die Wärmebehandlungstemperatur 450 bis 900°C beträgt und die Wärmebehandlungszeit 1 bis 12 Stunden beträgt; Die bevorzugte Wärmebehandlungstemperatur beträgt 500-800 ° C und die Behandlungszeit 4-8 Stunden.

10 Positives Elektrodenmaterial mit hohem Nickelgehalt, hergestellt nach dem Verfahren nach einem der Ansprüche 1 bis 9.

Drawing

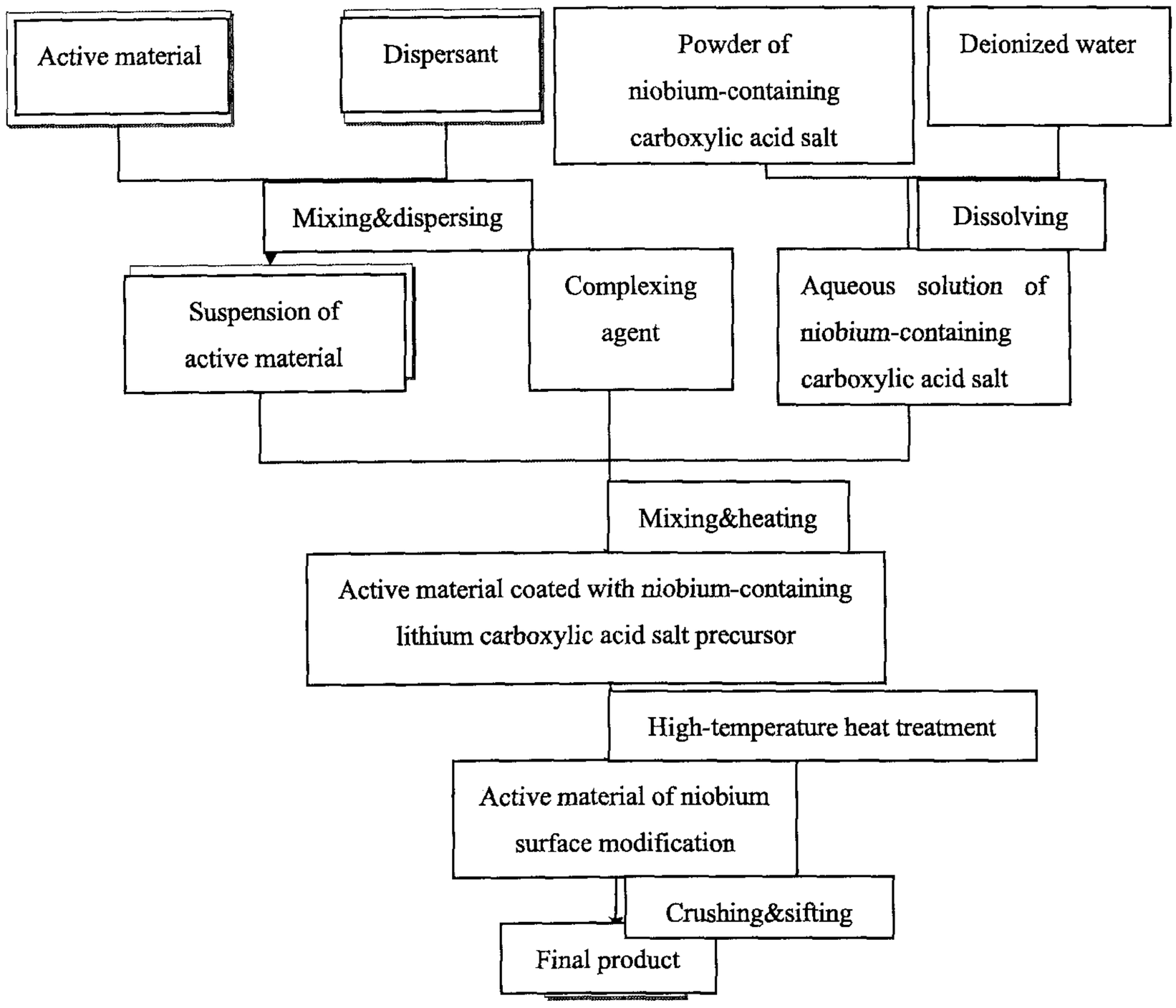


FIG. 1