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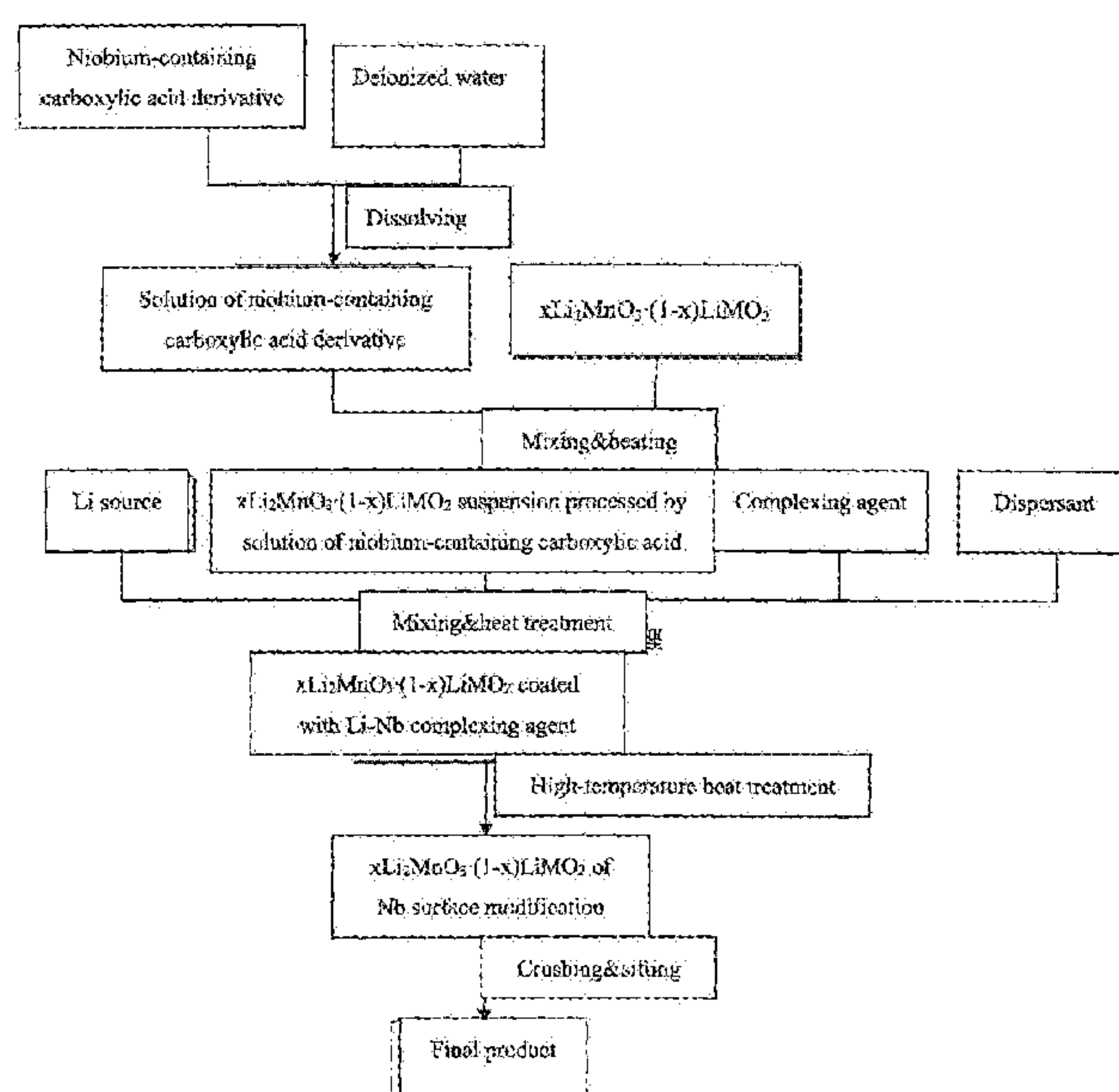
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Lithium-rich Manganese-based Electrode Material and Preparation Method.

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A preparation method of a lithium-rich manganese-based positive electrode material, including the following steps of: (1) dissolving a carboxylic acid derivative of niobium in deionized water to prepare a solution with a pH value of 1~3; (2) mixing a lithium-rich manganese-based material with the solution of the carboxylic acid derivative of niobium, and stirring and heating the mixture to a temperature of 55-80°C, preferably 60-65°C, to form a suspension; (3) adding a lithium source, a complexing agent and a dispersant into the suspension according to a molar ratio of 1:1-3:0.01-0.5, performing heating at a temperature of 60-100°C for 2-10 h to form a lithium-rich manganese-based material coated with a Li-Nb precursor; and (4) calcinating the lithium-rich manganese-based material, which is obtained in Step (3) and coated with Li-Nb precursor, at a temperature of 500-900°C for 5-15 h to obtain a manganese-based positive electrode material. By using the mild acidity of the solution of the carboxylic acid derivative of niobium, this method constructs Li⁺/H⁺ structure defects at the surface of the lithium-rich manganese-based material, and constructs an "Nb-doped/LiNbO₃-coated" dual-shell surface reconstruction layer via the addition of the lithium source and the high-temperature solid-phase reaction, thereby significantly improving the electrochemical performance of the lithium-rich manganese-based material.



Specification

Lithium-rich Manganese-based Electrode Material and Preparation Method

Technical Field

The present invention relates to a method of surface modification on a lithium-rich manganese-based positive electrode material and an electrode prepared by this method, belonging to the technical field of lithium batteries.

Background

Due to a discharge specific capacity of $250 \text{ mAh}\cdot\text{g}^{-1}$ and its low cost, lithium-rich manganese base ($x\text{Li}_2\text{MnO}_3\cdot(1-x)\text{LiMO}_2$) is hopeful to be the next-generation positive electrode material for the electric vehicle power batteries. Nevertheless, its application is limited by its inherent disadvantages, which include: (1) comparatively low coulomb efficiency caused by irreversible phase transition during the first cycle; (2) dissolution of transition metal ions when being charged to a high voltage; (3) voltage attenuation during a long period cycle; (4) poor ratio and cycling performance. To solve these problems, researchers proposed some solutions, such as bulk phase doping, surface coating and so on. The main doped elements include Al^{3+} , Mg^{2+} , Ti^{4+} , etc., which mainly play a role of stabilizing the laminated structure of bulk phase materials and suppressing cation mixing; coating materials mainly include metal oxide, lithium conducting layer, polymer conducting layer and so on.

In recent years, Nb^{5+} has been applied, as a new type of doped ions, to the modification of laminated positive electrode materials, wherein Nb mainly plays the role of stabilizing the structure of laminated materials and accelerating ion diffusion; as a lithium fast ion conductor, LiNbO_3 has also been applied to the coating modification of various positive electrode materials such as LiCoO_2 , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, etc., which can isolate the active material from the organic electrolyte, function as a physical protective layer, suppress surface side reaction, as well as promote the transmission of lithium ions by using its ion conductivity as high as $10^{-6} \text{ S}\cdot\text{cm}^{-1}$.

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 niobate/spinel-type lithium manganese-based composite oxide (LNO/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 ratio 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.

The present invention adopts a “niobium-containing mild carboxylic acidity treatment--post-heating” method, and adds a certain amount of lithium source to combine Nb surface gradient doping and LiNbO_3 surface coating; this patent uses a “sol-gel” process to reduce the thickness of the coating layer to a nanometer scale and further improve its uniformity.

Summary of the Invention

A carboxylic acid derivative of niobium is a soluble Nb source, and its aqueous solution is mildly acidic, the pH value of which is 1-3 when the mass concentration is 0.1-1g/10mL. The present invention treats the surface of lithium-rich manganese-based (LMR) material by using the solution of the carboxylic acid derivative of niobium, which has a mild acidity, wherein: firstly, structural defects are formed on the surface of the material through Li^+/H^+ ion exchange reaction, and then high temperature sintering is performed. After these steps, Nb element can partially enter the lithium-rich manganese-based material, thereby enhancing the structural stability of the lithium-rich manganese-based (LMR) material and suppressing voltage attenuation. In the present invention, Li source is added to the niobium carboxylic acid derivative suspension of LMR so as to form a LiNbO_3 fast ion conductive layer on the surface of the lithium-rich manganese-based material (LMR), and also to function as a physical protective layer, thereby improving the ratio and cycling stability of the material. In the coating process, complexing agents and dispersants can also be added so as to form a uniform nano-scale coating layer on the material surface.

The present invention provides a method of preparing a lithium-rich manganese-based positive electrode material, including the following steps of:

- (1) dissolving a carboxylic acid derivative of niobium in deionized water to prepare a solution of the

carboxylic acid derivative of niobium with a pH value of 1~3;

(2) mixing a lithium-rich manganese-based material with the solution of the carboxylic acid derivative of niobium, and stirring and heating the mixture to a temperature of 55-80°C, preferably 60-65°C, to form a suspension;

(3) adding a lithium source, a complexing agent and a dispersant into the suspension according to a molar ratio of 1:1-3:0.01-0.5, performing heating at a temperature of 60-100°C for 2-10h to form a lithium-rich manganese-based material coated with a Li-Nb precursor; and

(4) calcinating the lithium-rich manganese-based material, which is obtained in Step (3) and coated with Li-Nb precursor, at a temperature of 500-900°C for 5-15h to obtain a manganese-based positive electrode material.

Said lithium-rich manganese-based material is $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$, wherein x is 0.01-0.99, preferably 0.1-0.5.

Said Li source is one or more of lithium hydroxide, lithium carbonate, lithium nitrate, and lithium oxalate.

The addition amount of said carboxylic acid derivative of niobium in Step (2) is 0.1-9wt% of the mass of LMR material, preferably 0.5~5.

Said complexing agent is one or more of citric acid, EDTA, ascorbic acid and maleic acid; said dispersant is one or more of ethylene glycol, glycerin, propylene glycol, polyvinyl alcohol, dimethyl ether and acetone.

Said carboxylic acid derivative of niobium is a mono- or dibasic carboxylic acid derivative, of which a carbon atom number of niobium is 2-5, preferably niobium oxalate or ammonium niobium oxalate.

Said mixing in Step (2) is one of the following ways: slowly pumping the solution of the carboxylic acid derivative of niobium into the suspension of the lithium-rich manganese-based material; slowly pouring a powder of the lithium-rich manganese-based material into the solution of the carboxylic acid derivative of niobium; and directly mixing the solution of the carboxylic acid derivative of niobium with the suspension of the lithium-rich manganese-based material.

Preferably, Step (4) is carried out in an oxidizing atmosphere in the presence of oxygen or air.

Preferably, the product obtained in Step (4) is crushed to 200-400 mesh to obtain the final product.

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

Beneficial effects of the Invention:

By using the mild acidity of the solution of the carboxylic acid derivative of niobium and through Li^+/H^+ ion exchange reaction, the present invention first constructs Li^+/H^+ structural defects on the surface of the lithium-rich manganese-based material; by means of high-temperature solid-phase reaction, Nb is solid-dissolved into the surface of the material, and exchange again with H^+ therein, thereby forming a lithium-rich manganese-based material doped on the surface of Nb. During the sintering process, undoped Nb reacts with the added lithium source and Li^+ separated out of the surface layer to form a LiNbO_3 fast ionic conductor phase on the material surface (the ion conductivity reaches $10^{-6} \text{ S}\cdot\text{cm}^{-1}$). In this way, after the three stages of “processing of a carboxylic acid derivative of niobium --addition of Li source--high-temperature sintering”, the “Nb-doped/ LiNbO_3 coated” double-shell surface reconstruction layer can be formed on the surface of the lithium-rich manganese-based material, thereby improving the electrochemical properties of the lithium-rich manganese-based material. The addition of the complexing agent and the dispersant is beneficial to the forming of nanometer coating with uniform thickness.

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

A method of preparing a lithium-rich manganese-based material, including the following steps of:

- (1) dissolving niobium oxalate in deionized water to prepare a solution with a pH value of 1;
- (2) mixing a lithium-rich manganese-based material with the solution of ammonium niobium oxalate, and stirring and heating the mixture to a temperature of 60°C to form a suspension; the addition amount of ammonium niobium oxalate is 2wt% of the mass of LMR ($0.5\text{Li}_2\text{MnO}_3\cdot 0.5\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$) material;
- (3) adding lithium nitrate, EDTA and dimethyl ether into the suspension according to a molar ratio of

1:1:0.1, performing heating at a temperature of 60°C for 10h to form a lithium-rich manganese-based material coated with a Li-Nb precursor; and

(4) calcinating the lithium-rich manganese-based material coated with Li-Nb precursor at a temperature of 900°C for 5h, and crushing the calcined manganese-based positive electrode material to 200 mesh.

Example 2

A method of preparing a lithium-rich manganese-based positive electrode material, including the following steps of:

(1) dissolving ammonium niobium oxalate in deionized water to prepare a solution with a pH value of 2;

(2) mixing a lithium-rich manganese-based material with the solution of ammonium niobium oxalate, and stirring and heating the mixture to a temperature of 80°C to form a suspension; the addition amount of ammonium niobium oxalate is 1wt% of the mass of LMR ($0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$) material;

(3) adding a lithium source, a complexing agent and a dispersant into the suspension according to a molar ratio of 1:2:0.3, performing heating at a temperature of 95°C for 2h to form a lithium-rich manganese-based material coated with a Li-Nb precursor; and

(4) calcinating the lithium-rich manganese-based material, which is obtained in Step (3) and coated with Li-Nb precursor, at a temperature of 600°C for 12h, and crushing the calcined manganese-based positive electrode material to 300 mesh.

Comparative Example 1

(1) Dissolving lithium ethoxide and niobium ethoxide in a certain amount of ethanol solution;

(2) dispersing a lithium-rich manganese-based material in said solution, and stirring the solution intensely;

(3) heating the dispersed solution at a temperature of 80°C till the solvent is completely evaporated, thereby obtaining a lithium-rich manganese-based material coated with ethanol niobium lithium; and

(4) drying the product obtained in Step (3) at a temperature of 500°C, obtaining the lithium-rich manganese-based material coated with LiNbO_3 , and crushing and sifting under 200 mesh the calcined manganese-based positive electrode material.

Comparative Example 2

A method of preparing a lithium-rich manganese-based positive electrode material, including the following steps of:

- (1) dissolving niobium oxalate in deionized water to prepare a solution with a pH value of 1;
- (2) mixing a lithium-rich manganese-based material with the solution of ammonium niobium oxalate, and stirring and heating the mixture to a temperature of 60°C to form a suspension; the addition amount of ammonium niobium oxalate is 2wt% of the mass of LMR ($0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$) material;
- (3) stirring and heating the suspension obtained in Step (2) to 60°C till the solvent is completely evaporated; and
- (4) calcinating the dried product obtained in Step (3) for 5h, and crushing the calcined lithium-rich manganese-based positive electrode material to 200 mesh.

Comparative Example 3

- (1) Dissolving ammonium niobium oxalate in deionized water to prepare a solution with a pH value of 1;
- (2) mixing a lithium-rich manganese-based material with the solution of ammonium niobium oxalate, and stirring and heating the mixture to a temperature of 60°C to form a suspension; the addition amount of the ammonium niobium oxalate is 1wt% of the mass of LMR ($0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$) material;
- (3) adding a complexing agent and a dispersant into the suspension according to a molar ratio of 2:0.3, performing heating at a temperature of 95°C for 2h to form a lithium-rich manganese-based material coated with Nb; and
- (4) calcinating the lithium-rich manganese-based material coated with Nb at a temperature of 900°C for 5h, and crushing the calcined manganese-based positive electrode material to 200 mesh.

The positive electrode materials prepared according to Examples 1-2 and Comparative Examples 1-3 will be mixed with conductive carbon black and polyvinylidene fluoride at a ratio of 8:1:1 by weight, and the mixture will be uniformly blended with N-methyl-2-pyrrolidone into a positive electrode slurry. The positive electrode slurry will be uniformly spread on an aluminum foil with a thickness of 0.02mm, and will be dried by using a hot air circulation at 80~150°C. After drying, a pressure of 300 tons will be used for rolling, and the required positive electrode for lithium batteries will be obtained after compaction.。

Performance tests were carried out on the products of Examples 1-2 and Comparative Examples 1-3,

and the results are as follows:

	First-cycle Coulomb efficiency, %	1C Capacity retention ratio after 100 cycles , %	1C Discharge medium voltage after 100 cycles, V
Example 1	85.2%	86.2%	3.34
Example 2	83.1%	85.6%	3.30
Comparative Example 1	79.5%	80.1%	3.15
Comparative Example 2	80.1%	82.0%	3.01
Comparative Example 3	81.4%	80.7%	2.92

Comparative Examples 1-3 use neutral niobium solutions for loading treatment; no lithium source, no complexing agent and no dispersant are added; no electrode material prepared with lithium source is added. According to the comparison between the embodiments of the present invention and the comparative examples, the electrode material prepared by the method of the present invention has a better capacity retention ratio after multiple cycles, the discharge voltage reduce is very small and coulomb efficiency is significantly enhanced, which indicate great improvement.

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.

Claims

1. A method of preparing a lithium-rich manganese-based positive electrode material, including the following steps of:

(1) dissolving a carboxylic acid derivative of niobium in deionized water to prepare a solution of the carboxylic acid derivative of niobium with a pH value of 1~3;

(2) mixing a lithium-rich manganese-based material with the solution of the carboxylic acid derivative of niobium, and stirring and heating the mixture to a temperature of 55-80°C, preferably 60-65°C, to form a suspension;

(3) adding a lithium source, a complexing agent and a dispersant into the suspension according to a molar ratio of 1:1-3:0.01-0.5, performing heating at a temperature of 60-100°C for 2-10h to form a lithium-rich manganese-based material coated with a Li-Nb precursor; and

(4) calcinating the lithium-rich manganese-based material, which is obtained in Step (3) and coated with Li-Nb precursor, at a temperature of 500-900°C for 5-15h to obtain a manganese-based positive electrode material.

2. The method according to claim 1, wherein the lithium-rich manganese-based material is $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$, wherein x is 0.01-0.99, preferably 0.1-0.5; the Li source is one or more of lithium hydroxide, lithium carbonate, lithium nitrate, and lithium oxalate.

3. The method according to claim 1, wherein the carboxylic acid derivative of niobium is a mono- or dibasic carboxylic acid derivative, of which a carbon atom number of niobium is 2-5, preferably niobium oxalate or ammonium niobium oxalate.

4. The method according to claim 1, wherein the addition amount of said carboxylic acid derivative of niobium in Step (2) is 0.1-9wt% of the mass of LMR material, preferably 0.5~5.

5. The method according to claim 1, wherein the complexing agent is one or more of citric acid, EDTA, ascorbic acid and maleic acid; the dispersant is one or more of ethylene glycol, glycerin, propylene glycol, polyvinyl alcohol, dimethyl ether and acetone.

6. The method according to claim 1, wherein the mixing in Step (2) is one of the following ways: slowly pumping the solution of the carboxylic acid derivative of niobium into the suspension of the lithium-rich manganese-based material; slowly pouring a powder of the lithium-rich manganese-based material into the solution of the carboxylic acid derivative

of niobium; and directly mixing the solution of the carboxylic acid derivative of niobium with the suspension of the lithium-rich manganese-based material.

7. The method according to claim 1, wherein Step (4) is carried out in an oxidizing atmosphere in the presence of oxygen or air.

8. The method according to claim 1, wherein the product obtained in Step (4) is crushed to 200-400 mesh to obtain the final product.

9. A lithium-rich manganese-based positive electrode material prepared by the method of any of the claims 1-8.

10. Application of the lithium-rich manganese-based positive electrode material prepared by the method of any of the claims 1-8 to batteries.

1. Ein Verfahren zur Herstellung eines lithiumreichen positiven Elektrodenmaterials auf Manganbasis, einschließlich der folgenden Schritte:

(1) Lösen eines Carbonsäurederivats von Niob in entionisiertem Wasser, um eine Lösung des Carbonsäurederivats von Niob mit einem pH-Wert von 1 bis 3 herzustellen;

(2) Mischen eines lithiumreichen Materials auf Manganbasis mit der Lösung des Carbonsäurederivats von Niob und Rühren und Erhitzen der Mischung auf eine Temperatur von 55-80 ° C, vorzugsweise 60-65 ° C, um eine Suspension zu bilden;

(3) Hinzufügen einer Lithiumquelle, eines Komplexbildners und eines Dispergiermittels zu der Suspension gemäß einem Molverhältnis von 1: 1-3: 0,01-0,5, Durchführen eines Erhitzens auf eine Temperatur von 60-100 ° C für 2-10 Stunden, um ein lithiumreiches Material auf Manganbasis zu bilden, das beschichtet mit einem Li-Nb-Präkursor ist; und

(4) Kalzinieren des lithiumreichen Materials auf Manganbasis, das in Schritt (3) erhalten und mit einem Li-Nb-Präkursor beschichtet wird, bei einer Temperatur von 500 bis 900 ° C für 5 bis 15 Stunden, um ein positives Elektrodenmaterial auf Manganbasis zu erhalten .

2. Verfahren nach Anspruch 1, wobei das lithiumreiche Material auf Manganbasis $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ist , wobei x 0,01 bis 0,99, vorzugsweise 0,1 bis 0,5 beträgt; Die Li-Quelle besteht aus eine oder mehrere von Lithiumhydroxid, Lithiumcarbonat, Lithiumnitrat und Lithiumoxalat.

3. Verfahren nach Anspruch 1, wobei das Carbonsäurederivat von Niob ein- oder zweibasisches Carbonsäurederivat ist, von dem eine Kohlenstoffatomzahl von Niob 2 bis 5 beträgt, vorzugsweise Nioboxalat oder Ammoniumniobiumoxalat.

4. Verfahren nach Anspruch 1, wobei die Zugabemenge des Carbonsäurederivats von Niob in Schritt (2) 0,1 bis 9 Gew .-% der Masse des LMR-Materials beträgt, vorzugsweise 0,5 bis 5.

5. Verfahren nach Anspruch 1, wobei das Komplexbildner eines oder mehrere von Zitronensäure, EDTA, Ascorbinsäure und Maleinsäure ist; Das Dispergiermittel ist eines oder mehrere von Ethylenglykol, Glycerin, Propylenglykol, Polyvinylalkohol, Dimethylether und Aceton.

6. Verfahren nach Anspruch 1, wobei das Mischen in Schritt (2) eine der folgenden Möglichkeiten ist: langsames Pumpen der Lösung des Carbonsäurederivats von Niob in die

Suspension des lithiumreichen Materials auf Manganbasis; langsames Gießen eines Pulvers des lithiumreichen Materials auf Manganbasis in die Lösung des Carbonsäurederivats von Niob ; und direktes Mischen der Lösung des Carbonsäurederivats von Niob mit der Suspension des lithiumreichen Materials auf Manganbasis.

7. Verfahren nach Anspruch 1, wobei Schritt (4) in einer oxidierenden Atmosphäre in Gegenwart von Sauerstoff oder Luft durchgeführt wird.

8. Verfahren nach Anspruch 1, wobei das in Schritt (4) erhaltene Produkt auf 200 bis 400 mesh zerkleinert wird, um das Endprodukt zu erhalten.

9. Lithiumreiches positives Elektrodenmaterial auf Manganbasis, das nach dem Verfahren nach einem der Ansprüche 1 bis 8 hergestellt wird.

10. Verwendung des lithiumreichen positiven Elektrodenmaterials auf Manganbasis, das nach dem Verfahren nach einem der Ansprüche 1 bis 8 hergestellt wurde, auf Batterien.

Drawing

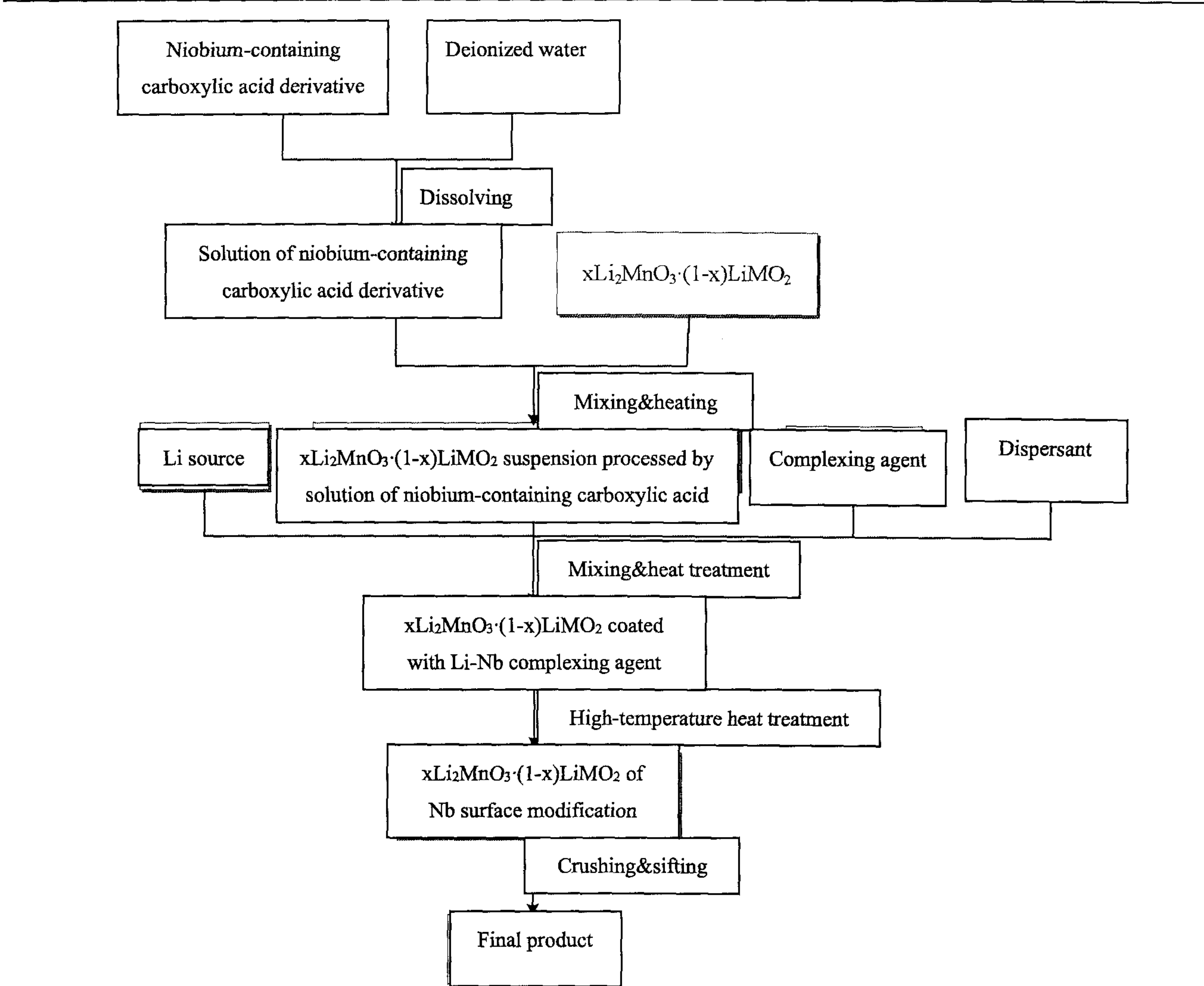


FIG. 1