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(54) **Title:** METHOD OF MAKING MIXED LITHIUM OXIDES SUITABLE AS ACTIVE MATERIAL FOR A POSITIVE ELECTRODE IN A LITHIUM ION BATTERY

(57) **Abstract:** Method of making an oxide of M, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof, comprising at least steps (S1) and (S2): (S1) mixing a composition comprising water and at least one cation of at least one M with a composition comprising water and at least one anion selected from the group consisting of hydroxide, hydrogen carbonate, and carbonate, or a mixture of two or more thereof, in a colloid mill; (S2) precipitating an oxide or hydroxide or hydrogen carbonate or carbonate or a mixture of two or more thereof of M from the milled mixture obtained in step (S1).

## **METHOD OF MAKING MIXED LITHIUM OXIDES SUITABLE AS ACTIVE MATERIAL FOR A POSITIVE ELECTRODE IN A LITHIUM ION BATTERY**

### **FIELD OF THE INVENTION**

[0001] The invention relates to a method of making mixed lithium oxides comprising at least one transition metal, preferably at least one of Ni, Mn, or Co. The invention further relates to precursors from which said mixed lithium oxides are made. The invention further relates to a positive electrode comprising said mixed lithium oxides, and to a battery comprising said positive electrode. Moreover, the invention relates to the use of a colloid mill for making mixed lithium oxides comprising at least one transition metal M, preferably selected from Ni, Mn, or Co, and precursors thereof.

### **BACKGROUND OF THE INVENTION**

[0002] It is known to use mixed lithium oxides comprising at least one of Ni, Mn, or Co as active material for a positive electrode in a lithium ion battery. Known processes for the manufacture of such mixed oxides include the preparation of suitable precursors such as oxides of Ni, Mn, or Co, or a mixture of two or more thereof. Said precursors are subsequently subjected to a lithiation reaction in order to obtain the mixed lithium oxides comprising at least one transition metal such as Ni, Mn, or Co, or a mixture of two or more thereof.

[0003] For instance, aqueous solutions of Ni, Mn, and/or Co salts such as the sulfates may be reacted with hydroxide ions to result in the respective hydroxides, which, after sintering to the respective oxides, may be further reacted with suitable lithium compounds such as lithium hydroxide to said mixed lithium oxides. Typically, such processes include a mixing step of said Ni, Mn, and/or Co salts such as the sulfates with a suitable base such as hydroxide ions. This mixing step is frequently termed as nucleation step. This nucleation step is accompanied or followed by a step of crystal growth in which a precursor of said mixed lithium oxide is formed. Nucleation and crystal growth may be carried out in parallel in two different reactors, i.e. in a continuous manner, or subsequently, e.g. in a batch process in one reactor.

[0004] It is known that the continuous process typically results in a particle size distribution of the respective precursors which is above 11.5  $\mu\text{m}$  (measured as D90, D50 and D10). However, such particle size distribution may negatively affect the properties of the respective mixed lithium oxides in terms of capacity and cycle number of the respective lithium ion battery due to inhomogeneity.

### **OBJECTS OF THE INVENTION**

[0005] It is the object of the present invention to develop precursors for mixed lithium oxides comprising at least one transition metal such as Ni, Mn, and/or Co, having improved homogeneity, which in turn allow the manufacture of mixed lithium oxides comprising preferably Ni, Mn, and/or Co also having improved homogeneity. This would support the performance of a cathode comprising said mixed oxide, respectively the performance of a lithium battery comprising said cathode.

### **SUMMARY OF THE INVENTION**

[0006] The inventors of the present invention discovered that the use of a colloid mill in a method of making precursors for mixed lithium oxides comprising at least one transition metal such as Ni, Mn, and/or Co allows the preparation of products having advantageous properties in view of homogeneity over products which are made according to methods discussed in the Background section above. Furthermore, nucleation and crystal growth may be carried out separately from one another, which advantageously may increase throughput of produced precursor.

[0007] According to a **first aspect**, the invention relates to a method of making an oxide comprising at least M, and optionally further comprising one or more of Al, Si, Mg, and B, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof, comprising at least steps (S1) and (S2):

- (S1) mixing a composition comprising water and at least one cation of at least one M with a composition comprising water and at least one anion selected from the group consisting of hydroxide, hydrogen carbonate, and carbonate, or a mixture of two or more thereof, in a colloid mill;

(S2) precipitating an oxide or hydroxide or hydrogen carbonate or carbonate, or a mixture of two or more thereof, of M from the milled mixture obtained in step (S1).

[0008] In one embodiment, in step (S1) the rotor of the colloid mill is rotated at a speed of from 1,000 to 9,000 rpm.

[0009] In one embodiment, in step (S1) the mixing is carried out at a temperature of from 10 °C to 30 °C.

[0010] In one embodiment, in step (S2) the temperature is above 30 °C.

[0011] In one embodiment, steps (S1) and (S2) are carried out in parallel, wherein the milled mixture obtained in step (S1) is fed to a reactor in which step (S2) is carried out.

[0012] In one embodiment, the method further comprises step (S3):

(S3) isolating said oxide or hydroxide or hydrogen carbonate or carbonate, or a mixture of two or more thereof, of M precipitated in step (S2).

[0013] In one embodiment, the method further comprises step (S4):

(S4) sintering the compound isolated in step (S3).

[0014] In one embodiment, the method further comprises at least steps (S1) to (S4):

(S1) mixing a composition comprising water and at least one cation of M with a composition comprising water and a carbonate in a colloid mill;

(S2) precipitating at least a carbonate of M from the milled mixture obtained in step (S1).

(S3) isolating the carbonate of M precipitated in step (S2).

(S4) sintering the carbonate isolated in step (S3).

[0015] In one embodiment, the distribution of the particle size (measured in terms of D90, D50 and D10) of the carbonate of M isolated in step (S3) is  $\leq 11.5 \mu\text{m}$ .

[0016] In a **second aspect**, the invention relates to a carbonate of M, optionally comprising one or more of Al, Si, Mg, and B, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof, wherein the distribution of the particle size (D90, D50 and D10) is  $\leq 11.5 \mu\text{m}$ .

[0017] In a **third aspect**, the invention relates to a method of making a mixed oxide comprising at least Li and M, and optionally one or more of Al, Si, Mg, and B, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof, comprising at least steps (T1) and (T2):

- (T1) mixing a lithium oxide, lithium hydroxide, lithium carbonate or lithium hydrogen carbonate, or a mixture of two or more thereof, with a product obtained according to step (S3) or (S4) as defined in the **first aspect**; or the carbonate defined in the **second aspect**;
- (T2) sintering the mixture obtained in step (T1).

[0018] In **fourth aspect**, the invention relates to a mixed oxide comprising at least Li and M, and optionally one or more of Al, Si, Mg, and B, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof, obtained by the method of as defined in the **third aspect**.

[0019] In a **fifth aspect**, the invention relates to a cathode of a lithium ion battery, comprising the mixed oxide obtained in the method as defined in the **third aspect**.

[0020] In a **sixth aspect**, the invention relates to a lithium ion battery, comprising the cathode as defined in the **fifth aspect**.

[0021] In a **seventh aspect**, the invention relates to the use of a colloid mill for making a hydroxide, a hydrogen carbonate, a carbonate or an oxide of M, or a mixed

oxide comprising at least Li and M, and optionally one or more of Al, Si, Mg and B, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof.

### **DETAILED DESCRIPTION OF THE INVENTION**

[0022] According to a **first aspect**, the invention relates to a method of making an oxide at least comprising M, and optionally further comprising one or more of Al, Si, Mg, and B, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof, comprising at least steps (S1) and (S2):

- (S1) mixing a composition comprising water and at least one cation of at least one M with a composition comprising water and at least one anion selected from the group consisting of hydroxide, hydrogen carbonate, or carbonate, or a mixture of two or more thereof, in a colloid mill;
- (S2) precipitating an oxide or hydroxide or hydrogen carbonate or carbonate, or a mixture of two or more thereof, of M from the milled mixture obtained in step (S1).

[0023] The term “oxide of M, wherein M at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof” as used in this disclosure encompasses oxides of one or more transition metals.

[0024] The term “transition metal” as used in this disclosure encompasses the transition metals having atomic numbers of from 21 to 30, 39 to 48, and 71 to 80, as defined in the Periodic Table.

[0025] Preferably, the transition metal is selected from transition metals having atomic numbers of from 21 to 30, further preferably from one or more of the following transition metals: Sc, V, Cr, Mn, Fe, Co, Ni or Cu.

[0026] More preferably, the transition metal is selected from one or more of the following transition metals: Mn, Fe, Co, Ni or Cu.

[0027] Still more preferred, transition metals are selected from one or more of the following: Mn, Co, or Ni.

[0028] In one embodiment, the term “*oxide of M, wherein M at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof*” encompasses oxides of the individual elements Ni, Mn, or Co.

[0029] In another embodiment, the oxide is a mixed oxide of Ni with Mn, or Ni with Co, or Mn with Co, or Mn.

[0030] In still another embodiment, the oxide is a mixed oxide of Ni with Mn and Co.

[0031] The oxide of M may be doped with one or more compounds of Al, Si, Mg, or B, preferably in the form of oxides.

[0032] According to step (S1), a composition comprising water and at least one cation of at least one M is mixed in a colloid mill with a composition comprising water and at least one anion selected from the group consisting of hydroxide, hydrogen carbonate, and carbonate.

[0033] The term “*composition comprising water and at least one cation of at least one M*” as used in this disclosure encompasses a water-soluble salt of said at least one M.

[0034] The term “*water-soluble salt of M*” as used in this disclosure encompasses any salt of said at least one M having a solubility of at least 1 g per 100 g water.

[0035] Preferred salts are inorganic salts such as halogenides, nitrates or sulfates. Organic salts such as formiates or acetates or oxalates may also be used.

[0036] The term “*composition comprising at least one anion selected from the group consisting of hydroxide, hydrogen carbonate, and carbonate*” as used in this disclosure encompasses aqueous bases of said hydroxides, hydrogen carbonates and carbonates. Suitable cations are preferably selected from alkali metal such as so-

dium and potassium. The reaction may also be carried out in the presence of ammonia or organic amines, preferably ammonia. Without being bound by theory, it is believed that ammonia or organic amines act as chelating agents for M, thus supporting in step (S1) solubility of the salt of M in water. This ammonia or amines may also be generated under basic conditions from respective ammonium salts being present in step (S1). Suitable forms of ammonia or amine are ammonia or amine in water, or salts such as ammonium sulfate, ammonium chloride, and ammonium carbonate.

[0037] In one embodiment, said composition comprising water and at least one cation of at least one M, and optionally ammonia or an amine, and said composition comprising water and at least one anion selected from the group consisting of hydroxide, hydrogen carbonate, and carbonate are fed separately from one another to said colloid mill in order to be mixed.

[0038] In another embodiment, it is possible to combine said composition comprising water and at least one cation of at least one M and said composition comprising water and at least one anion selected from the group consisting of hydroxide, hydrogen carbonate, and carbonate prior to the mixing in said colloid mill.

[0039] The term "*colloid mill*" encompasses a device comprising a rotor and stator between which a compound may be subjected to a high shear force. The term "*colloid mill*" has a well-accepted meaning in the art.

[0040] In one embodiment, the rotor of the colloid mill in step (S1) is rotated at a speed of from 1,000 to 9,000 rpm, preferably of from 2,000 to 8,000 rpm, more preferred of from 3,000 to 7,000 rpm, still more preferred of from 3,000 to 6,000 rpm or 3,000 to 5,000 rpm.

[0041] In one embodiment, the mixing in step (S1) is carried out at a temperature of from 10 °C to 30 °C.

[0042] In one embodiment, said composition comprising water and at least one cation of at least one M, and said composition comprising water and at least one anion selected from the group consisting of hydroxide, hydrogen carbonate, and carbonate,



are fed separately from one another to said colloid mill at a rate of from 30-40 mL/min, wherein the rotating speed of the rotor of said colloid mill is in the range of from 3,000-5,000 rpm, and the reaction temperature is in the range of from 15-25 °C.

[0043] Step (S1) according to the invention may be regarded as a nucleation step.

[0044] Typically, if in step (S2) the temperature is raised above 30 °C, a water-insoluble compound starts precipitating. Preferably, said compound is an oxide, a hydroxide, a hydrogen carbonate or a carbonate of said at least one M, or a mixture of two or more thereof.

[0045] In one embodiment, the temperature of step (S2) is  $\geq 30$  °C, preferably in the range of from 35 to 80 °C, more preferred of from 40 to 70 °C.

[0046] In one embodiment, the milled mixture generated in step (S1) is fed in step (S2) to a stirred reactor at a feeding rate of from 5-10 mL/min and a stirring rate of from 900 rpm, wherein the temperature is kept in a range of from 40 to 50 °C.

[0047] Said step (S2) may be regarded as a step of crystal growth.

[0048] In one embodiment, steps (S1) and (S2) may be carried out in parallel. The term "*in parallel*" means that both steps are carried out simultaneously, i.e. in different reactors. Thus, the reaction sequence according to steps (S1) and (S2) may be carried out in a continuous manner, wherein the milled mixture obtained in step (S1) is fed to a reactor in which step (S2) is carried out.

[0049] In another embodiment, step (S2) may be carried out subsequently to step (S1). Accordingly, the sequence may be carried out as a batch process wherein steps (S1) and (S2) are carried out in the same reactor.

[0050] In one embodiment, the method further comprises step (S3):

(S3) isolating said water-insoluble compound precipitated in step (S2).

[0051] Said isolation according to step (S3) may be carried out according to methods which are well known in the art. Preferably, said isolation may be performed by filtration or centrifugation.

[0052] In one embodiment, said method further comprises step (S4):

(S4) sintering the compound isolated in step (S3).

[0053] Step (S4) removes water and, if carbonates and/or hydrocarbonates are present in the product formed in step (S3), carbon dioxide.

[0054] Suitable sintering temperatures are  $\geq 100$  °C, preferably in the range of from 200 to 900 °C, more preferred from 300 to 800 °C, still more preferred from 400 to 700 °C. In one embodiment, said sintering may be carried out in a suitable device such as a muffle furnace.

[0055] In one embodiment, sintering is performed for a period of time in the range of from 4 to 10 h such as 6 h.

[0056] If desired, sintering may be carried out in air or oxygen. This further supports the formation of oxides.

[0057] In one embodiment, further suitable compounds used as dopants based on compounds selected from Al, Si, Mg, and B compounds may be present in any one of steps (S1), (S2), (S3), or (S4). Suitable compounds are e.g. oxides. Respective halogenides e.g. may be added to step (S1) or (S2).

[0058] In a specific embodiment, the method according to the invention comprises:

- (S1) mixing a composition comprising water and at least one cation of M with a composition comprising water and a carbonate in a colloid mill;
- (S2) precipitating at least a carbonate of M from the milled mixture obtained in step (S1).

[0059] Preferably, a sulfate or halogenide or nitrate or oxalate of M is employed in step (S1).

[0060] Preferably, the carbonate used in step (S2) is sodium carbonate or ammonium carbonate or a mixture thereof.

[0061] This specific embodiment further comprises step (S3):

(S3) isolating the carbonate of M precipitated in step (S2).

[0062] This specific embodiment further comprises step (S4):

(S4) sintering the carbonate isolated in step (S3).

[0063] The carbonate obtained in step (S4) according to the invention has a very homogeneous particle size distribution. In one embodiment, said particle size distribution (measured as D90, D50 and D10 via laser diffraction as is common in the art) is  $\leq 11.5 \mu\text{m}$  or  $\leq 11.0 \mu\text{m}$ . Said particle size distribution is advantageously improved over the respective distribution of a product which has been prepared according to a process as defined in the Background section. If such a product is prepared according to the referenced continuous method, the respective distribution is about  $20 \mu\text{m}$ , and about  $12 \mu\text{m}$  according to the batch process known in the art.

[0064] According to a **second aspect**, the invention relates to a carbonate of M, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof, wherein the distribution of the particle size (D90, D50 and D10) is  $\leq 11.5 \mu\text{m}$  or  $\leq 11.0 \mu\text{m}$ .

[0065] In order to obtain a mixed oxide comprising at least Li and M, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof, the oxide obtained according to the method defined in the **first aspect**, or the carbonate defined in the **second aspect**, is mixed with a suitable lithium

compound. Subsequently to the mixing, the generated composition is subjected to a sintering step.

[0066] In one embodiment, the product isolated in step (S3) may be subjected to a lithiation reaction.

[0067] In another embodiment, the product sintered in step (S4) may be subjected to a lithiation reaction.

[0068] Suitable lithium compounds for lithiation are preferably selected from lithium oxide, lithium hydroxide, lithium carbonate, or lithium hydrogen carbonate, or a mixture of two or more thereof. The compounds may be employed in hydrated form. In one embodiment, lithium hydroxide may be employed in hydrated form such as  $\text{LiOH}\cdot\text{H}_2\text{O}$ .

[0069] Thus, according to a **third aspect**, the invention relates to a method of making a mixed oxide comprising at least Li and at least one M, and optionally one or more of Al, Si, Mg, and B, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof, from the oxide obtained according to the method defined in the **first aspect**, or from the carbonate defined in the **second aspect**, comprising:

- (T1) mixing a lithium oxide, lithium hydroxide, lithium carbonate or lithium hydrogen carbonate, or a mixture of two or more thereof, with a product obtained according to step (S3) or (S4) as defined in the **first aspect**, or with the carbonate defined in the **second aspect**,
- (T2) sintering the mixture obtained in step (T1).

[0070] In one embodiment, sintering according to step (T2) is carried out at a temperature  $\geq 500$  °C, preferably of from 500 to 1,500 °C, more preferred of from 600 to 1,400 °C, and still more preferred of from 700 to 1,100 °C. In one embodiment, sintering is performed at a temperature of 900 °C.

[0071] In one embodiment, further suitable compounds used as dopants based on compounds selected from Al, Si, Mg, and B compounds may be present in any one of steps (T1) or (T2). Suitable compounds are e.g. oxides.

[0072] Accordingly, in one embodiment, the invention relates to a method of making a mixed oxide comprising at least Li and M, and optionally one or more of Al, Si, Mg, and B, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof, comprising:

- (S1) mixing a composition comprising water and at least one cation of at least one M with a composition comprising water and at least one anion selected from the group consisting of hydroxide, hydrogen carbonate, or carbonate, or a mixture of two or more thereof, in a colloid mill;
- (S2) precipitating an oxide or hydroxide or hydrogen carbonate or carbonate, or a mixture of two or more thereof, of M from the milled mixture obtained in step (S1);
- (S3) isolating said water-insoluble compound precipitated in step (S2);
- (S4) sintering the compound isolated in step (S3);
- (T1) mixing a lithium oxide, lithium hydroxide, lithium carbonate or lithium hydrogen carbonate, or a mixture of two or more thereof, with a product obtained according to step (S3) or (S4);
- (T2) sintering the mixture obtained in step (T1).

[0073] The mixed oxide obtained according to the method defined in the **third aspect** has improved homogeneity due to the homogeneous precursor used as starting material compared to the known respective precursors.

[0074] Accordingly, in a **fourth aspect**, the invention relates to a mixed oxide comprising at least Li and M, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof, obtained by the method as defined in the **third aspect**.

[0075] The mixed oxide comprising at least Li and M, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof, obtained according to the method as defined in the **third aspect** may be processed as an active material for a cathode of a lithium ion battery.

[0076] The term “*active material*” as used in this disclosure encompasses the material which reversibly may absorb or may release lithium ions.

[0077] The term “*cathode*” as used in this disclosure encompasses the electrode which may absorb electrons upon discharging the battery.

[0078] The term “*lithium ion battery*” as used in this disclosure encompasses terms such as “*lithium battery*”, “*secondary lithium ion battery*”, or “*lithium ion accumulator*”, i.e. a rechargeable lithium ion battery.

[0079] Thus, according to a **fifth aspect**, the invention relates to a cathode of a lithium ion battery, comprising the mixed oxide obtained in the method as defined in the **third aspect**, or comprising the mixed oxide defined in the **fourth aspect**.

[0080] According to a **sixth aspect**, the invention relates to a lithium ion battery comprising the cathode as defined in the **fifth aspect**.

[0081] According to a **seventh aspect**, the invention relates to the use of a colloid mill for making a hydroxide, a hydrogen carbonate or a carbonate or an oxide of M, or a mixed oxide comprising at least Li and M, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof.

## CLAIMS

1. Method of making an oxide comprising at least M, and optionally further comprising one or more of Al, Si, Mg, and B, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof, comprising at least steps (S1) and (S2):  
  
(S1) mixing a composition comprising water and at least one cation of at least one M with a composition comprising water and at least one anion selected from the group consisting of hydroxide, hydrogen carbonate, and carbonate, or a mixture of two or more thereof, in a colloid mill;  
(S2) precipitating an oxide or hydroxide or hydrogen carbonate or carbonate, or a mixture of two or more thereof, of M from the milled mixture obtained in step (S1).
2. Method of claim 1, wherein in step (S1) the rotor of the colloid mill is rotated at a speed of from 1,000 to 9,000 rpm.
3. Method of claim 1 or 2, wherein in step (S1) the mixing is carried out at a temperature of from 10 °C to 30 °C,
4. Method of any one of the preceding claims, wherein in step (S2) the temperature is above 30 °C.
5. Method of any one of the preceding claims, wherein steps (S1) and (S2) are carried out in parallel, wherein the milled mixture obtained in step (S1) is fed to a reactor in which step (S2) is carried out.
6. Method of any one of the preceding claims, further comprising step (S3):  
  
(S3) isolating said oxide or hydroxide or hydrogen carbonate or carbonate, or a mixture of two or more thereof, of M precipitated in step (S2).

7. Method of claim 6, further comprising step (S4):
  - (S4) sintering the compound isolated in step (S3).
8. Method of any one of the preceding claims, comprising at least steps (S1) to (S4):
  - (S1) mixing a composition comprising water and at least one cation of M with a composition comprising water and a carbonate in a colloid mill;
  - (S2) precipitating at least a carbonate of M from the milled mixture obtained in step (S1).
  - (S3) isolating the carbonate of M precipitated in step (S2).
  - (S4) sintering the carbonate isolated in step (S3).
9. Method of any one of the preceding claims, wherein the distribution of the particle size (measured in terms of D90, D50 and D10) of the carbonate of M isolated in step (S3) defined in claim 8 is  $\leq 11.5 \mu\text{m}$ .
10. Carbonate of M, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof, wherein the distribution of the particle size (D90, D50 and D10) is  $\leq 11.5 \mu\text{m}$ .
11. Method of making a mixed oxide comprising at least Li and M, and optionally one or more of Al, Si, Mg, and B, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof, comprising at least steps (T1) and (T2):
  - (T1) mixing a lithium oxide, lithium hydroxide, lithium carbonate or lithium hydrogen carbonate, or a mixture of two or more thereof, with a product obtained according to step (S3) or (S4) as defined in any one of claims 1 to 9, or with the carbonate defined in claim 10;
  - (T2) sintering the mixture obtained in step (T1).



12. Mixed oxide comprising at least Li and M, and optionally one or more of Al, Si, Mg, and B, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof, obtained by the method of claim 11.
13. Cathode of a lithium ion battery, comprising the mixed oxide obtained in the method of claim 11.
14. Lithium ion battery, comprising the cathode of claim 13.
15. Use of a colloid mill for making a hydroxide, a hydrogen carbonate, a carbonate or an oxide of M, or a mixed oxide comprising at least Li and M, and optionally one or more of Al, Si, Mg and B, wherein M is at least one transition metal, preferably selected from Ni, Mn, or Co, or a mixture of two or more thereof.

## INTERNATIONAL SEARCH REPORT

International application No.

**PCT/CN2015/075440**

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
H01M 4/131(2010.01)i; H01M 4/1391(2010.01)i; H01M 10/052(2010.01)i		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
H01M		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
CNABS, CNTXT, VEN: colliod mill, lithium, battery, positive, electrode, cathode, sinter		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 102769142 A (UNIV BEIJING CHEM TECHNOLOGY) 07 November 2012 (2012-11-07) description, paragraphs [0006]-[0021]	1-10
Y	CN 102769142 A (UNIV BEIJING CHEM TECHNOLOGY) 07 November 2012 (2012-11-07) description, paragraphs [0006]-[0021]	11-15
Y	CN 103326012 A (SHANGQIU JINGTAI MATERIAL TECHNOLOGY CO LTD) 25 September 2013 (2013-09-25) description, paragraphs [0008]-[0022]	11-15
Y	CN 103500825 A (DONGGUAN AMPEREX TECHNOLOGY CO LTD) 08 January 2014 (2014-01-08) description, paragraphs [0020]-[0027]	11-15
A	CN 101847715 A (UNIV BEIJING CHEM TECHNOLOGY) 29 September 2010 (2010-09-29) the whole document	1-15
A	CN 101577326 A (WANG S) 11 November 2009 (2009-11-11) the whole document	1-15
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents:		
“A”	document defining the general state of the art which is not considered to be of particular relevance	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“E”	earlier application or patent but published on or after the international filing date	“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“L”	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“O”	document referring to an oral disclosure, use, exhibition or other means	“&” document member of the same patent family
“P”	document published prior to the international filing date but later than the priority date claimed	
Date of the actual completion of the international search		Date of mailing of the international search report
21 July 2015		30 July 2015
Name and mailing address of the ISA/CN		Authorized officer
STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA 6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088, China		GAO,Yu
Facsimile No. (86-10)62019451		Telephone No. (86-10)62089424

INTERNATIONAL SEARCH REPORT

International application No.

**PCT/CN2015/075440**

<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 103413944 A (NINGBO NEXT NEW MATERIAL TECHNOLOGY CO) 27 November 2013 (2013-11-27) the whole document	1-15
.....		

**INTERNATIONAL SEARCH REPORT**  
**Information on patent family members**

International application No.

**PCT/CN2015/075440**

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	102769142	A	07 November 2012	None			
CN	103326012	A	25 September 2013	None			
CN	103500825	A	08 January 2014	None			
CN	101847715	A	29 September 2010	CN	101847715	B	25 July 2012
CN	101577326	A	11 November 2009	CN	101577326	B	18 May 2011
CN	103413944	A	27 November 2013	None			