

LOW TEMPERATURE SYNTHESIS OF LAYERED
LITHIATED TRANSITION METAL OXIDES

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BACKGROUND OF THE INVENTION

The increasing commercial importance of rechargeable
10 lithium ion battery cells has prompted a desire to identify and
to prepare cathode materials better able to reversibly
intercalate lithium ions at higher voltages. There are three
prominent reversible lithium intercalation compounds used for
lithium ion rechargeable batteries; namely, LiCoO_2 and LiNiO_2
15 compounds, and LiMn_2O_4 spinel.

The present invention relates to a method of making
hexagonal lithiated metal oxide materials at reduced
temperatures. More particularly, the invention relates to a
20 method of synthesizing lithium cobalt oxide or lithium nickel
oxide products which is economical and which yields products
having good electrochemical properties. The invention also
relates to a method of producing a cobalt hydroxide precursor.

25 LiCoO_2 cells are of particular interest because of their
ability to insert/deinsert lithium reversibly at voltages
greater than 4 V, resulting in batteries that have an output
voltage and an energy density three times greater than Ni-Cd
cells. Lithium cobalt oxide adopts a hexagonal structure
30 consisting of CoO_2 layers separated by Van der Waals gap. The
octahedral sites within the Van der Waals gap are occupied by

the Li ions. This results in the reversible intercalation of lithium. LiNiO_2 is isostructural with LiCoO_2 and is commercially viable for use in secondary lithium ion batteries.

5 Lithium secondary batteries are described for instance in U.S. Patent Nos. 5,296,318 and 5,418,091 to Gozdz et al., both of which are incorporated in their entirety herein by reference. Lithium metal-free "rocking chair" batteries may be viewed as comprising two lithium-ion-absorbing electrode
10 "sponges" separated by a lithium-ion conducting electrolyte usually comprising a Li^+ salt dissolved in a non-aqueous solvent or mixture of such solvents. Numerous such salts and solvents are known in the art as evidenced in Canadian Patent Publication No. 2,002,191, dated January 30, 1991.

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 U.S. Patent No. 5,192,629, which is herein incorporated by reference in its entirety, provides a class of electrolyte compositions that are exceptionally useful for minimizing electrolyte decomposition in secondary batteries comprising
20 strongly oxidizing positive electrode materials. These electrolytes are uniquely capable of enhancing the cycle life and improving the temperature performance of practical "rocking chair" cells. These electrolyte compositions have a range of effective stability extending up to about 5.0 V at 55°C, as well
25 as at room temperature (about 25°C).

 A substantial cost in the fabrication of lithium secondary batteries is the cost of electrode material resulting from the price of Co- or Ni-based precursors plus the processing
30 cost. Prior methods of synthesizing LiCoO_2 include heating to temperatures of from 800°C to 900°C. Reduction of the synthesis

temperature of LiCoO_2 would result in significant savings in the energy and cost in the production of these electrode materials.

Barboux et al., *Journal of Solid State Chemistry*, 94, (1191) 185, have reported a low temperature sol-gel approach to the synthesis of LiCoO_2 , but temperatures greater than 700°C are still necessary to obtain poorly crystalline powders of LiCoO_2 . R.J. Gummow et al., *Mat. Res. Bull.*, 27 (1992), 327, and E. Rossen et al., *Solid State Ionics*, 62 (1993) 53, tried to prepare LiCoO_2 at low temperature (400°C) from CoCO_3 and obtained a compound which they called "LT LiCoO_2 ". This material adopts a spinel (cubic) rather than an hexagonal structure. The LT LiCoO_2 phase, which does not present any interest from an electrochemical point of view, transforms to the hexagonal LiCoO_2 phase at temperatures greater than 600°C . Such a LiCoO_2 spinel structure results most likely from the fact, as suggested by Barboux et al., that the phase grows or nucleates from the cubic Co_3O_4 spinel.

Reimers et al., in *J. Electrochem. Soc.* (May 1993), reported a low-temperature synthesis method for LiMnO_2 . The material produced by Reimers et al. at low temperatures, e.g., 400°C , however, was unlike lithium manganese oxide produced at high temperatures and exhibited inferior electrochemical properties. Other low temperature processes have been attempted; for example, Fernandez-Rodriguez et al., in *Mat. Res. Bull.*, Vol. 23, pp. 899-904, report unsuccessful attempts to form LiCoO_2 from HCoO_2 at 200°C .

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SUMMARY OF THE INVENTION

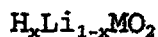
Applicants have discovered an advantageous method of forming layered structure lithium cobalt dioxide and lithium nickel dioxide materials which employs low temperatures, i.e., not exceeding 150°C, yet provides good electrochemical properties in the materials. The present invention is directed to this simple and cost-efficient method of making lithiated transition metal oxides at low temperatures.

In one aspect, the invention relates to a method of making an alkali metal oxide of the formula



wherein A is an alkali metal of group Ia, x is a number from 0.99 to 0 (depending upon the progress of the synthesis reaction), and M is a transition metal, the method comprising reacting an alkali metal ion source in a basic solution with MOOH, wherein M is as defined above, in the presence of water at a temperature of from about 50°C to about 150°C and at a pressure greater than atmospheric.

In another aspect, the invention relates to a method of making a lithium transition metal oxide of the formula



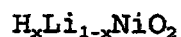
wherein x is a number from 0.99 to 0 and M is a transition metal, the method comprising reacting a lithium ion source in a basic solution with MOOH, wherein M is as defined above, in the presence of water at a temperature of from about 50°C to about 150°C and at a pressure greater than atmospheric.

In a further aspect, the invention relates to a method of making lithium cobalt oxide of the formula



5 wherein x is a number from 0.99 to 0, the method comprising reacting a lithium ion source in a basic solution with CoOOH in the presence of water at a temperature of from about 50°C to about 150°C and at a pressure greater than atmospheric.

10 In a still further aspect, the invention relates to a method of making a lithium nickel oxide of the formula



wherein x is a number from 0.99 to 0, the method comprising reacting a lithium ion source in a basic solution with NiOOH in the presence of water at a temperature of from about 50°C to
15 about 150°C and at a pressure greater than atmospheric.

BRIEF DESCRIPTION OF THE DRAWING

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The present invention will be described with reference to the accompanying drawing of which:

25 FIG. 1 shows X-ray diffraction patterns of LiCoO₂ prepared according to the present invention at varying degrees of H₂O saturation.

FIG. 2 shows the X-ray diffraction patterns of the
30 respective precursor and reaction products in the method of preparing LiCoO₂ according to the present invention.

FIG. 3 shows the similarity of X-ray diffraction patterns of LiCoO_2 prepared according to the present invention and according to prior high temperature practice.

5 FIG. 4 shows an X-ray diffraction pattern of LiNiO_2 prepared according to the present invention, along with a standard LiNiO_2 pattern.

10 FIG. 5 shows the initial reversible cycling of a rechargeable battery cell comprising an electrode of LiCoO_2 prepared according to the present invention.

15 FIG. 6 shows the initial reversible cycling of a rechargeable battery cell comprising an electrode of LiCoO_2 prepared according to prior high temperature practice.

20 FIG. 7 shows extended reversible cycling of a rechargeable battery cell comprising an electrode of LiCoO_2 prepared according to the present invention.

25 FIG. 8 shows extended reversible cycling of a rechargeable battery cell comprising an electrode of LiCoO_2 prepared according to another embodiment of the present invention.

DESCRIPTION OF THE INVENTION

30 According to the present invention lithium cobalt oxide and lithium nickel oxide having desirable properties can be

synthesized at temperatures well below 800-900°C. This has been accomplished through the use of an MOOH starting material in which M is a transition metal.

5 More particularly, an alkali metal oxide material of the formula



wherein A is an alkali metal of group Ia, x is a number from 0.99 to 0 (depending upon the progress of the synthesis
10 reaction), and M is a transition metal, can be synthesized by reacting an alkali metal ion source in a basic solution with MOOH, wherein M is a transition metal, in the presence of an ion exchange medium, such as water, at a pressure greater than atmospheric. Preferably M is selected from cobalt and nickel.
15 Preferably A is an alkali metal of group Ia selected from lithium, sodium, and potassium. More preferably, the alkali metal for use in the present invention is lithium.

20 The temperature of the reaction is preferably from about 50°C to about 150°C, more preferably from about 80°C to about 130°C, and most preferably from about 100°C to 130°C. The reaction is preferably carried out at a pH of from about 8 to about 14, preferably from about 12 to about 14. Generally, the reaction temperature may be lowered with increased pH of the
25 composition.

30 The pressure is selected to maintain the presence of water. The pressure of the reaction should therefore be at least greater than atmospheric. The pressure of the reaction is preferably from 1×10^5 Pa to about 3×10^6 Pa, more preferably between about 2×10^5 Pa and about 1×10^6 Pa, most preferably

between about 6×10^5 Pa and about 1×10^6 Pa. It may be possible, with a high pH to run the reaction under reflux. The skilled artisan will clearly understand the relationship of temperature, pressure and pH and can readily select appropriate conditions.

The reaction is carried out at the selected temperature and pressure to synthesize the desired alkali metal oxide. The reaction time is preferably from about 1 day to about 20 days, more preferably from about 2 days to about 10 days and most preferably from about 3 days to about 5 days.

This reaction may be carried out at a 1 to 1 ratio of alkali metal to transition metal; however, it is preferably carried out in a stoichiometric excess of alkali metal. More preferably the reaction is carried out in a molar excess of alkali metal from about 1.05 to about 5.0, most preferably in a molar excess of about 1.5 to about 2.5.

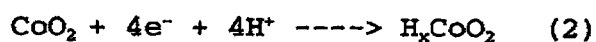
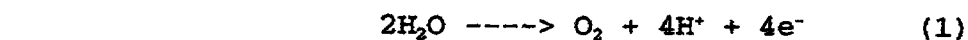
The reaction is further preferably carried out in a saturation of water. The effect of the degree of water saturation on the reaction product is shown in the LiCoO_2 X-ray diffraction patterns of FIG. 1 which were obtained in a series of syntheses where the amount of water ranged from 0 to 0.8 ml/0.4 grams of CoOOH . A substantially total saturation of the reaction composition occurred at about 0.4 ml. The skilled artisan can readily determine the appropriate water content necessary to carry the reaction to substantial completion, as described.

It has been demonstrated that Li can be completely removed from LiCoO_2 while maintaining a layered structured.

Electrochemically synthesized CoO_2 powders are able to reintercalate lithium in a secondary battery to give the LiCoO_2 phase, a direct indication of the fully reversible Li insertion process within the LiCoO_2 phase.

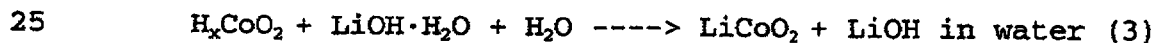
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The CoO_2 phase which is made electrochemically at a voltage of 5 V is significantly unstable in a moisture-containing environment. Indeed, this phase reacts as follows:



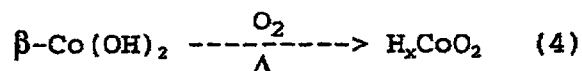
The resulting H_xCoO_2 , or CoOOH , phase has the same layered structure as LiCoO_2 , and is known in the literature, e.g., JCPDS Powder Diffraction Files, under the name of heterogenite-(3R).
15 The heterogenite phase reported in Kondrashev and Fedorova, *Doklady Akad. Nauk.*, 94, 229, 1954, was prepared by boiling $\beta\text{-Co(OH)}_2$ in water.

20 H_xCoO_2 formed from electrochemically synthesized CoO_2 , as described in reaction (2) above, is a starting material from which lithium cobalt oxide can be produced at low temperatures. An exchange of the proton can be effected at low temperatures by reacting H_xCoO_2 with $\text{LiOH}\cdot\text{H}_2\text{O}$ according to following reaction.



The electrochemical preparation of CoO_2 being volume limited, it was desired to find alternative methods of preparing the H_xCoO_2 precursor phase. It has now been discovered
30 that large amounts of single phase H_xCoO_2 can be obtained by

thermal oxidation of $\beta\text{-Co(OH)}_2$ under oxygen, as follows:



5 The reaction is preferably carried out at a temperature
of from about 120°C to about 130°C for a period of from about 10
hours to about 2 days. The reaction is more preferably carried
out at a temperature of about 125°C for a period of about 24
hours. In preferred embodiments, the material is removed and
ground at intervals. The resulting H_xCoO_2 can now be used as the
10 precursor in reaction (3) to obtain single phase LiCoO_2 at a
temperature of about 100°C according to the present invention.

After the lithiated oxide is formed it may be rinsed in a
suitable rinsing agent, for example, water, acetonitrile, an
15 aqueous solution of tetramethyl ammonia hydroxide, or mixtures
of the same. Excess LiOH is removed during the washing step.
X-ray diffraction powder patterns for the $\beta\text{-Co(OH)}_2$ precursor,
the CoOOH and LiCoO_2 products of reactions (4) and (3), and the
washed LiCoO_2 are shown respectively at (a)-(d) in FIG. 2.
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The lithiated material may further be heated to a
temperature between 100°C and 950°C for a time sufficient to
drive off interfering groups. Lithium cobalt oxide may also be
annealed at a temperature of greater than 950°C for a period of
25 from 1 to 5 hours to further improve the capacity of the
material.

The following are examples of the practice of the present
invention. It will be appreciated by those skilled in the art
30 that these examples are not to be construed as limiting the
present invention, which is defined by the appended claims.

Example 1

Lithium cobalt oxide was prepared from a mixture 0.4 g of CoOOH and 0.4 g of LiOH·H₂O (2 times molar) with 0.4 ml of H₂O, providing a pH of about 14. The mixture was sealed in a quartz ampoule (25 ml capacity) and the synthesis reaction was carried out at a temperature of 100°C, generating a calculated pressure of about 6.6×10^5 Pa, for about 5 days.

FIG. 3 compares X-ray diffraction pattern (a) of the LiCoO₂ formed in this example at 100°C with X-ray diffraction pattern (b) of an LiCoO₂ formed according to prior practices at about 850°C. The lattice parameters of the example material are 2.8163 ± 0.001 for the "a" value and 14.069 ± 0.01 for the "c" value. These values agree with the JCPDS.

Example 2

2 g of H_xCoO₂, 2 g of LiOH·H₂O, and 10 ml of water, providing a pH of about 10, were measured into a glass receptacle which was then placed in an autoclave. The mixture was heated for 2 days at a temperature of about 140°C and a pressure of $30\text{--}35 \times 10^5$ Pa. An X-ray diffraction pattern of the LiCoO₂ produced was substantially the same as that of the material of Example 1.

Example 3

An LiNiO₂ material was formed in the same manner as in Example 1, except that NiOOH was used at a reaction temperature of about 140°C. The X-ray diffraction pattern for this material

and a standard LiNiO_2 reference pattern are shown respectively at (a) and (b) in FIG 4.

Example 4

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To examine the electrochemical efficacy of the synthesized lithium metal oxide compounds, simple test cells were assembled using as the positive electrode a film of composition cast from a fluid dispersion comprising the finely-
10 divided oxide compound with about 10% carbon and 5% binder polymer, such as polyvinylidene fluoride, in an organic solvent, e.g., 1-methyl-2-pyrrolidinone. A boro-silicate glass paper separator element saturated with an electrolyte solution of 1 M LiPF_6 in a 2:1 mixture of ethylene carbonate and dimethyl
15 carbonate was then arranged between the positive electrode element and a lithium foil negative electrode element in a Swagelock test cell which compressed the electrode and separator elements into intimate contact. The resulting cell was then tested in the usual manner over charge/discharge
20 cycles in the range of about 3 V to 4.5 V.

The results of test cycling indicated that the initial reversible intercalation properties of a LiCoO_2 prepared according to Example 1 (FIG. 5) compared favorably with such a
25 compound prepared at about 850°C according to prior practice (FIG. 6). The exemplary results of extended cycling tests of the LiCoO_2 material of Example 1 and of the same material prepared in Example 2 are shown respectively in FIGs. 7 and 8.

30 Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein.

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What is claimed is:

1. A method of making a single phase layered alkali metal oxide material of the formula

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wherein A is an alkali metal of the group Ia, x is a number from 0.99 to 0, and M is a transition metal

characterized in that
an alkali metal ion source is reacted in a basic solution with
10 MOOH, wherein M is as defined above, in the presence of water
and at a temperature of from about 50°C to about 150°C and a
pressure greater than atmospheric.

2. The method of claim 1 wherein M is Co or Ni.

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3. The method of claim 1 wherein the alkali metal ion source is LiOH or LiOH·H₂O.

4. The method of claim 1 wherein the reaction pressure is from
20 about 1x10⁵ Pa to about 3x10⁶ Pa.

5. The method of claim 1 wherein the reaction is carried out at a temperature of from about 80°C to about 130°C.

25 6. The method of claim 1 wherein A is selected from the group consisting of Li, Na, or K.

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