

PARTICLES OF DOPED LITHIUM COBALT OXIDE, METHOD FOR PREPARING THE SAME AND THEIR USE IN LITHIUM ION BATTERIES

Field of the invention

The present invention is in the field of inorganic chemistry and in the field of electricity. More specifically the present invention provides the compounds containing metals used in processes and means for conversion of chemical into electrical energy.

Discussion of the state of the art

Nowadays, lithium batteries are used principally as energy sources in telecommunications means (portable or cell phones, video cameras, portable computers, portable stereophonic equipment, pagers, facsimile devices, etc.). The principal advantages of lithium batteries are high energy density and long service life. The batteries have potential uses for a wide range of electrical systems, ranging from memory components for electronic apparatuses to electric vehicles.

Whereas the demand for electronic apparatuses in international markets is growing strongly, safety requirements are becoming more stringent. In this connection, research and development is proceeding aimed at introducing rechargeable lithium ion batteries into transportation means, particularly electric vehicles (Katz et al., U.S. Patent 6,200,704; Gao et al., U.S. Patent 6,589,499; Nakamura et al., U.S. Patent 6,103,213).

The qualities needed in lithium ion storage batteries for the major applications are:

- good energy storage;
- good thermal stability;
- good safety; and
- long service life.

The desirable qualities are greatly affected by the characteristics of the active materials used for the cathode and anode. In recent years, great progress has been made in anode materials. The set of problems relating to the cathode is still the subject of substantial research. The material most commonly used for the cathode is lithium cobalt oxide (LiCoO_2); however, alternative materials are used as well. LiNiO_2 would be a candidate also, because it has very high discharge capacity; however, its use has been impeded by serious problems relating to manufacturing difficulties and low thermal stability. LiMnO_2 is less expensive and is essentially environmentally benign; but as a practical matter it is not used, because of its low specific capacity.

Lithium cobalt oxide is widely used in batteries in commercially successful applications as a result of the high voltage of the batteries and the ease of their manufacture. Nonetheless, this material has drawbacks relating to storage capacity, namely:

- capacity fade rate with increasing numbers of cycles of charging/discharging; and
- poor energy storage at elevated temperatures (see Mao et al., U.S. Patent 5,964,902).

As a result a great amount of research has been devoted to alleviating these problems.

As a general requirement, a rechargeable battery must have high electrochemical capacity. In the case of a lithium ion battery, this can be achieved if the positive and negative electrodes can accommodate a large amount of lithium. In order to achieve long service life, the positive and negative electrodes should have sufficient lability to accommodate and release lithium in a reversible manner, i.e. they should have minimal "capacity fade". In this connection, the structural stability of the electrodes should be maintained during the deposition and extraction of lithium over a large number of cycles.

According to Needham (Needham, S.A., "Synthesis and electrochemical performance of doped LiCoO_2 materials" (Ref. 1)), the choice of dopant and the amount of dopant are important factors in the improvement of the electrochemical performance of LiCoO_2 via suppression of anisotropic structural changes which can occur in the structure of the lithium cobalt oxide.

Further, the physicochemical properties of LiCoO_2 which is commonly used as a positive electrode material in lithium ion batteries tend to depend on the preparation method, the choice of precursors and the conditions of preparation. The control of these parameters has effects on the particle size

distribution, and on the morphology and purity of the cobalt oxide (see Lundblad, A. and Bergman, (Ref. 2); and Lala, S.M. et al., (Ref. 9)).

With the aim of stabilizing the crystalline structure of the lithium cobaltate and to improve the properties of the material, inter alia its characteristics during the charging/discharging cycle, incorporation of magnesium into the lithium cobalt oxide lattice was studied (Maeda et al., U.S. 7,192,539; and Antolini, E. et al., (Ref.3)).

According to the invention made by A. Masashi and al. (Japan patent application No. 08 – 171755, (1998)), several chemical trivalent elements were used as doping agent in the cobalt lithium oxide in order to obtain compositions of uniform size distribution and morphology.

A large number of similar studies have been conducted, studying the effect of doping with different elements (particularly, transition elements) on the electrochemical performance of batteries using such compounds in the cathode. Lithium cobalt oxides doped with manganese and titanium have been studied and considered as promising materials for cathodes of storage batteries (see Kumar et al., U.S. Patent 6,749,648).

According to the work of Needham, S.A. (Ref. 1), doping with tetravalent elements is more promising than with divalent or trivalent elements. Dong Zhang (Dong Zhang et al., (Ref. 10)) showed that doping of lithium cobalt oxide with chromium provides an initial capacity of 230 mAh/g.

According to Jang (Jang, S.W. et al., (Ref. 4)), the structural stability of lithium cobalt oxide, which crystallizes in the hexagonal system, greatly influences the electrochemical performance. It was concluded that the phase transition from hexagonal to monoclinic during cycling of the battery is the cause of the loss in capacity of batteries using lithium cobalt oxide.

In the invention it is proposed to remediate these problems by providing nano-particles for use in the manufacture of cathodes of rechargeable lithium batteries in order to obtain enhanced energy storage, high thermal stability and very high charge / discharge capacities compared to the known conventional lithium ion batteries.

Summery of the invention

The object of the present invention has been achieved by the Applicants by providing particles of doped lithium cobalt oxide of formula $\text{LiCo}_y\text{O}_z \cdot t \text{ MO}_x$, wherein the doping agent MO_x is selected from the group of lanthanide oxides, wherein the molar ratios expressed by y, z, t and x are selected so as to produce desired stoichiometric ratios in said particles of doped lithium cobalt oxide, and wherein said doping agent MO_x is nano-sized.

The present invention also provides a cathode for lithium ion batteries comprising the particles of doped lithium cobalt oxide according to the invention as an active electrochemical material.

In this context, a further object of the present invention is to provide a lithium ion battery comprising at least one negative electrode, at least one positive electrode, and at least one separation electrolyte, wherein the positive electrode comprises the cathode according to the invention.

Other objects of the present invention are to provide a method of improving the stability and storage capacity of rechargeable lithium ion batteries and to provide a method of producing particles of doped lithium cobalt oxide according to the invention.

Other characteristics and advantages of the invention will be apparent from the description which follows herein below. The accompanying Figures are offered solely for purposes of example.

Brief description of the Figures

Figure 1 shows the crystalline structure of the CeO_2 lattice;

Figure 2 (a and b) is simplified flow chart of the method of preparation;

Figure 3 shows charge and discharge capacities of LiCo_yO_z , 0.02 CeO_x without nano-sized cerium

oxide.

Figure 4 shows XDR diffraction patterns of the synthesized cerium oxide: a) microscopic CeO_2 ; b) nanoscopic $\text{CeO}_{2-\delta}\square_\delta$ ($\square$: Oxygen vacancies)

Figure 5 shows the charging and discharging curves for lithium cobalt oxide sample combined with nano-sized cerium oxide.

Figure 6 shows (DSC) measurements of LiCo_yO_z , 0.02 CeO_x : a) microscopic CeO_2 , b) nanoscopic CeO_2 .

Figure 7 shows XDR diffraction patterns of LiCo_yO_z , 0.02 CeO_x : a) microscopic CeO_2 ; b) nanoscopic $\text{CeO}_{2-\delta}\square_\delta$.

Figure 8 shows SEM photograph of microscopic LiCo_yO_z , 0.02 CeO_x

Figure 9 shows SEM photograph of nanoscopic LiCo_yO_z , 0.02 CeO_x

Detailed description of the invention

Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety. The publications and applications discussed herein are provided solely for their disclosure prior to the filing date of the present application. Nothing herein is to be construed as an admission that the present invention is not entitled to antedate such publication by virtue of prior invention. In addition, the materials, methods, and examples are illustrative only and are not intended to be limiting.

Novel cathode materials for rechargeable batteries are produced by a novel method which consists of doping lithium cobalt oxide with the aim of improving its electrochemical performance and its safety characteristics. These characteristics are of particular and critical importance in order to fulfill the increasing needs in energy especially on an industrial scale.

The invention relates to novel particles of doped lithium cobalt oxide of formula $\text{LiCo}_y\text{O}_z \cdot t \text{MO}_x$ wherein the doping agent MO_x is selected from the group of lanthanide oxides, wherein the molar ratios expressed by y, z, t and x are selected so as to produce desired stoichiometric ratios in said particles of doped lithium cobalt oxide and wherein said doping agent MO_x is nano-sized.

The terms “nano-sized” or “nanoscopic” or “nanoparticles” or “nanoscale”, used interchangeably herein, define controlled geometrical size of particles below 100 nanometers (nm) (see “Nanotechnology and patents”, EPO 2009, <http://www.epo.org/about-us/publications/general-information/nanotechnology.html>)

The originality of the invention lies in the fact that such doping by nano-sized lanthanide oxide group dopants has never been previously envisioned and especially it has never been studied as to the nano-structural properties and the resulting electrochemical properties of the lithium cobalt oxide. Merely it has been known that the lanthanides (rare earths) have exceptional properties which have been exploited to great advantage in numerous industrial sectors.

The invention relates particularly to the study of combining the impact of doping by lanthanide oxides of exceptional properties and effect of crystallites size of doping compound especially at form of nanoscale particles, in the absence of any indications in the literature of the implications of such doping.

The rare earths (lanthanides) (e.g. Ce, La, Nd, Eu) comprise 15 scarce elements of atomic numbers in the range 57-71 (lanthanum to lutetium), having similar chemical properties. They comprise the 15 members of the "internal transition series" in Mendeleev's table of the elements.

Preferably, the doping agent MO_x in the doped lithium cobalt oxide is selected from the group consisting of oxides of Nd, Eu, Sm, Ce, Tb, and / or combinations thereof.

In the inventive particles of doped lithium cobalt oxide ($\text{LiCo}_y\text{O}_z \cdot t \text{MO}_x$), the preferable values of the molar ratios are:

$$0.7 \leq x \leq 1.1$$

$$0.005 \leq t \leq 0.3, \text{ more preferably } 0.01 \leq t \leq 0.2$$

$$1.55 \leq z \leq 1.993$$

$$y = 1 - t$$

The molar ration x of Oxygen content in the lattice of the lanthanide oxide depends on the non stoichiometric behavior of nano-sized lanthanide oxide. The molar ratio z of Oxygen in lithium cobalt oxide is such as to ensure electrical neutrality of the particles.

In particular, the molar ratio z (or index) depends on the molar ratio t for the dopant, and an increased t essentially increases z ; since the doping causes structural vacancies in the structure of lithium cobalt oxide. In practice, the value (molar ratio) of z will be in the range of $1.55 \leq z \leq 1.993$.

According to a preferred embodiment of the invention, the doping agent MO_x is cerium (Ce) oxide (ceria).

Most preferably, the formula for the doped lithium cobalt oxide particles is $LiCo_{0.98}O_{1.97} \cdot 0.02CeO_x$

Surprisingly, the choice of nano-sized cerium oxide as a doping agent has demonstrated exceptional properties. Cerium oxide is a compound which has recently been the subject of much study for potential uses in numerous industrial sectors. This interest is explained by the following:

- Cerium oxide is characterized by high structural and thermal stability (it crystallizes into a fluorine-type structure, and does not undergo a phase transition until its fusion point T_f of 2750°K);
- It has lability such that it acts as an "oxygen reservoir"; this property is known as "OSC" (oxygen storage capacity);
- It has mixed electrical conductivity (electronic and ionic).

Cerium dioxide, CeO_2 , commonly called ceria, crystallizes in a structure of the fluorine type (CaF_2), in the space group $Fm3m$, over a wide range of temperatures up to its fusion temperature (M. Mogensen et al., (Ref. 5)).

The crystalline structure of this oxide is presented in Figure 1. Cerium dioxide is characterized by, inter alia, its non-stoichiometric behavior, which allows it to serve as a reservoir of oxygen, which has effects on the mixed electrical conductivity properties (electronic and ionic) of this oxide. A summary of physical properties of cerium oxide is presented in Tables 1 and 2.

Table 1: Physical properties of cerium dioxide

Crystallographic data	CeO₂
Crystalline system	Cubic
Space group	Fm3m
Lattice parameter (nm)	0,5411
Asymmetric units	Ce (0,0,0) O (1/4,1/4,1/4)
Inter-reticular distances which relate to the most intense bands (nm)	d ₁₁₁ =0,312 d ₁₁₀ =0,383

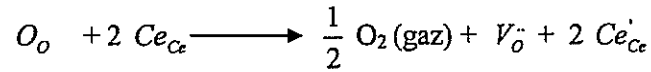
Table 2: Physical properties of cerium dioxide

Property	value
Density	7,22 g/cm ³
Fusion temperature	2750 K
Thermal conductivity	12 W.m ⁻¹ .K ⁻¹
Specific heat	460 J.Kg ⁻¹ .K ⁻¹
Young's modulus	165.10 ⁹ N.m ⁻¹

The advantage provided by introduction of an oxygen reservoir into the structure of lithium cobalt oxide may lie in the fact that, when CeO₂ is reduced to CeO_{2-x}, defects appear in the form of Ce³⁺

ions (indicated as Ce'_{Ce} in the notation of Kröger and Vink), wherewith the Ce^{3+} has a charge which is negative with respect to the Ce^{4+} of the normal lattice of CeO_2 . It is generally accepted that the principal means by which the oxygen vacancies in CeO_{2-x} are compensated for is the creation of Ce'_{Ce} defects (Zhu, T. et al., (Ref. 7); Trovarelli, A. et al., (Ref. 8) and I. Akalay et al, (Ref. 11)).

The process of reduction of CeO_2 is represented as follows:



wherein :

Ce_{Ce} : represents the cerium present in the normal CeO_2 lattice,

O_o : represents an oxygen in the normal ceria lattice: namely an ion O^{2-}

$V_o^{\cdot\cdot}$: represents an oxygen vacancy

The introduction of these oxygen vacancies can both improve the electrical properties of the material by introducing of oxygen species with high mobility, to better adapt to the fluctuations of oxygen taking place and furthermore to promote textural stability of systems based on cobalt lithium oxide and therefore the introduction of nano-sized cerium oxide in the development of electrochemically active compounds have a double effect:

- Improve the safety aspect by the restitution of oxygen released resulting from the interactions between cathode – electrolyte.
- Improve the charge / discharge capacities compared to conventional products based on lithium cobalt oxide, the second advantage is provided by the introduction of new mobile species that lead to the improvement of electrical transport properties and the subsequent electrochemical performance in terms of charge / discharge capacities. The mobility of these oxygen species is becoming more important when miniaturizing the average size of crystallites to the nano - scale.

Indeed, studies show that the transition from micro - size to a nano - size (average size of crystallites smaller than 100 nm) has a great influence on the physical and chemical properties of

materials. These variations in properties can be explained by the number of surface atoms greater than 70% compared to the number of atoms in volume for the nanoscale materials, resulting in an exceptional improvement of all the phenomena of surface compared to conventional materials (microscopic scale) (N.G.Millot (Ref. 14)).

Carrying out electrochemically active systems involving a cathode with an average crystallite size falls belonging to the nano - field and the combination with the effects resulting in integration of a catalytic phase has never been studied, according to our knowledge.

In this context the present invention deals with proving that the performance of these new systems in terms on the safety aspect and charge / discharge capacities are greatly improved compared to conventional products (microscopic scale).

The particles of LiCo_yO_z in doped lithium cobalt oxide according to the invention have a mean diameter of preferably ≤ 200 nm, more preferably ≤ 180 nm (see Example 2).

The particles of MO_x have a mean diameter less than or equal to 50 nm.

The particles of doped lithium cobalt oxide according to the invention also have difference between the charging and discharging capacity of $< 0.3\%$. Preferably, the specific discharge capacity of the particles is ≥ 165 mAh/g.

The particles of doped lithium cobalt oxide according to the invention show a high structural stability and have been characterized by various techniques.

The electrochemical characteristics displayed by these materials demonstrate that doping by nano-sized rare earth oxides, particularly cerium oxide, confers upon the material an improved charging/discharging capacity compared to materials based on lithium cobalt oxide which have been studied in the literature. Furthermore, the small capacity loss between the charging/discharging cycles which is one of the characteristic of materials according to the present invention means that they have a high reversibility in battery cycling, and long life, which makes them excellent candidates

for use in storage battery technology (secondary batteries).

According to the invention it is proposed to provide a cathode (positive electrode) as an active electrochemical material for lithium ion batteries (also called rechargeable electrochemical lithium batteries), wherein said cathode comprises the particles of doped lithium cobalt oxide according to the present invention.

In particular, the particles of doped lithium cobalt oxide according to the present invention may be used for the manufacture of cathodes of lithium ion rechargeable batteries.

For example, an electrode according to the invention comprises a conductive support serving as a power collector which is coated by the electrochemically active material (particles) according to the invention, and further comprises a binder and a conductive material.

The power collector is preferably a two-dimensional conductive support, such as a solid strip of material or perforated strip of material, which is containing carbon or metal, e.g. copper, aluminum, nickel, steel, or stainless steel. Preferably, a positive electrode comprises a collector in aluminum. In the event of excessive discharging or inversion of the battery, one thus avoids short-circuiting by dendrites of copper (which might occur if the collector is in copper).

The binder may contain one or more of the following compounds: polyvinylidene fluoride (PVDF) and its copolymers, polytetrafluoroethylene (PTFE), polyacrylonitrile (PAN), polymethyl methacrylate, polybutyl methacrylate, polyvinyl chloride (PVC), polyvinyl formal, block polyester amides and polyether amides; polymers of acrylic acid, acrylamide, itaconic acid, and sulfonic acid; elastomers; and cellulosic compounds.

Among the numerous elastomers which may be used are: ethylene-propylene-diene rubber (EPDM), styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR), styrene-butadiene-styrene block copolymers (SBS), styrene-acrylonitrile-styrene block copolymers (SIS), styrene-ethylene-butylene-styrene copolymers (SEBS), styrene-butadiene-vinylpyridine terpolymers (SBVR), polyurethanes (PUR), neoprenes, polyisobutylenes (PIB), and butyl rubbers; and mixtures of these.

The cellulosic compound may be chosen among for example carboxymethylcellulose (CMC), hydroxypropylmethylcellulose (HPMC), hydroxypropylcellulose (HPC), or hydroxyethylcellulose (HEC).

The conductor material may be chosen among graphite, carbon black, 15 acetylene black (AB), or derivatives and/or mixtures thereof.

It is another object of the present invention to provide a lithium ion battery (also know as secondary or storage battery) comprising at least one negative electrode, at least one positive electrode, and at least one separation electrolyte; wherein the positive electrode comprises the cathode according to the present invention.

Preferably the separation electrolyte is a liquid, a gel, or a solid. More preferably, the electrolyte is chosen among a non-aqueous electrolyte comprising a lithium salt dissolved in a solvent; and a polymeric solid conductive electrolyte which is an ionic conductor of lithium ions, e.g. polyethylene oxide (PEO).

The lithium salt is chosen among lithium perchlorate (LiClO_4), lithium hexafluoroarsenate (LiAsF_6), lithium hexafluorophosphate (LiPF_6), lithium tetrafluoroborate (LiBF_4), lithium trifluoromethanesulfonimide ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$) (LiTFSI), lithium trifluoroethanesulfonemethide ($\text{LiC}(\text{CF}_3\text{SO}_2)_3$) (LiTFSM), and lithium bisperfluoroethylsulfonimide ($\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$) (BETI); and mixtures thereof.

Preferably, the solvent is a solvent or mixture of solvents, chosen among usual or customary organic solvents, particularly: saturated cyclic carbonates, unsaturated cyclic carbonates, non-cyclic carbonates, alkyl esters (such as formiates, acetates, propionates, or butyrates), ethers, lactones (such as gamma-butyrolactone), tetrahydrothiophene dioxide (commercialized as SULFOLANE), nitrile solvents; and mixtures of these. Among the cyclic saturated carbonates which might be mentioned are: ethylene carbonate (EC), propylene carbonate (PC), and butylene carbonate (BC); and mixtures of these. Among the cyclic unsaturated carbonates which might be mentioned are, e.g., vinylene

carbonate (VC), and its derivatives; and mixtures of these. Among the non-cyclical carbonates which might be mentioned are, e.g.: dimethyl carbonate (DMC), diethyl carbonate (DEC), methyl ethyl carbonate (EMC), and dipropyl carbonate (DPC); and mixtures of these. Among the alkyl esters which might be mentioned are, e.g.: methyl acetate, ethyl acetate, methyl propionate, ethyl propionate, butyl propionate, methyl butyrate, ethyl butyrate, and propyl butyrate; and mixtures of these. Among the ethers which might be mentioned are, e.g., dimethyl ether (DME) and diethyl ether (DEE); and mixtures thereof. Other solvents which might be mentioned are 1,2-dimethoxyethane, 1,2-diethoxyethane, 2-methyltetrahydrofuran, and 3-methyl-1,3-dioxolane.

In general, the negative electrode comprises a conductor support serving as a power collector, which is coated with a layer comprising the electrochemically active material and further comprising a binder and a conductive material. The collector of this negative electrode may be made of copper or nickel, advantageously copper. The electrochemically active material is chosen among metallic lithium, lithium alloys, a carbon material wherein lithium can be inserted in the structure (e.g. graphite, coke, carbon black, or vitreous carbon), and a mixed oxide of lithium and a transition metal such as nickel, cobalt, or titanium.

Generally, improved electrochemical performance of rechargeable batteries involves an elevated reversibility of the process of intercalation and de-intercalation of Li^+ in the battery, which results in a low difference between the charging and discharging capacities (Levasseur, Stéphane (Ref. 6)).

A major problem faced by investigators and industrial exploiters is the operational safety of rechargeable batteries. Without adequate safety, the range of applications is limited. This applies in particular to the use of advanced rechargeable batteries in electrical and hybrid vehicles. Safety is a factor of major concern in addition to high ratings in capacity per unit weight and per unit volume, and in service life.

Generally, the battery safety tests comprise three steps:

- Progressive increasing of the potential difference between anode and cathode;
- Heating of the battery to a maximum temperature prescribed for the safety testing;
- Perforation, by prescribed means. Three sets of data are recorded, namely the potential difference

(Volts), temperature ($^{\circ}\text{C}$), and power (Amps).

Example 2 demonstrates that the safety of the batteries according to the invention is much better than that of standard commercial lithium cobalt batteries.

The Applicants have shown that the temperature increase compared to the increase with standard LiCoO_2 batteries is minor. In particular, the temperature increase with the lithium ion battery according to the invention in classical safety tests is less than 15°C (generally in the range $+7^{\circ}\text{C}$ to $+15^{\circ}\text{C}$). The doped material of the present invention leads to a temperature increase which is slightly more than half that of a battery using non-doped lithium cobalt oxide.

The lithium ion battery according to the present invention have the specific discharge capacities of cobalt lithium oxide doped with nano-sized ceria greater or equal to 165 mAh/g.

The lithium ion battery according to the present invention generates heat of less than 50 J/g.

The invention additionally proposes a method of improving the stability and storage capacity of rechargeable lithium ion batteries wherein, the positive electrode (cathode) of said batteries comprises the particles of doped lithium cobalt oxide according to the invention as the active electrochemical material.

Another object of the invention is a method of producing the particles of doped lithium cobalt oxide $\text{LiCo}_y\text{O}_z \cdot t \text{ MO}_x$ according to the invention. This method comprises:

- a) the preparation of nano-sized doping agent MO_x (lanthanide oxide) comprising the steps of:
 - (i) obtaining MO_x precursor starting from acetate or nitrate of lanthanide by co-precipitation or sol-gel method,
 - (ii) calcinating MO_x precursor to obtain nano-sized MO_x having a controlled crystallites size,
- b) the preparation of LiCo_yO_z particles comprising mixing of cobalt oxide Co_3O_4 with lithium carbonate Li_2CO_3 to obtain a homogenous LiCo_yO_z particles,

and wherein said particles of doped lithium cobalt oxide $\text{LiCo}_y\text{O}_z \cdot t \text{ MO}_x$ are obtained by:

- 1) mixing the LiCo_yO_z particles of step b) with the nano-sized MO_x of step a.ii),
- 2) homogenizing and milling of the mixture of step 1), and
- 3) calcinating the result of step 2).

Additives may be used in step 1) and mixed together with LiCo_yO_z particles and nano-sized MO_x to influence the size and shape of the particles according to the invention. Several additives were studied, especially of organic nature such as acetone or PVA.

Preferably the calcination of step a.ii) is carried out at temperatures in the range of 450°C to 700°C; the calcination of step 3), is carried out at temperatures in the range of 600°C to 1200°C during a time comprised in the range of 3 to 40 hours.

Co- precipitation method:

- a) The starting materials, such as nitrates of cerium hexahydrate, are dissolved in distilled water (in the case of nitrates).
- b) A precipitating agent for co-precipitation is added under stirring until a determined value of pH (5-12).
- c) The obtained precipitate is then subjected to successive steps of washing with deionized water in order to remove residual trace of the precipitation agent.
- d) Then, the washed precipitate is dried at temperature ranging from 80 to 130°C.
- e) The dried precipitate (MO_x precursor) is calcinated to obtain nano-sized MO_x (lanthanide oxide) particles having a controlled crystallites size.

Sol - gel method:

This method involves:

- a) Dissolution of lanthanide acetate, such as cerium acetate, in appropriate medium (acetic acid). The obtained sol is continuously stirred.
- b) A precipitating agent is added until formation of gel for a value of pH varying between 5 and 12.
- c) The obtained gel is dried at temperature varying between 50°C and 100°C.

- d) The dried gel (MO_x precursor) is calcinated to obtain nano-sized MO_x (lanthanide oxide) particles having a controlled crystallites size.

The above-mentioned precipitating agent may be NH_4OH solution or any other suitable solution known to the person skilled in the art.

In a preferred embodiment of the invention, the chosen lanthanide oxide is cerium oxide.

The invention further proposes to provide particles of doped lithium cobalt oxide of formula $\text{LiCo}_y\text{O}_z \cdot t \text{MO}_x$ obtainable according to the method of the present invention, wherein the doping agent MO_x being selected from the group of lanthanide oxides, the molar ratios expressed by y, z, t and x are selected so as to produce desired stoichiometric ratios in said particles of doped lithium cobalt oxide, and wherein doping agent MO_x is nano-sized.

The originality of this invention is that for the first time it is proved that the particles of doped lithium cobalt oxide with nano-sized doping agent exhibit exceptional properties compared to conventional products whose average particle size exceeds 100 nm. The particles of doped lithium cobalt oxide ($\text{LiCo}_y\text{O}_z \cdot t \text{MO}_x$) of the present invention are developed based on two components: (1) the particles of LiCo_yO_z having a mean diameter less than or equal to 200 nm, and (2) the particles of doping agent MO_x have a mean diameter less than or equal to 50 nm. The combination of these two components leads to the electrochemically active particles having:

- High thermal stability reflecting improved safety aspect compared to the conventional products made of lithium cobalt oxide,
- Very high charge / discharge capacities (about 165 mAh / g).

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications without departing from the spirit or essential characteristics thereof. The invention also includes all of the steps, features and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations or any two or more of said steps or features. The present disclosure is therefore to

be considered as in all aspects illustrated and not restrictive, the scope of the invention being indicated by the appended Claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

Other characteristics and advantages of the invention will be apparent from the following exemplary embodiments, which are presented for purposes of example and do not limit the scope of the invention, and in the accompanying Figures.

Examples

(1) Experimental method:

The particles produced were identified with the use of an "Xpert" X-ray diffractometer. In this connection, the lattice parameters were calculated and refined with the use of a program based on the method of least squares.

The mean lattice size of the crystallites of the particles used as cathode materials was calculated from the X-ray diffraction spectra, using the Scheerer formula:

$$D = \frac{k \cdot \lambda}{\beta \cdot \cos \theta}$$

where k is the shape factor (≈ 0.9 if the width is half the height);

D is the mean lattice parameter of the crystallites ($\text{\AA}$);

λ is the wavelength of the incident beam ($\text{\AA}$); and

β is the width at half height, corrected by an apparatus factor relating to the broadening of the diffraction rays.

References for the Scheerer formula:

- Muller, C., (Ref. 15);
- Millot, N.G., (Ref. 14).

The morphology of the produced samples was characterized with the use of a scanning electron microscope.

The electrochemical performance of the batteries was evaluated by tests on batteries comprising the cathode (using the particles according to the invention) and an anode, separated by an electrolyte. The safety of synthesized particles was evaluated using differential scanning Calorimetry (DSC).

Example 1

This example illustrates the structural properties of cerium oxide crystallites, which have a nanoscopic size compared to microscopic cerium oxide sample.

The preparation of cerium oxide can be achieved through co-precipitation process or a sol-gel route. The starting material can be acetates or nitrates of cerium. The precipitating agent consisting of NH_4OH solution is added to the nitrate or acetate cerium solution until a pH reaches a value varying between 9 and 11. The obtained precipitate (CeO_2 precursor) is then washed to remove residual NH_4^{4+} ions. Drying is then carried out at optimum temperature. Calcinations allow thereafter obtaining nano crystallites cerium oxide. The desired average size of crystallites is governed by the choice of temperature and the duration of calcinations (K. Ouzaouit, and al., (Ref. 12)). Calcining temperature ranges from 450°C to 700°C according to the co-precipitation or sol-gel process route, the precursors used and the desired size.

The average size of crystallites estimated according to the semi - empirical relationship:

$D = D_0 \exp (-E_a/k_B T)$ where E_a is the activation energy of crystallization, k_B the Boltzmann constant and D_0 the pre-exponential factor. The D size tends to infinity for a temperature near the melting temperature of CeO_2 at 2750°K (S. Saitzek, (Ref. 16)).

Figure 4 shows the X-ray patterns of two samples of cerium oxide prepared: a) of microscopic crystallites size, b) nanoscopic crystallites size.

The identification of the two samples is carried out by comparing experimental data to reference

ones which are the JCPDS file. This study shows that the diffraction lines are characteristic of pure cerium oxide, in accordance with the standard JCPDS file (34 – 0394) for both samples a) and b). There is also a peak broadening observed for a produced sample b). This strong increase of the peak width is explained generally by two effects: the size of crystallites or micro-strains in the lattice. In the Applicants' case, the expansion is mainly attributed to the average crystallites size.

Table 1 lists the average crystallites size of synthesized cerium oxide prepared in the nanoscopic form compared to a microscopic sample and their refined cells parameters.

Table 1: Cell Parameters and average crystallite size of synthesized microscopic and nanoscopic cerium oxide

	Microscopic sample « CeO ₂ » (a)	Nanoscopic ceria « CeO _{2-δ} » (b)
<i>Cell parameter a (Å)</i>	5.405 ± 0.002	5.391 ± 0.005
<i>Cell volume V(Å³)</i>	157.9 ± 0.1	156.7 ± 0.4
<i>Average crystallites size (nm)</i>	162.2 ± 0.1	32.4 ± 0.1

The Applicants note that the cell parameters of different synthesized cerium oxide samples nanoscopic and microscopic size are in perfect agreement with those of literature.

Procedure for obtaining cerium oxide having a controlled average crystallite size was carried out through specifically choice of elaboration parameters (see above-mentioned co-precipitation and sol-gel methods). Controlling preparation conditions allow not only to control the average crystallites size but also allow to control a non-stoichiometry oxygen ($0.05 < \delta < 0.2$).

This non- stoichiometric behavior in oxygen amount contained in the prepared cerium oxide is the source of catalytic properties as a reservoir of oxygen that can present this material.

The prepared nano-sized cerium oxide according to the method of the present invention (having the

average crystallite size of about 32nm, as presented in Table 1) is used in the method of producing the particles of doped lithium cobalt oxide of formula $\text{LiCo}_y\text{O}_z \cdot t \text{ MO}_x$ for performing electrochemically active cathode and safe compared to conventional products.

Example 2:

The second example presents results corresponding to two samples of cobalt lithium oxide prepared with micro-sized and nano-sized cerium oxides as described in Example 1.

The particles of doped lithium cobalt oxide were prepared in order to have a formula $(\text{LiCo}_y\text{O}_z, 0.02 \text{ CeO}_x)$ chosen after a series of tests, the coefficients x, y and z chosen were the same for both samples prepared from synthesized cerium oxide referenced by a) (microscopic) and b) (nanoscopic) in the first example.

Several samples were synthesized with different values of x, y and z varying within defined ranges as claimed in the present invention. These samples have been subjected to different characterizations, such as structural and electrochemical performance, which allowed the selection of the preferred particles of doped lithium cobalt oxide for use according to the present invention.

The method used to prepare particles of doped lithium cobalt oxide $(\text{LiCo}_y\text{O}_z, 0.02 \text{ CeO}_x)$ in form of nanoparticles implies a solid - state reaction adopting a specific thermal treatments and using a specific additional in mixture with starting precursors consisting in cobalt lithium oxide and different synthesized cerium oxide as described in example 1.

The homogenization of precursors used in the preparation of the electrochemically active phase is achieved via the addition of a specific organic additive. The purpose of this additional organic product was to have composites presenting highly homogeneous morphologies.

1- Structural characterisation

Figure 7 shows X - Ray patterns of doped lithium cobalt oxide $(\text{LiCo}_y\text{O}_z, 0.02 \text{ CeO}_x)$. As already mentioned above, the choice of $\text{LiCo}_y\text{O}_z, 0.02 \text{ CeO}_x$ was achieved after several series of tests whose results showed that $\text{LiCo}_y\text{O}_z, 0.02 \text{ CeO}_x$ present the stoichiometry leading to a best

structural performance and consequently electrochemical ones.

X – Rays patterns of LiCo_yO_z , 0.02 CeO_x (Figure 7) shows in addition to the diffraction lines attributed to cobalt lithium oxide, additional peaks assigned to cerium oxide. In order to obtain the best performances, the amount of residual cerium oxide in the doped lithium cobalt oxide is optimized. Indeed, the amount of cerium oxide was chosen to be greater than the limit of a solid solution $\text{LiCo}_y\text{O}_z - \text{CeO}_x$ with a well determined quantity. Table 2 lists the average crystallites size of synthesized doped lithium cobalt oxides based on cobalt lithium oxide and cerium oxide.

Table 2: Cell Parameters and average crystallites size of synthesized doped lithium cobalt oxide based on cobalt lithium oxide and microscopic or nanoscopic cerium oxide

Structural parameter	LiCo_yO_z , 0.02 CeO_x « Microscopic » (a)	LiCo_yO_z , 0.02 $\text{CeO}_{2.5}\square_\delta$ « Nanoscopic » (b)
Structural ordering factor	$R = 0.52$	$R = 0.46$
Cell parameter ($\text{\AA}$)	$a = 2.813 \pm 0.001$ $c = 14.042 \pm 0.001$	$a = 2.806 \pm 0.005$ $c = 13.996 \pm 0.002$
Cell volume ($\text{\AA}^3$)	$V = 96.2 \pm 0.5$	$V = 96.1 \pm 0.3$
Average cristallites size (nm)	$D = 173.7 \pm 0.2$	$D = 89.2 \pm 0.3$
c/a	4.99	4.99

By analyzing results listed in Table 2, one can conclude that cells parameters of all the doped lithium cobalt oxides containing microscopic and nanoscopic cerium oxide (a) and (b) are in good agreement with literature data. The factor describing crystalline order of the sample prepared using nanosized cerium oxide is lower than that synthesized via microscopic cerium oxide and thereafter the lithium cobalt oxide particles doped by the nano-sized cerium oxide exhibit a more ordered crystalline structure. One recall that the factor reflecting the crystalline disorder is defined by:

$$R = \frac{I(102) + I(006)}{I(101)} \quad \text{where } I(102), I(006) \text{ and } I(101) \text{ are respectively the intensities of}$$

diffraction peaks (102), (006) and (101). However, as well as the value of R factor characteristic of crystalline disorder decreases, the order crystalline becomes better.

The average crystallites size of lithium cobalt oxide is much lower in the case when doped by nanoscopic (b) compared to the microscopic cerium oxide (a).

2 - Morphological characterization of LiCo_yO_z , 0.02 CeO_x wherein CeO_x is nano-sized

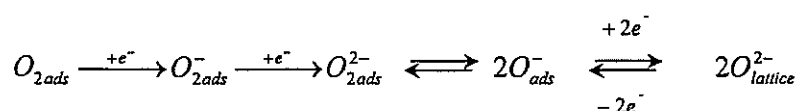
Figures 8 and 9 show the morphological characterization achieved by scanning electron microscopy of LiCo_yO_z , 0.02 CeO_x particles having micro-sized or nano-sized cerium oxide. The images show that the morphologies of those two types of particles are homogeneous, the coalescence of grains exhibiting a well determined sides. The LiCo_yO_z , 0.02 CeO_x particles, prepared with cerium oxide microscopic or nanoscopic, present regular forms (pseudo hexagonal) which reflects a better microstructural organization of the system. The particles having microscopic cerium oxide exhibit a quite variable grains size (Figure 8). The presence of porosity is quite noticeable in the sample prepared with nanoscopic cerium oxide, as seen in Figure 9.

3 – Electrochemical performance:

Figures 3 and 5 show the curves of charge / discharge capacities for the designed batteries manufactured based on particles whose synthesis and characterization have been described in example 2.

Both particles exhibit better electrochemical performance, i.e. the charge / discharge capacities of about 150mAh / g for the particles containing non-nanoscope cerium oxide and the capacities exceeding 165 mAh / g for the particles containing nanoscopic cerium oxide. The obtained discharge capacities for both particles are higher than the value of non-doped lithium cobalt oxide samples (140 mAh/g).

The synthesized doped lithium cobalt oxide containing nano-sized cerium oxide leads to an excellent improvement of discharge capacity of about 12% compared to the conventional products. This phenomena can be interpreted by the introduction of new oxygen species in the lattice of cobalt lithium oxide attributed to the non- stoichiometric behavior regarding oxygen and the increased mobility of these species. This property generates the production of oxygen species type responsible for the improvement of electrical transport properties. The chemical reaction describing the creation of these species (A. Trovarelli, Ref. 8):



Consequently the electrochemical properties show a good improvement as a result of combining the two effects: introduction of catalytic product to the electrochemical system and synthesis of nanoscale electrochemically active materials.

Synthesis of electrochemical system for rechargeable batteries in form of nanoscale crystallites present a key factor to a significant enhancement in terms of charge/discharge capacities.

4 – Safety of $LiCo_yO_z$, $0.02 CeO_x$ particles

The operational safety of rechargeable batteries continues to be the main challenge for researchers and industrial users. Safety is so important because insufficient safety limits the use of advanced rechargeable batteries in numerous applications, particularly electric and hybrid vehicles.

Lamellar oxides such as lithium cobalt oxide tend to release oxygen when they are highly delithiated during the charging process or when they are subjected to constrained thermal conditions. The mechanism of degradation of the lithium ion battery can be explained by the reaction between oxygen released from the oxide forming the cathode and the electrolyte. In other words the combustion of organic solvents in the presence of oxygen is the origin of the exothermic reactions observed by differential scanning calorimetry (DSC), for example an organic solvent of general formula $C_xH_yO_z$ may be oxidized in the presence of O_2 and release heat energy in the future according to the reaction: $C_xH_yO_z + (2x+y/2-z)/2O_2 \longrightarrow xCO_2 + y/2H_2O$.

This type of reaction is very exothermic and is activated by heat and presence of oxygen. There are several techniques for safety inspection of lithium ion batteries such as:

- 1- Nail – penetration
- 2- Crush
- 3- Dropping from height of 1.5 m.

4- Heat evolution (DSC).

Differential scanning calorimetry can detect the thermal effects (endo or exothermic phenomena) occurring during a transformation or a structural transition. The used measure consists in determining ΔH enthalpy (the quantity may be positive or negative) when the material is subjected to temperature change perfectly linear with time.

Regarding safety characterization of rechargeable lithium ion, two quantities are essential and provide an indication of the thermal behavior of the rechargeable battery, namely:

- $T_{on\ set}$ temperature ($^{\circ}C$): indicates the start of the reaction between the electrolyte and cathode. More the value of this temperature is high; the better is thermal stability of battery.
- ΔH (J / g): is the energy released during the reaction electrolyte – cathode; lower this value is, the cathode becomes more stable - concerning reactivity with the electrolyte.

Figure 6 shows the characterization by differential calorimetry (DSC) of particles based on lithium cobalt oxide and cerium oxide prepared in the form of nanoscopic and microscopic scale respectively. The main information's that can be drawn from the analysis of Figure 6 are listed in Table 3.

Table 3: (DSC) measurements of $LiCo_yO_z$, 0.02 CeO_x : a) nanosized, b) micro sized.

Sample	Onset Temperature ($^{\circ}C$)	ΔH area (J/g)
$LiCo_yO_z$ - 0.02 CeO_x CeO_x micro sized	240	191
$LiCo_yO_z$ - 0.02 $Ce\Box_8O_{2.5}$ $Ce\Box_8O_{2.5}$ nanosized	228	35.6
Literature (Ref. 13)	176 $LiCoO_2$	2102

In order to prove the originality of using nanoscopic cerium oxide in doped lithium cobalt oxide particles as electrochemically active cathode presenting high performance, the characterization of the safety aspect of the particles (using microscopic and nanoscopic cerium oxide) shows that reducing the size at the nanoscale form leads to an excellent improvements in terms of thermal stability of

electrochemical active systems based on cobalt lithium oxide as seen in Figure 6.

The heat energy released by marketed lithium cobalt oxide is: LiCoO_2 (4.2 V) = - 770 j/g.

Compared to the marketed lithium cobalt oxide, it can be noticed that $\text{LiCo}_x\text{O}_2 - 0.02 \text{ CeO}_x$ particles having microscopic cerium oxide exhibit a marked decrease of about 4 times regarding liberated heat. A significant decrease of the heat energy released during the reaction between cathode and electrolyte of about 22 times for the particles having nanoscopic cerium oxide compared to the marketed ones. In the light of these results, it can be concluded that the particles with nanoscopic cerium oxide leads to an excellent thermal stability and consequently to a high safety compounds for cathodes of rechargeable batteries.

Another potential feature of the particles of doped lithium cobalt oxide of the present invention is the temperature of starting reactivity ($T_{\text{on set}}$) of the cathode with the electrolyte, which exhibits a net increase of 30% compared to marketed products which reflects another excellent performance related to a safety of the particles of the present invention.

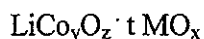
It goes without saying that the present invention is not limited in scope to the described embodiments but extends to numerous variants accessible to one skilled in the art. In particular it is within the scope of the invention to employ a conductive electrode support of a different nature and structure than described. Further, various ingredients may be employed in preparing the homogeneous paste, in various proportions. In particular, various additives may be used which facilitate forming of the electrode, such as thickeners and texture stabilizers.

References

- 1 - « Synthesis and electrochemical performance of doped LiCoO_2 materials », S.A.Needham et al., *Journal of Power Sources* (2007).
- 2 - « Synthesis of LiCoO_2 starting from carbonate precursors», A.Lundblad, B.Bergman, *Solid State Ionics* **96** (1997) 173 – 181
- 3 - « Synthesis and Thermal Stability of LiCoO_2 », E.Antolini et al., *Journal of Solid State Chemistry* **117**, 1-7 (1995)
- 4 - « Synthesis and electrochemical of Li_xCoO_2 for lithium – ion batteries », Serk-Won Jang et al. *Materials and Research Bulletin* **38** (2003) 1- 9
- 5 - « Physical, chemical and electrochemical properties of pure and doped ceria», M.Mogensen, N.Sammes, G.A.Tompsett, *Solid State Ionics* **129** (2000) 63-94.
- 6 - Stéphane LEVASSEUR, Doctoral dissertation, université de Bordeaux I, 2001.
- 7 - « Redox chemistry over CeO_2 -based catalysts: SO_2 reduction by CO or CH_4 », T.Zhu, L.Kundakovic, A.Dreher, M.F.Stephanopoulos *Catalysis Today* **50** (1999) 381-397.
- 8 - « Catalytic Properties of Ceria and CeO_2 -Containing Materials», A.Trovarelli, *Rev* **38** (1996) 439 – 450.
- 9 - « Synthesis of LiCoO_2 by metallo-organic decomposition-MOD», S.M.Lala et al., *Journal of Power Sources* **114** (2003) 127 – 132.
- 10 - « Dong Zhang et al., *Journal of Power Sources* **83** (1999) 121 – 127 »
- 11 - I.Akalay et al, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 1137 – 1148
- 12 - K. Ouzaout, and al. *Journal de Physique IV*, (2005), Volume 123, Issue 1, pp.125 -130
- 13 - Y-K.Sun, S-W.Cho, S-T.Myung, K.Amine, Jai.Prakash, *Electrochimica Acta* **53**(2007) 1013-1019
- 14 - N.G.Millot, thesis, University of Borgogne (1998)
- 15 - Muller, C., 1996, thesis, Joseph Fourier University, Grenoble
- 16 - S. Saitzek, Thesis University of south Toulon Var (2003)

Claims

1. Particles of doped lithium cobalt oxide of formula



wherein the doping agent MO_x is selected from the group of lanthanide oxides, and wherein the molar ratios expressed by y, z, t and x are selected so as to produce desired stoichiometric ratios in said particles of doped lithium cobalt oxide, characterized in that said doping agent MO_x is nano-sized and wherein the molar ratio y of cobalt is $y = 1 - t$, the molar ratio z of oxygen is such as to ensure electric neutrality of said particles of doped lithium cobalt oxide and the molar ratio x of oxygen is from 0.7 to 1.1.

2. Particles of doped lithium cobalt oxide according to claim 1, characterized in that the doping agent MO_x is selected from the group consisting of oxides of Nd, Eu, Sm, Ce, Tb, and / or combinations thereof.

3. Particles of doped lithium cobalt oxide according to any of claims 1 to 2, characterized in that the doping agent MO_x is cerium (Ce) oxide.

4. Particles of doped lithium cobalt oxide according to claim 1 to 3, characterized in that the molar ratio t of the doping agent MO_x is in the range of 0.005 to 0.3.

5. Particles of doped lithium cobalt oxide according to any of claims 1 to 4, characterized in that the molar ratio t of the doping agent MO_x is in the range of 0.01 to 0.2.

6. Particles of doped lithium cobalt oxide according to claims 1 to 5, characterized in that the molar ratio z of oxygen is in the range of 1.55 to 1.993.

7. Particles of doping agent according to claims 1 to 6, characterized in that the molar ratio y of cobalt is 0.98.

8. Particles of doped lithium cobalt oxide according to claims 1 to 7, characterized in that the particles consist in $\text{LiCo}_{0.98}\text{O}_{1.97}$, 0.02 CeO_x .

9. Particles of doped lithium cobalt oxide according to any of claims 1 to 8, characterized in that the particles of LiCo_yO_z have a mean diameter less than or equal to 200 nm.
10. Particles of doped lithium cobalt oxide according to any of claims 1 to 8, characterized in that the particles of LiCo_yO_z have a mean diameter less than or equal to 180 nm.
11. Particles of doped lithium cobalt oxide according to any of claims 1 to 8, characterized in that the particles of doping agent MO_x have a mean diameter less than or equal to 50 nm.
12. Particles of doped lithium cobalt oxide according to any of claims 1 to 11, characterized in that the difference between the charging and discharging capacity is less than 0.3%.
13. A cathode for lithium ion batteries comprising the particles of doped lithium cobalt oxide according to any of claims 1 to 12 as an active electrochemical material.
14. Use of the particles of doped lithium cobalt oxide according to any of claims 1 to 12, for manufacture of cathodes for rechargeable lithium ion batteries.
15. A lithium ion battery comprising at least one negative electrode, at least one positive electrode, and at least one separation electrolyte, characterized in that the positive electrode comprises the cathode according to claim 13.
16. The lithium ion battery according to claim 15, characterized in that the separation electrolyte is a liquid, a gel, or a solid.
17. The lithium ion battery according to any of claims 15 to 16, characterized in that the specific discharge capacities of cobalt lithium oxide doped with nanosized ceria is greater or equal to 165 mAh/g.
18. The lithium ion battery according to any of claims 15 to 17, characterized in that said battery generates heat of less than 50 J/g.

19. A method of improving the stability and storage capacity of rechargeable lithium ion batteries, characterized in that the positive electrode in said batteries comprises the particles of doped lithium cobalt oxide according to any of claims 1 to 12 as an active electrochemical material.

20. A method of producing particles of doped lithium cobalt oxide $\text{LiCo}_y\text{O}_z \cdot t \text{MO}_x$ according to any of claims 1 to 12, said method comprises:

- a) the preparation of nano-sized doping agent MO_x (lanthanide oxide) comprising the steps of:
 - i. obtaining MO_x precursor starting from acetate or nitrate of lanthanide by co-precipitation or sol-gel method,
 - ii. calcinating MO_x precursor at temperatures in the range of 450°C to 700°C to obtain nano-sized MO_x having a controlled crystallites size,
- b) the preparation of LiCo_yO_z particles comprising mixing of cobalt oxide Co_3O_4 with lithium carbonate Li_2CO_3 to obtain a homogenous LiCo_yO_z particles,

and wherein said particles of doped lithium cobalt oxide $\text{LiCo}_y\text{O}_z \cdot t \text{MO}_x$ are obtained by:

- 1) mixing the LiCo_yO_z particles of step b) with the nano-sized MO_x of step a.ii),
- 2) homogenizing and milling of the mixture of step 1), and
- 3) calcinating the result of step 2) at temperatures in the range of 600°C to 1200°C.

21. The method of claim 20, characterized in that additives are mixed together with LiCo_yO_z particles and nano-sized MO_x in step 1).

22. The method of claim 20, characterized in that the calcination step 3), is carried out during a time comprised in the range of 3 to 40 hours.