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(54) Title: PULVERULENT COMPOUNDS, A PROCESS FOR THE PREPARATION THEREOF AND THE USE THEREOF IN LITHIUM SECONDARY BATTERIES

(57) Abstract: The present invention relates to pulverulent compounds of the formula $\text{Li}_a\text{Ni}_b\text{M}_1\text{cM}_2\text{d}(\text{O})_2(\text{SO}_4)_x$, a process for preparation thereof and the use thereof as active electrode material in.



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Pulverulent compounds, a process for the preparation thereof and the use thereof in lithium secondary batteries

5 The present invention relates to pulverulent compounds of the formula $\text{Li}_a\text{Ni}_b\text{M1}_c\text{M2}_d(\text{O})_2(\text{SO}_4)_x$, a process for the preparation thereof and the use thereof as active electrode material in lithium secondary batteries.

10 Portable and cordless electric devices are very widely used nowadays. Owing to the continued miniaturization of these portable electronic devices, the demand for increasingly small and increasingly light secondary batteries having a high energy density, which serve as an
15 energy source for such devices, has very rapidly increased in recent years. Secondary batteries used are mainly nickel metal hydride batteries as well as lithium ion batteries. In consumer applications (e.g. mobile phone, laptop, digital camera), virtually exclusively
20 only lithium ion secondary batteries occur since they have a substantially higher energy density compared with the nickel metal hydride batteries.

This type of secondary battery is distinguished by active
25 materials on the cathode and anode side which can reversibly incorporate and release lithium ions. When this battery type was launched in the early 90s, lithium cobalt oxide LiCoO_2 was used as the electrochemically active substance for the positive electrode. However,
30 this LiCoO_2 which currently still dominates the market for active cathode materials in lithium ion secondary batteries, has a disadvantage of a very high cobalt price and greatly limited availability of cobalt. Against a background of the greatly expanding markets for Li ion

technology (i.e. power tools, hybrid engine vehicles (HEV) as new applications), the limited availability of cobalt gives cause for concern that LiCoO_2 alone will not be able in future to supply the market for active cathode materials for Li ion batteries. Even at present, more than 25% of the annual cobalt production is used in the battery sector. Alternative cathode active materials are therefore urgently necessary.

Inter alia, against this background, the use of LiNiO_2 as active cathode material for Li ion batteries has already been discussed for a relatively long time. Nickel is both substantially more economical than cobalt and available in much larger amounts. In addition, LiNiO_2 has a substantially higher electrochemical capacity than LiCoO_2 .

However, such an LiNiO_2 has the disadvantage that, when used in secondary batteries, it leads to insufficient thermal stability of the battery. A significant change in the crystal structure during the charging/discharging process furthermore means that the long-life properties/cycle stability of the batteries with such an active material does not meet the market requirements.

For improving the abovementioned parameters, various doping elements for LiNiO_2 , such as, for example, Co, Al, Mn, Fe and Mg, were therefore tested over the years, which led to a significant improvement in the parameters discussed above. Example compounds having the dopants mentioned are $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$. These dopants permitted the market launch of the nickel-containing lithium mixed metal compounds, which are currently used in addition to the original active

material, LiCoO_2 .

In the case of the required, high-energy density of the storage media (secondary batteries), a distinction may be made between the volumetric energy density, expressed in watt hours/litres (Wh/l), and the gravimetric energy density, expressed in Wh/kg. The volumetric energy density of the secondary battery is influenced, inter alia, by the electrode density (g/cm^3) both on the side of the cathode and on the side of the anode. The higher the electrode density of the cathode or anode, the higher is the volumetric energy density of the storage medium. The electrode density in turn is influenced both by the production process of the electrodes and by the active cathode material used. The higher the density of the cathode material (for example, determined as tapped density, compacted density or compressed density), the higher is the resultant electrode density under otherwise constant conditions during electrode manufacture (e.g. processes for electrode manufacture, electrode composition). This discovery is already reflected in some documents.

Thus, DE 19849343 A1 describes the compacted density of lithium-containing mixed oxides of the formula LiNiCoMO_2 . Here, M is at least one of the metal elements Al, Ca, Mg and/or B. The compacted densities of these materials, the primary particles of which have rectangular or square structure, and the secondary particles of which are spherical, are in the range of 2.4 to 3.2 g/cm^3 .

In DE 19849343 A1 it is pointed out that the morphology and particle shape of the precursor are of major importance for the shape of the product (the LiNiCoMO_2)

and hence also the compacted density thereof. Furthermore, it is stated that a higher compacted density increases the relative packing quantity of an active material for a positive electrode, with the result that
5 the capacitance of an electrochemical cell is increased. The importance of spherical particles for achieving high compacted densities is also mentioned.

The relationship between tapped density of the active
10 cathode material and electrode density and hence volumetric energy density of the Li ion battery is described in Journal of The Electrochemical Society, Vol. 15 (2004), 10, pages A1749-A1754.

15 Since a certain pressure is applied during the electrode preparation, the tapped density or compacted density determined for the powder need not, however, permit direct conclusions about the electrode density when this powder is used. A compressed density of a powder which is
20 determined under a defined pressure represents a variable which permits more reliable conclusions about the electrode density with this powder. A precondition for the abovementioned measurement of the compressed density as well as for the electrode manufacture should be that
25 the particles do not break during the compression. Breaking of the particles would mean firstly uncontrolled manufacture of the electrode and furthermore such comminution of the particles during the electrode production would lead to inhomogeneities. Thus, the
30 internal fracture surfaces of the comminuted particles would not have such good contact with the binder and the conductive additive of the electrode as the external surface of the particles. US 2004/023113 A1 is concerned with the determination of the compressed density and

compressive strength of cathode powders.

Substances of the general formula $\text{Li}_x\text{M}_{(1-y)}\text{N}_y\text{O}_2$ in which $0.2 \leq x \leq 1.2$, $0 \leq y \leq 0.7$, are mentioned therein. Here, M is a transition metal and N is a transition metal differing from M, or an alkaline earth metal. In US 2004/023113 A1, particular value is placed on the fact that the particle size distribution must have a defined form so that the pressure applied during the compression during electrode manufacture can spread particularly gently over the particle bed. In addition to the particle size distribution, it is also mentioned that the particles of the powder should have pores which are as small as possible and the pore volume of the pores up to a diameter of $1 \mu\text{m}$ should not exceed a value of $0.03 \text{ cm}^3/\text{g}$ (Hg porosimetry). However, no particular process engineering measures are described for achieving said product parameters. In the determination of the compressed density, the powder is compressed under a pressure of 0.3 t/cm^2 .

In the examples, mainly lithium cobalt oxides are described. At the abovementioned compression pressure of 0.3 t/cm^3 , compressed densities in the range of $2.58\text{--}3.32 \text{ g/cm}^3$ are reached.

In addition to the compressed density itself, value is furthermore placed on the fact that, after the compression of the material, the volume fraction of the particles smaller than $1 \mu\text{m}$ is not greater than 0.1%. A significant increase in the fine particles after the compression would indicate that particles are destroyed during the application of pressure. Such a phenomenon would endanger the homogeneity of the electrode.

It is however to be assumed that a pressure of 0.3 t/cm^2 does not correspond to the pressures which are actually applied during the electrode manufacture. During the
5 electrode manufacture, the material must be built to withstand at least a pressure of 1 t/cm^2 . In JP 2001-80920 A, a pressure of 2 t/cm^2 is stated in example 1 for the electrode manufacture. JP 2001-80920 A mentions the compressive strength of lithium mixed metal oxides (LNCO),
10 which comprise three metallic components in addition to lithium.

The materials thus produced have a compressive strength of $0.001 - 0.01 \text{ N}$. According to this document, it is desirable for the particles to disintegrate into their primary
15 constituents during the electrode manufacture, which is contrary to the argumentation of US 2004/023113 A1. According to JP 2001-80920 A the material which has disintegrated into smaller constituents must have a certain flowability to enable the particles to be distributed
20 uniformly over the electrode.

The compressive strength of lithium mixed metal oxides is also discussed in US 2005/0220700 A1. There, the compounds have the formula $\text{Li}_p\text{Ni}_x\text{Co}_y\text{Mn}_z\text{M}_q\text{O}_{2-a}\text{F}_a$. Whereas
25 US 2004/023113 A1 only states the value 0.3 t/cm^2 for the compressive strength, compressive strengths of at least 50 MPa are stated in US 2005/0220700 A1 for the lithium mixed metal compounds, which corresponds to 0.5 t/cm^2 . However, the formula for the relevant compounds in
30 US 2005/0220700 A1 is defined substantially more narrowly than that in US 2004/023113 A1. Thus, manganese is a fixed constituent of all compounds in US 2005/0220700 A1. US 2005/0220700 A1 does not consider why the compounds mentioned have a particular compressive strength. Only a

defined particle size range and a defined range for the specific surface area of the materials are mentioned. Particular process engineering peculiarities which make the material particularly pressure-resistant are not
5 mentioned.

US 2005/0220700 A1 discloses compounds which contain fluoride as a further anionic component in addition to the anionic oxygen. EP 1450423 A1 claims an active
10 material for positive electrodes of a nonaqueous secondary battery, which material can be expressed substantially by a lithium mixed metal oxide compound, that has sulphate anions in the range from 0.4% by weight to 2.5% by weight. The high proportion of sulphate anion
15 is intended to ensure that the carbon content in the end product (substantially as alloy to Li_2CO_3) is kept low.

It is an object of the present invention to provide a lithium mixed metal oxide in which the secondary
20 particles are not broken or not comminuted during the electrode manufacture (cathode).

The preservation of the secondary particle during electrode manufacture is of major importance for the
25 homogeneity of the electrode. At the same time, it should be possible to achieve a high electrode density and good electrochemical properties with such a lithium mixed metal oxide. The object of the present invention is furthermore to provide a process for the preparation of
30 the lithium mixed metal oxide.

The object is achieved by a pulverulent compound of the formula $\text{Li}_a\text{Ni}_b\text{M1}_c\text{M2}_d(\text{O})_2(\text{SO}_4)_x$ (subsequently also referred to as LNMOS or lithium mixed metal oxides), in which M1

denotes at least one element selected from the group consisting of Fe, Co, Cr, Mg, Zn, Cu and/or mixtures thereof, M2 denotes at least one element selected from the group consisting of Mn, Al, B, Ca, Sr, Ba, Si and/or mixtures thereof, and $0.95 \leq a \leq 1.1$, $0.3 \leq b \leq 0.83$, $0.1 \leq c \leq 0.5$, $0.03 \leq d \leq 0.5$ and $0.001 \leq x \leq 0.03$, the secondary particles of which have a compressive strength of at least 100 MPa.

10 Compounds which are part of the invention are shown in the table below.

Compound No.	a	b	M1	c	M2	d	x
001	1.09	0.333	Co	0.333	Mn	0.333	0.015
002	1.05	0.50	Co	0.20	Mn	0.30	0.015
003	1.03	0.77	Co	0.13	Mn	0.10	0.009
004	1.03	0.80	Co+Mg	0.10	Mn	0.10	0.007
005	1.03	0.70	Co	0.10	Mn+Al	0.20	0.006
006	1.05	0.30	Co	0.30	Mn+Al	0.40	0.015
007	1.03	0.80	Co	0.17	Al	0.03	0.005
008	1.04	0.75	Co+Fe	0.20	Al	0.05	0.006
009	1.02	0.80	Co	0.16	Al+B	0.04	0.003
010	1.03	0.80	Co	0.17	Sr	0.03	0.002
011	1.03	0.60	Mg	0.10	Mn	0.30	0.004
012	1.04	0.45	Mg	0.10	Mn	0.45	0.009
013	1.02	0.333	Co	0.333	Mn	0.333	0.015
014	1.04	0.45	Co	0.10	Mn	0.45	0.009
015	1.04	0.40	Co+Mg	0.20	Mn	0.40	0.007
016	1.02	0.77	Co	0.20	B	0.03	0.003
017	1.03	0.60	Co	0.20	Mn	0.20	0.005
018	1.03	0.80	Fe	0.10	Mn	0.10	0.004
019	1.02	0.70	Co	0.25	Al+Ca	0.05	0.002
020	1.01	0.80	Co	0.16	Al	0.04	0.001

The secondary particles of the pulverulent LNMOS compound according to the invention preferably have a compressive strength of at least 200 MPa, particularly preferably of at least 300 MPa. Secondary particles are understood as meaning compact particles composed of a multiplicity of primary particles. Primary particles are particles which form from nuclei, for example during a crystallization process.

10

The compressive strength of the secondary particles according to the invention can be determined by the method mentioned in US 2004/0023113 A1, page 6, Example 1.

15

The pulverulent lithium mixed metal oxides according to the invention are distinguished by their very low porosity. According to the invention, the pulverulent lithium mixed metal oxides have a porosity, measured according to ASTM D 4222, of up to 0.01 cm³/g, preferably up to 0.008 cm³/g, with particular preference up to 0.006 cm³/g.

20

The pulverulent lithium mixed metal oxide according to the invention can be prepared both in spheroidal and in regular (non-spheroidal) particle shapes.

25

Preferred pulverulent lithium mixed metal oxides according to the invention are distinguished in particular by the spheroidal particle shape of the secondary particles, the shape factor of which has a value greater than 0.8, with particular preference greater than 0.9.

30

The shape factor of the secondary particles can be determined by the method mentioned in US 5476530, columns 7 and 8 and Figure 5. This method determines the shape factor of the particles, which is a measure of the sphericity of the particles. The shape factor of the secondary particle can also be determined from the scanning electron micrographs of the materials.

The shape factor is determined by evaluating the particle circumference and the particle area and determining the diameter derived from the respective variables. Said diameters are obtained from

$$d_U = U/\pi$$

$$d_A = (4A/\pi)^{1/2}.$$

The shape factor of the particles f is derived from the particle circumference U and the particle area A according to:

$$f = \left(\frac{d_A}{d_U} \right)^2 = \left(\frac{4\pi A}{U^2} \right)$$

In the case of an ideal spherical particle, d_A and d_U are of equal magnitude, and a shape factor of exactly one would result.

Fig. 1 shows, by way of example, an image, recorded using a scanning electron microscope (SEM), of the pulverulent lithium mixed metal oxide according to the invention, which was prepared according to Example 1.

Preferably, the pulverulent lithium mixed metal oxides according to the invention have a D10 value, measured according to ASTM B 822, which changes by not more than

1 μm , preferably by not more than 0.5 μm , after
compression of the powder at a pressure of 200 MPa
compared with the starting powder.

- 5 A decrease in the D10 value after the compression means
that a fraction of the particles has been broken into
smaller particles. Thus, the change in the D10 value is a
quantitative measure for determining the compressive
strength of the powders according to the invention.

10

Preferably, the pulverulent lithium mixed metal oxides
according to the invention have a D90 value, measured
according to ASTM B 822, which changes by not more than
1 μm after compression of the powder at a pressure of
15 200 MPa compared with the starting material.

Fig. 2 shows, by way of example, a scanning electron
micrograph of the pulverulent lithium mixed metal oxide
according to the invention after compression at 200 MPa,
20 which lithium mixed metal oxide was prepared according to
Example 1.

Fig. 2 shows that the spheroidal secondary particles have
retained their shape even after compression and have not
25 broken into fragments of a spheroidal particle. It is
clear from this that the material bed of the compound
prepared according to Example 1 withstands a pressure of
200 MPa without the particles breaking.

30 The pulverulent lithium mixed metal oxides according to
the invention preferably have a normalized width of the
particle size distribution, measured according to the
Formula (1)

$$\frac{D90 - D10}{D50} \quad (1)$$

in which D denotes the diameter of the secondary particles, of less than 1.4, particularly preferably less than 1.2.

Preferably, the pulverulent lithium mixed metal oxides according to the invention have a compressed density of at least 3.2 g/cm³, preferably of at least 3.5 g/cm³, measured at a compression pressure of 200 MPa.

The pulverulent lithium mixed metal oxides according to the invention are also distinguished in that they have a tapped density of at least 2.2 g/cm³, preferably of at least 2.4 g/cm³, measured according to ASTM B527.

The invention furthermore relates to a novel process for the preparation of pulverulent lithium mixed metal oxides according to the invention.

The invention therefore relates to a process for the preparation of the pulverulent lithium mixed metal oxides, comprising the following steps:

- a. provision of a co-precipitated nickel-containing precursor having a porosity of less than 0.05 cm³/g, measured according to ASTM D 4222,
- b. mixing the precursor according to a) with a lithium-containing component and production of a precursor mixture,
- c. calcination of the precursor mixture with multistage heating to temperatures of 1000°C with the use of a CO₂-free (≤ 0.5 ppm of CO₂), oxygen-containing carrier gas and production of a pulverulent product,
- d. deagglomeration of the powder by means of ultrasound

and sieving of the deagglomerated powder.

For the preparation of lithium mixed metal oxides according to the invention, nickel-containing precursors
5 which have a low porosity of less than $0.05 \text{ cm}^3/\text{g}$, preferably of less than $0.04 \text{ cm}^3/\text{g}$, particularly preferably of less than $0.03 \text{ cm}^3/\text{g}$, are required. Suitable nickel-containing precursors are in particular mixed oxides, mixed hydroxides, mixed oxyhydroxides,
10 partially oxidized mixed hydroxides, partially oxidized mixed hydroxysulphates of the metals Ni, Co, Mn, Al, Fe, Cr, Mg, Zr, B, Zn, Cu, Ca, Sr, Ba and/or mixtures thereof.

15 The preparation of the co-precipitated nickel-containing precursor is carried out by precipitation from aqueous metal salt solutions at a PH of 8-14, preferably of 9-13, by feeding alkali metal hydroxide solutions and optionally ammonia, in gaseous form or as an aqueous
20 solution. Although the reaction to give the nickel-containing precursor can be effected batchwise or semicontinuously, this precipitation reaction is preferably carried out continuously. In the continuous process, metal salt solution and the alkali metal
25 hydroxide solution are fed simultaneously to a precipitation reactor with continuous removal of the product suspension. Suitable metal salts are water-soluble metal salts, e.g. nitrates, sulphates, halides, such as for example, chlorides or fluorides. When
30 carrying out the precipitation, hydroxides of the alkali metals, preferably sodium hydroxide or potassium hydroxide, are used as alkali metal salt solutions.

The nickel-containing precursors can be prepared both in

spheroidal and in nonspheroidal particle shape, the preparation of the first-mentioned being carried out in the presence of ammonia or ammonium salts.

- 5 For the preparation of the lithium mixed metal oxides, the co-precipitated nickel-containing precursors are thoroughly mixed with a lithium-containing component so that a homogeneous mixture of the components is produced. Lithium carbonate, lithium hydroxide, lithium oxide,
10 lithium nitrate, lithium hydroxide monohydrate and/or mixtures thereof are preferably used as the lithium-containing components. For the reaction of the precursor mixture to give the lithium mixed metal oxides according to the invention it is important for the thermal
15 treatment (calcination) to be effected over a plurality of temperature stages. Preferably, the calcination is carried out in three stages, the precursor mixture being heated at a temperature of 200-400°C for 2-10 hours in the first stage, at 500-700°C for 2-10 hours in the
20 second stage and at 700-1000°C for 2-20 hours in the third stage. Preferably, the precursor mixture is calcined at a temperature of 250-350°C for 2-10 hours in the first stage, at 550-650°C for 2-10 hours in the second stage, and at 725-975°C for 2-20 hours in the
25 third stage, particularly preferably at a temperature of 250-350°C for 4-8 hours in the first stage, at 550-650°C for 4-8 hours in the second stage and at 725-975°C for 5-15 hours in the third stage.
- 30 As a result of the temperature hold stages and associated controlled reaction a material is obtained which has no secondary particle agglomerates that are strongly sintered together. Agglomerates that are strongly sintered together are understood as meaning agglomerates

which do not disintegrate into the individual secondary particles in the case of ultrasound sieving. Such a material without agglomerates which are strongly sintered together has the advantage that milling, as is usually
5 required after calcination, can be dispensed with. Milling has the disadvantage that destruction of individual spheroidal secondary particles leads to the formation of angular and square-edged particles. It is in particular these particles which, during electrode
10 manufacture, owing to their shape, result in further particles being destroyed within the material bed under high pressure.

The lithium mixed metal oxide which is obtainable after
15 the calcination according to the invention and may be present in slightly agglomerated form is subjected to gentle deagglomeration by means of ultrasound and subsequent sieving. The ultrasound causes the isolated, loose agglomerates which are optionally formed during the
20 calcination, to disintegrate in a gentle manner into their constituents (secondary particles), but without the secondary particles themselves being destroyed.

Furthermore, it is important that the reaction to give
25 the LNMOS takes place in an oxygen-containing carrier gas atmosphere which is free of CO₂. A CO₂-free carrier gas atmosphere is understood as meaning a carrier gas which contains ≤ 0.5 ppm (part per million) of CO₂. The absence of CO₂ in the carrier gas prevents incorporation of the
30 CO₂ into the end product, with the result that formation of crystal lattice defects is reduced.

Preferably, the carrier gas contains 20 to 100% by volume, particularly preferably 40 to 100% by volume, of

oxygen. The process according to the invention is distinguished by the fact that the reaction of the nickel-containing precursor takes place with retention of the shape of the secondary particles and/or particle size distribution.

The process according to the invention makes it possible, for example, to convert the spherical nickel-containing precursors having a very narrow particle size distribution into the lithium mixed metal oxide with retention of the shape of the secondary particles.

The pulverulent lithium mixed metal oxides according to the invention are suitable in particular for the production of secondary lithium batteries. Preferably, they are used as electrode material (anode, cathode) for lithium secondary batteries together with the material known to the person skilled in the art.

The invention is explained in more detail below with reference to the following example.

Example 1

A spheroidal $\text{Ni}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}(\text{O})_{0.2}(\text{OH})_{1.8}(\text{SO}_4)_{0.01}$ was used as co-precipitate Ni precursor. This material had a porosity of $0.0372 \text{ cm}^3/\text{g}$. An Li_2CO_3 of $< 40 \mu\text{m}$ (Chemetall) was dry-blended with the Ni precursor in the molar $\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})$ ratio of 1.05:1.00. The dry blend thus formed (also referred to as premix) was then placed in an oven at room temperature and first heated to 300°C and kept at this temperature for 6 hours. The heating of the material and the entire oven process were effected with the use of oxygen as a carrier gas stream which is

substantially free of CO₂ (≤ 0.5 ppm). At said 300°C, controlled release of water from the nickel-containing precursor took place.

5 After this temperature hold stage, the material was heated further to 600°C and kept at this temperature for 6 hours. At this oven temperature a very controlled reaction of the two starting components to give
10 $\text{Li}_{1.04}\text{Ni}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2(\text{SO}_4)_{0.01}$ took place. The reaction temperature was deliberately kept low in order to be able to achieve a slow and hence controlled reaction of the two components to give the end product. By means of this controlled reaction, the formation of crystal lattice defects and the significant inclusion of pores in the
15 particle structure were avoided. A "breathing"/gas expulsion from the material during the reaction is permitted. Finally, the material is heated to 860°C and then kept at this temperature for 10 hours in order to carry out ripening of the crystals and to produce high
20 crystallinity.

Thereafter the material is brought to room temperature and then poured directly on to a sieve having a mesh size of 50 μm . The sieve was additionally equipped with an
25 ultrasound generator having an ultrasound power of 200 W. The deagglomerated and sieved material thus obtained has a tapped density of 2.2 g/cm³. The porosity of the material was 0.0029 cm³/g. The D10, D50 and D90 values were 5.67 μm , 8.96 μm and 13.62 μm . For the normalized
30 particle size width, the value of $(13.62 \mu\text{m} - 5.67 \mu\text{m}) / 8.96 \mu\text{m} = 0.89$ was obtained therefrom.

The material had a density of 3.0 g/cm³ after the determination of the compressed density at 100 MPa, and a

density of 3.3 g/cm³ after the determination at 200 MPa.

The D10 value had decreased by 0.2 µm compared with the original material after determination of the compressed density at a pressure of 100 MPa, and the D10 value had decreased by 0.4 µm compared with the original material at a pressure of 200 MPa. The particle size distributions of the material before the compression and after the compression at a pressure of 200 MPa are shown in Fig. 3.

The LNMOS prepared in the example was measured as positive active material in an electrochemical half-cell with lithium metal as the negative electrode (anode). The electrolyte used was a 1:1:1 mixture of ethylene carbonate, dimethyl carbonate and diethyl carbonate, which contained LiPF₆ in a concentration of 1 mol/l. The positive electrode consists of 83% by weight of active material, 10% by weight of carbon black super P and 7% by weight of polytetrafluoroethylene (PTFE) as binder. The initial electrochemical capacity was determined in a voltage range of 2.75 to 4.3 V at a constant current rate of 0.1 C (10 hours per complete charging or discharging). Under said measuring conditions an initial discharge capacity of 160 mAh/g was achieved.

The electrochemical cyclic behaviour was determined in a voltage range of 2.75 to 4.3 V at a constant current rate of 1 C (1 hour per complete charging or discharging). After 40 electrochemical charging and discharging cycles, the cell still exhibited 98.5% of the initial discharge capacity at a constant current rate of 1 C.

CLAIMS

1. Pulverulent compound of the formula $\text{Li}_a\text{Ni}_b\text{M1}_c\text{M2}_d(\text{O})_2(\text{SO}_4)_x$, in which M1 denotes at least one
5 element selected from the group consisting of Fe, Co, Cr, Mg, Zn, Cu and/or mixtures thereof, M2 denotes at least one element selected from the group consisting of Mn, Al, B, Ca, Sr, Ba, Si and/or mixtures thereof, and $0.95 \leq a \leq 1.1$, $0.3 \leq b \leq 0.83$, $0.1 \leq c \leq 0.5$,
10 $0.03 \leq d \leq 0.5$ and $0.001 \leq x \leq 0.03$, characterized in that the secondary particles have a compressive strength of at least 100 MPa.
2. Pulverulent compound according to Claim 1,
15 characterized in that it has a compressive strength of at least 200 MPa.
3. Pulverulent compound according to Claim 1,
20 characterized in that it has a compressive strength of at least 300 MPa.
4. Pulverulent compound according to at least one of Claims 1 to 3, characterized by a porosity of up to $0.01 \text{ cm}^3/\text{g}$ measured according to ASTM D 4222.
25
5. Pulverulent compound according to at least one of Claims 1 to 3, characterized by a porosity of up to $0.008 \text{ cm}^3/\text{g}$ measured according to ASTM D 4222.
- 30 6. Pulverulent compound according to at least one of Claims 1 to 3, characterized by a porosity of up to $0.006 \text{ cm}^3/\text{g}$ measured according to ASTM D 4222.
7. Pulverulent compound according to at least one of

Claims 1 to 6, characterized in that the secondary particles have a spheroidal shape.

8. Pulverulent compound according to Claim 7,
5 characterized in that the secondary particles thereof have a shape factor greater than 0.8.

9. Pulverulent compound according to Claim 7,
10 characterized in that the secondary particles thereof have a shape factor greater than 0.9.

10. Pulverulent compound according to at least one of Claims 1 to 9, characterized in that the D10 value, measured according to ASTM B 822, after compression of
15 the material at a pressure of 200 MPa changes by not more than 0.5 μm compared with the starting material.

11. Pulverulent compound according to at least one of Claims 1 to 9, characterized in that the D90 value,
20 measured according to ASTM B 822, after compression of the material at a pressure of 200 MPa changes by not more than 1 μm compared with the starting material.

12. Pulverulent compound according to at least one of
25 Claims 1 to 11, characterized in that the normalized width of the particle size distribution, measured according to the Formula (1)

$$\frac{D90 - D10}{D50} \quad (1)$$

30

in which D denotes the diameter of the secondary particles, is less than 1.4.

13. Pulverulent compound according to at least one of

Claims 1 to 11, characterized in that the normalized width of the particle size distribution, measured according to the Formula (1)

$$5 \quad \frac{D90 - D10}{D50} \quad (1)$$

in which D denotes the diameter of the secondary particles, is less than 1.2.

10 14. Pulverulent compound according to at least one of Claims 1 to 13, characterized in that it has a compressed density of at least 3.2 g/cm³ at a compression pressure of 200 MPa.

15 15. Pulverulent compound according to at least one of Claims 1 to 14, characterized in that it has a tapped density measured according to ASTM B 527, of at least 2.2 g/cm³.

20 16. Pulverulent compound according to at least one of Claims 1 to 14, characterized in that it has a tapped density measured according to ASTM B 527, of at least 2.4 g/cm³.

25 17. Process for the preparation of the pulverulent compound according to at least one of Claims 1-16, comprising the following steps:

30 a. provision of a co-precipitated nickel-containing precursor having a porosity of less than 0.05 cm³/g, measured according to ASTM D 4222,

b. mixing the precursor according to a) with a lithium-containing component,

c. calcination of the mixture with multistage heating to temperatures of 1000°C with the use of a CO₂-free (≤ 0.5 ppm of CO₂), oxygen-containing carrier gas and
5 production of a pulverulent product,

d. deagglomeration of the powder by means of ultrasound and sieving of the deagglomerated powder.

10 18. Process according to Claim 17, characterized in that the nickel-containing component is a mixed oxide, mixed hydroxide, mixed oxyhydroxide, partially oxidized mixed hydroxide, partially oxidized mixed hydroxysulphate of the metals Ni, Co, Mn, Al, Fe, Cr, Mg, Zr, B, Zn, Cu, Ca,
15 Sr, Ba and/or mixtures thereof.

19. Process according to Claim 17, characterized in that the lithium-containing component is lithium carbonate, lithium hydroxide, lithium hydroxide monohydrate, lithium
20 oxide, lithium nitrate and/or mixtures thereof.

20. Process according to at least one of Claims 17 to 19, characterized in that the calcination of the precursor mixture is effected at a temperature of 200-
25 400°C for 2-10 hours in the first stage, at 500-700°C for 2-10 hours in the second stage and at 700-1000°C for 2-20 hours in the third stage.

21. Process according to at least one of Claims 17 to
30 19, characterized in that the calcination of the precursor mixture is effected at a temperature of 250-350°C for 2-10 hours in the first stage, at 550-650°C for 2-10 hours in the second stage and at 725-975°C for 2-20 hours in the third stage.

22. Process according to at least one of Claims 17 to 19, characterized in that the calcination of the precursor mixture is effected at a temperature of 250-
5 435°C for 4-8 hours in the first stage, at 550-650°C for 4-8 hours in the second stage and at 725-975°C for 5-15 hours in the third stage.

23. Process according to at least one of Claims 17 to
10 22, characterized in that the carrier gas contains 20 to 100% by volume of oxygen.

24. Process according to at least one of Claims 17 to 22, characterized in that the carrier gas contains 40 to
15 100% by volume of oxygen.

25. Process according to at least one of Claims 17 to 24, characterized in that the reaction of the nickel-containing precursor takes place with retention of the
20 shape of the secondary particles and/or particle size distribution.

26. Pulverulent compounds obtainable according to at least one of Claims 17 to 25.

25 27. Use of the pulverulent compound according to at least one of Claims 1 to 26 as electrode material in lithium secondary batteries.

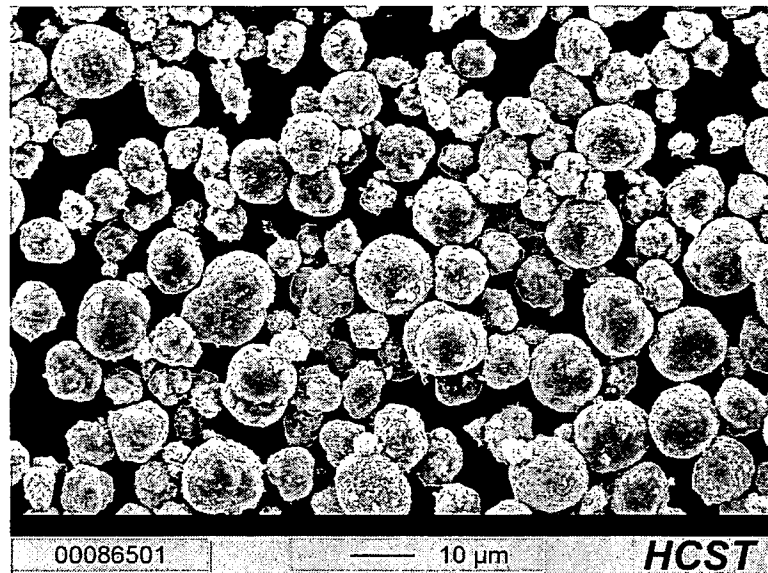


Fig. 1

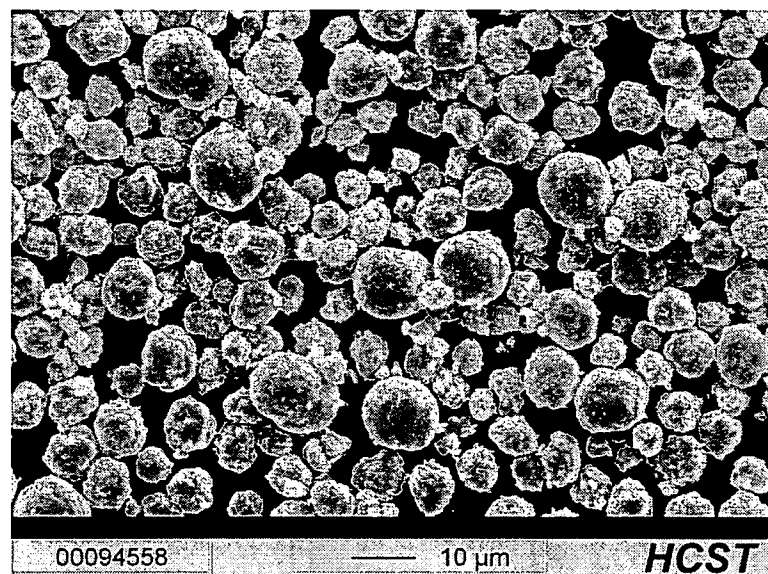


Fig. 2

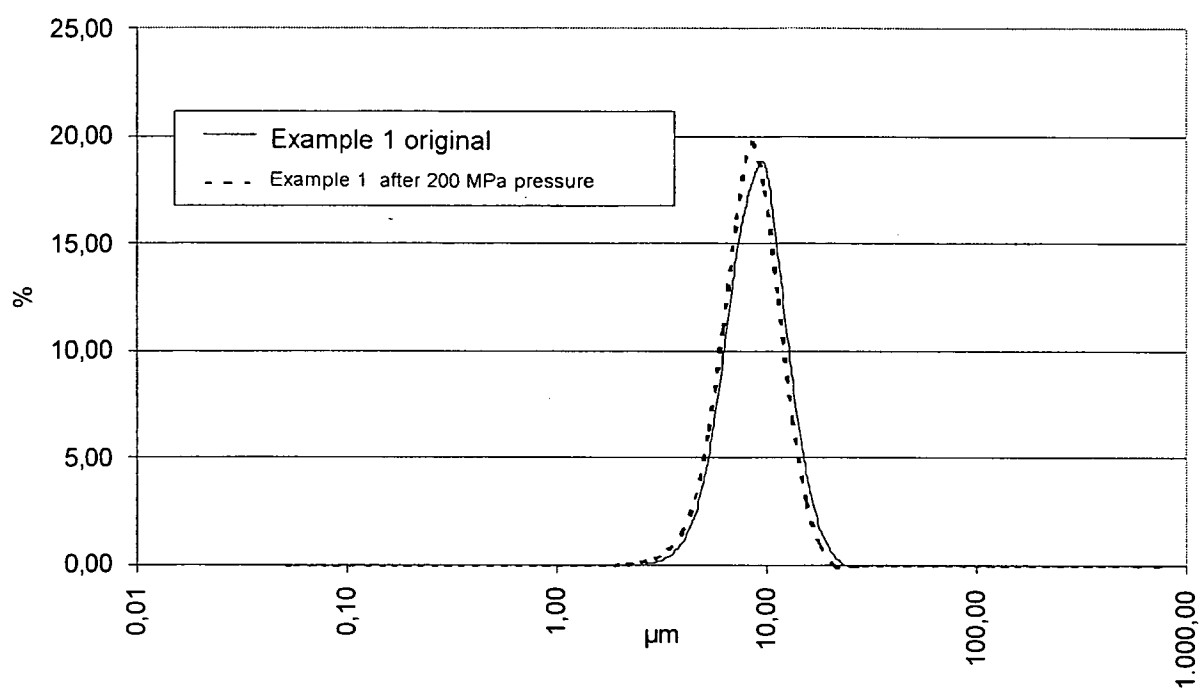


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/008848

A. CLASSIFICATION OF SUBJECT MATTER INV. H01M4/48 H01M4/52 H01M4/50 H01M10/40		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED 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 practical, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/057466 A1 (SUHARA MANABU [JP] ET AL) 16 March 2006 (2006-03-16) paragraph [0076]; examples Comparative-1	1,7,26,27
X	US 2005/271944 A1 (SUHARA MANABU [JP] ET AL) 8 December 2005 (2005-12-08) paragraph [0065]; example 4	1,7-9,26,27
X	US 2005/220700 A1 (SUHARA MANABU [JP] ET AL) 6 October 2005 (2005-10-06) examples 1-3,5	1,7-9,26,27
A	EP 1 450 423 A (TOYOTA MOTOR CO LTD [JP]) 25 August 2004 (2004-08-25) page 3, lines 33-35 paragraphs [0024], [0043] - [0047]	1,17-25
<div style="display: flex; justify-content: space-between;"> <input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex. </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents:</p> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*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)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>*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</p> <p>*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</p> <p>*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.</p> <p>* & * document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-size: 1.2em;">16 January 2008</div>		Date of mailing of the international search report <div style="text-align: center; font-size: 1.2em;">28/01/2008</div>
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-size: 1.2em;">Fitzpatrick, John</div>

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Information on patent family members

International application No

PCT/EP2007/008848

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