



(51) International Patent Classification:
C01G 53/00 (2006.01)

(21) International Application Number:
PCT/EP2024/067376

(22) International Filing Date:
21 June 2024 (21.06.2024)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
23184506.6 10 July 2023 (10.07.2023) EP

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(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG,
KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY,
MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA,
NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO,
RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH,

TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS,
ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, CV,
GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST,
SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ,
RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ,
DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT,
LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE,
SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN,
GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a
patent (Rule 4.17(ii))

Published:

— with international search report (Art. 21(3))

(54) Title: PROCESS FOR MAKING A CATHODE ACTIVE MATERIAL AND ITS PRECURSORS

(57) Abstract: Process for making a particulate (oxy)hydroxide of TM wherein TM comprises nickel and one transition metal selected from Co and Mn and at least one further element selected from Ca, Si, Ti, Zr, Mo, W, Al, Mg, Nb, and Ta and wherein said process comprises the steps of: (a) Providing an aqueous solution (α) containing sulfates of Ni and of at least one transition metal selected from Co and Mn, and a water-soluble compound of at least one further element selected from Ca, Si, Ti, Zr, Mo, W, Al, Mg, Nb, and Ta, and an aqueous solution (β) containing an alkali metal hydroxide and, optionally, an aqueous solution (γ) containing ammonia, (b) combining solution (α) and solution (β) and, if applicable, a solution (γ) at a pH value in the range of from 12.5 to 14.0 in a stirred tank reactor, thereby creating particles of a hy- droxide containing nickel, said particles being slurried, (c) adding solution (α) and solution (β) and, if applicable, a solution (γ) to slurry from step (b) at a pH value in the range of from 9.6 to 11.6 in a stirred tank reactor, thereby growing particles of hydroxide of TM, (d) terminating the addition of solution (α) but continuing the addition of solution (β) and, if applicable, of solution (γ), to adjust the pH value to 12.0 to 14.0, and (e) removing the particulate (oxy)hydroxide of TM by a solid/liquid separation method, followed by drying.

WO 2025/011920 A1

Process for making a cathode active material and its precursors

The present invention is directed towards a process for making a particulate (oxy)hydroxide or oxide of TM wherein TM comprises nickel and one transition metal selected from Co and Mn and at least one further element selected from Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta and wherein said process comprises the steps of:

- (a) Providing an aqueous solution (α) containing sulfates of Ni and of at least one transition metal selected from Co and Mn, and a water-soluble compound of at least one further element selected from Ca, Si, Ti, Zr, Mo, W, Al, Mg, Nb, and Ta, and an aqueous solution (β) containing an alkali metal hydroxide and, optionally, an aqueous solution (γ) containing ammonia,
- (b) combining solution (α) and solution (β) and, if applicable, solution (γ) at a pH value in the range of from 12.5 to 14.0 in a stirred tank reactor, thereby creating particles of a hydroxide containing nickel, said particles being slurried,
- (c) adding solution (α) and solution (β) and, if applicable, a solution (γ) to slurry from step (b) at a pH value in the range of from 9.6 to 11.6 in a stirred tank reactor, thereby growing particles of hydroxide of TM in a stirred tank reactor, thereby growing particles of hydroxide of TM,
- (d) terminating the addition of solution (α) but continuing the addition of solution (β) and, if applicable, of solution (γ), to adjust the pH value to 12.0 to 14.0, and
- (e) removing the particulate hydroxide of TM by a solid/liquid separation method, followed by drying.

Lithiated transition metal oxides are currently used as electrode active materials for lithium-ion batteries. Extensive research and developmental work have been performed in the past years to improve properties like charge density, specific energy, but also other properties like the reduced cycle life and capacity loss that may adversely affect the lifetime or applicability of a lithium-ion battery. Additional effort has been made to improve manufacturing methods.

In a typical process for making cathode materials for lithium-ion batteries, first a so-called precursor is being formed by co-precipitating the transition metals as carbonates, oxides or preferably as hydroxides that may or may not be basic, for example oxyhydroxides. The precursor is then mixed with a source of lithium such as, but not limited to LiOH, Li₂O or Li₂CO₃ and calcined

(fired) at high temperatures. Lithium source(s) can be employed as hydrate(s) or in dehydrated form. The calcination – or firing – often also referred to as thermal treatment or heat treatment of the precursor – is usually carried out at temperatures in the range of from 600 to 1000 °C. During the thermal treatment a solid-state reaction takes place, and the electrode active material is formed. The thermal treatment is performed in the heating zone of an oven or kiln.

To a major extent, properties of the precursor translate into properties of the respective cathode active material to a certain extent, such as particle size distribution, content of the respective transition metals and more. It is therefore possible to influence the properties of cathode active materials by steering the properties of the precursor.

Certain impurities that are introduced during the precursor manufacture are difficult to remove. They are retained in the cathode active material. In case such impurities are disadvantageous methods to avoid such impurities are highly welcomed.

One impurity that is unwelcome is sulfate, e.g., as Li_2SO_4 , see, e.g., EP 2 289 849 A1. Sulfate can be incorporated easily through the sulfates that are starting materials for the precursor manufacture. Since sulfates – unlike chlorides – do not cause corrosion problems and are commonly the cheapest water-soluble salts of transition metals such as nickel and cobalt and manganese they are popular starting materials. In cathode active materials, though, sulfate is unwelcome because it may capture lithium during the calcination process under formation of an electrically inactive compound, Li_2SO_4 . Under certain circumstances, Li_2SO_4 may create nanopores in the crystallites of the cathode active material that can deteriorate its performance in lithium-ion battery application, see, e.g., ACS Nano 2019, 13, 9, 10694–10704.

In particular in cathode active materials that are made from recycled transition metals that contain at least one of Ca, Si, Ti, Zr, Mo, W, Al, Mg, Nb, and Ta, a higher sulfate content is undesired. Especially, cathode active materials with a sulfate content of more than one wt% suffer from low processability and crystallinity.

It was an objective of the present invention to provide a process that allows the production of a cathode active material with a low content of sulfate. It was further an objective of the present invention to provide a process that allows the production of a precursor with a low content of sulfate. It was further an objective of the present invention to provide a cathode active material with a low sulfate content and a suitable precursor wherein such precursor can be made easily.

Accordingly, the process as defined at the outset has been found, hereinafter also defined as “inventive process” or “process according to the (present) invention”. The inventive process

comprises at least three steps, hereinafter also referred to as step (a), step (b) and step (c) and step (d) and step (e), or – even more briefly – (a), (b), (c), (d) and (e), respectively. The inventive process may include further – optional – steps. Steps (a) to (e) are performed consecutively. Steps (a) to (e) are described in more detail below. By the inventive process, a precursor with a low sulfate content is obtained.

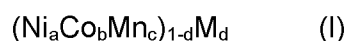
The inventive process is a process for making a particulate (oxy)hydroxide or oxide of TM. Said particulate (oxy)hydroxide then serves as a precursor for cathode active materials, and it may therefore also be referred to as precursor.

In one embodiment of the present invention, the resultant precursor is comprised of secondary particles that are agglomerates of primary particles.

In one embodiment of the present invention the specific surface (BET) of the resultant precursor is in the range of from 1 to 70 m²/g, determined by nitrogen adsorption, for example in accordance with to DIN-ISO 9277:2003-05. The outgassing temperature is 120°C.

The precursor is an (oxy)hydroxide of TM wherein TM comprises Ni and at least one metal selected from Co and Mn, and, optionally, at least one further element selected from Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta, preferably a combination of Al, W, Mg and Nb or a combination of Ti, Zr, Al and Mg.

In one embodiment of the present invention, TM is a combination of metals according to general formula (I)



wherein

a is in the range of from 0.6 to 0.95, preferably from 0.8 to 0.94,
b is in the range of from 0.025 to 0.2, preferably from 0.025 to 0.15,
c is in the range of from zero to 0.2, preferably from zero to 0.15, and
d is in the range of from 0.02 to 0.1,

M is selected from Mg, Al, Ca, Si, Ti, Zr, Mo, W, Al, Mg, Nb, and Ta, preferably selected from Al, Mg, Nb, W, Ti, and Zr, more preferably a combination of Mg and Al or a combination of Al, Mg, W and Nb or a combination of Mg and Al or a combination of Al, Mg, Ti and Zr.

$a + b + c = 1$, and $b + c > \text{zero}$ or M includes Al and $d > \text{zero}$.

In another embodiment of the present invention, TM corresponds to general formula (II)



with

a being in the range of from 0.25 to 0.4,

b being in the range of from zero to 0.2,

10 c being in the range of from 0.6 to 0.75, and

d being in the range of from 0.02 to 0.1,

M is selected from Mg, Ca, Si, Al, Ti, Zr, Mo, W, Al, Mg, Nb, and Ta, preferably selected from Al, Mg, Nb, W, Ti, and Zr.

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$a + b + c = 1$.

In each case, TM may contain traces of further metal ions other than the above, for example traces of ubiquitous metals such as sodium, iron, or zinc, as impurities but such traces will not
20 be taken into account in the description of the present invention. Traces in this context will mean amounts of 0.05 mol-% or less, referring to the total metal content of TM.

Precursors as used herein are particulate materials. In one embodiment of the present invention, precursors have an average particle diameter D50 in the range of from 3 to 20 μm , preferably from 4 to 16 μm . The average particle diameter may be determined, e. g., by light scattering or LASER diffraction or electroacoustic spectroscopy. The particles are composed of primary particles, in particular they are agglomerates of primary particles, and the above particle diameter refers to the secondary particle diameter. Although (D50) is – strictly speaking – the median value rather than an average diameter both expressions are used interchangeably.

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In one embodiment of the present invention, the span of the particle diameter distribution of precursors is in the range of from 0.2 to 2.0, preferably from 0.25 to 0.35 or from 0.6 to 1.5. The span is defined as $[(D90) - (D10)]/(D50)$, with the values of (D90), (D50) and (D10) being determined by dynamic light scattering or by X-ray diffraction.

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Said particles of precursors may have an irregular shape but in a preferred embodiment, said particulate material has a regular shape, for example spheroidal or even spherical. The aspect ratio may be in the range of from 1 and 10, preferably from 1 to 3 and even more preferably

from 1 to 1.5. The aspect ratio is defined as the ratio of width to length or specifically the particle diameter in the longest dimension versus the particle diameter in the shortest dimension. Perfectly spherical particles have an aspect ratio of 1.

- 5 Step (a) includes providing at least one aqueous solution (α) containing sulfates of Ni and of at least one transition metal selected from Co and Mn, and, of a water-soluble compound of at least one further element selected from Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta, and an aqueous solution (β) containing an alkali metal hydroxide and, optionally, an aqueous solution (γ) containing a complexing agent, for example ammonia.

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In one embodiment of the present invention, the nickel sulfate used as raw material in step (a) is at least partially made by recycling of lithium-ion batteries. Such recycling preferably includes a mechanical treatment of spent batteries or off-spec electrochemical cells followed by one or more chemical processes such as leaching processes, or by at least one smelting process followed by re-dissolving any reduced metal. Although strictly speaking not being a recycling, a re-introduction of off-spec cathode active materials is included in the term "recycling" in the context of the present invention. Depending on the recycling process used, a nickel is obtained that contains a measurable amount of at least one of Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta, preferably of at least two of Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta, for example 0.01 to 1.5% by weight, preferably at least one of Al, Mg, Nb, W, Ti, and Zr, more preferably a combination of Mg and Al or a combination of Al, Mg, W and Nb or a combination of Mg and Al or a combination of Al, Mg, Ti and Zr

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In the context of the present invention, the term "water-soluble compounds" refers to compounds that have a solubility in water at 20°C of at least 10 g/l.

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The term "water-soluble compounds of aluminum" then refers to compounds like $\text{Al}_2(\text{SO}_4)_3$, $\text{Al}(\text{NO}_3)_3$, $\text{KAl}(\text{SO}_4)_2$, NaAlO_2 and $\text{NaAl}(\text{OH})_4$. Depending on the choice of water-soluble compound of aluminum, the pH value of aqueous solution (α) may be in the range of from 1 to 3 or above 13.

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Examples of suitable compounds of Mg are MgSO_4 , $\text{Mg}(\text{NO}_3)_2$, magnesium acetate and MgCl_2 , with MgSO_4 being preferred.

35 Examples of suitable compounds of Ca are $\text{Ca}(\text{NO}_3)_2$, calcium acetate and CaCl_2 .

Examples of Suitable compounds of Si are sodium metasilicate, sodium orthosilicate, and silicic acid.

Examples of suitable compounds of Ti are $\text{Ti}(\text{SO}_4)_2$, TiOSO_4 , $\text{TiO}(\text{NO}_3)_2$, $\text{Ti}(\text{NO}_3)_4$, with $\text{Ti}(\text{SO}_4)_2$ being preferred.

- 5 Examples of suitable compounds of Zr are zirconium acetate, $\text{Zr}(\text{SO}_4)_2$, ZrOSO_4 , $\text{ZrO}(\text{NO}_3)_2$, $\text{Zr}(\text{NO}_3)_4$, with $\text{Zr}(\text{SO}_4)_2$ being preferred.

Examples of suitable compounds of Nb are $(\text{NH}_4)\text{Nb}(\text{C}_2\text{O}_4)_3$ and $(\text{NH}_4)\text{NbO}(\text{C}_2\text{O}_4)_2$. Examples of suitable compounds of Mo are MoO_3 , Na_2MoO_4 , and $(\text{NH}_4)_2\text{MoO}_4$.

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Examples of suitable compounds of W are WO_3 , $\text{WO}_3 \cdot \text{H}_2\text{O}$, Na_2WO_4 , ammonium tungstate and tungstic acid.

- 15 Solution (α) may have a pH value in the range of from 2 to 6. In embodiments wherein higher pH values are desired, ammonia may be added to solution (α). However, it is preferred to not add ammonia to solution (α). In case it is intended to provide a solution containing NaAlO_2 and $\text{NaAl}(\text{OH})_4$ it is preferred to provide at least two aqueous solutions, one containing nickel and at least one of cobalt and manganese and, optionally, at least one of Ti, Zr, Mo, W, Mg, Nb, and Ta, and another aqueous solution containing NaAlO_2 or $\text{NaAl}(\text{OH})_4$.

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The concentration of nickel and other constituents of TM, as the case may be, can be selected within wide ranges. Preferably, the respective total metal concentration is selected to be within a range of 1 to 1.8 mol of the metal/kg of solution, more preferably 1.3 to 1.7 mol of the metal/kg of solution.

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In addition, in step (a) an aqueous solution of alkali metal hydroxide is provided, hereinafter also referred to as solution (β). Examples of alkali metal hydroxides are potassium hydroxide and a combination of sodium and potassium hydroxide, and even more preferred is sodium hydroxide.

- 30 In one embodiment of the present invention, solution (β) mainly contains alkali metal hydroxide and some amount of carbonate, e.g., 0.1 to 2 % by weight, referring to the respective amount of alkali metal hydroxide, added deliberately or by aging of the solution (β) or the respective alkali metal hydroxide.

- 35 Solution (β) may have a concentration of hydroxide in the range from 0.1 to 12 mol/l, preferably 6 to 10 mol/l.

The pH value of solution (β) is preferably 13 or higher, for example 14.5.

Solution (γ) contains a complexing agent. Examples of complexing agents are ammonia and organic acids or their alkali or ammonium salts wherein said organic acid bears at least two functional groups per molecule and at least one of the functional groups is a carboxylate group.

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Examples of organic acids that bear two identical functional groups are adipic acid, oxalic acid, succinic acid and glutaric acid. An example of organic acids that bears three identical functional groups is citric acid.

10 In one embodiment of the present invention, said organic acid is selected from malic acid, tartaric acid, citric acid, and glycine.

In one embodiment of the present invention, the concentration of complexing agent(s) in solution (γ) is in the range of from 1 to 30 % by weight. In embodiments wherein the complexing agent is selected from ammonia its concentration is preferably in the range of from 10 to 30 % by weight. In embodiments wherein the complexing agent(s) is or are selected from organic acids or their alkali or ammonium salts wherein said organic acid bears at least two functional groups per molecule and at least one of the functional groups is a carboxylate group, the concentration of said complexing agent in solution (γ) may be in the range of from 0.2 to 10% by weight.

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More preferred complexing agent is ammonia.

In steps (b) and (c), solution (α) and solution (β) and – if applicable – solution (γ) are combined, under precipitation of a hydroxide. In step (b), essentially particles of hydroxide are formed and in step (c), such particles of hydroxide are grown. The continuous phase is also referred to as “mother liquor”. Said mother liquor contains the sulfate as well as alkali metal ions from the base in solution (β).

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30 Steps (b) and (c) may be performed in the same stirred tank reactor or in a cascade of at least two stirred tank reactors that are each equipped with an overflow system. Preferably, the stirred tank reactor(s) is or are equipped with a solid-liquid separation device through which mother liquor is removed. Examples of solid-liquid separation devices are clarifiers such as lamella clarifiers and filtration devices such as filter presses, hydrocyclones, and filters such as at least one candle filter. With the use of one or more of such solid-liquid separation devices, slurries with a solids content of up to 1200 g/l may be obtained.

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The percentage of mother liquor withdrawn in steps (b) and (c) may be in the range of from 200 to 1,200 g/l, preferably 800 to 1,200 g/l. However, despite the withdrawal of mother liquor, the slurry is still well stirrable.

- 5 Step (b) includes combining solution(s) (α) and solution (β) and, if applicable, solution (γ), in a continuous reactor, thereby creating solid particles of a hydroxide of TM. Said solid particles are slurried.

10 In one embodiment of the present invention, the particles resulting from step (b) have an average diameter in the range of from 2 to 10 μm , preferably 2 to 5 μm .

In step (b), the pH value of the liquid phase of the slurry is in the range of from 12.5 to 14.0. The pH value is determined at 23°C in the liquid phase.

- 15 In one embodiment of the present invention, the average hydraulic residence time of the slurry in step (b) is in the range of from 30 minutes to 16 hours, preferably in the range from 1 to 12 hours, more preferred in the range of 2 to 8 hours.

20 In one embodiment of the present invention, step (b) is performed at a temperature in the range from 10 to 85°C, preferably at temperatures in the range from 20 to 70°C.

In one embodiment of the present invention, step (b) is performed at constant pressure, for example at ambient pressure. In other embodiments, step (b) is performed at elevated pressure, for example up to 50 bar.

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In one embodiment of the present invention, mother liquor is removed from the continuous reactor during step (b). The mother liquor contains water and sodium sulfate.

30 After step (b), step (c) is performed. Step (c) may be performed in a different vessel or in the same vessel as step (b). In the latter case the inventive process is performed batch-wise.

In one embodiment of the present invention, the solids content of the slurry that is transferred to step (c) – or to a storage vessel, see below – is in the range of from 200 to 1200 g/l. Before the start-up of step (c), slurry from step (b) is preferably diluted in the reactor wherein step (c) is performed, for example with de-ionized water or with mother liquor, to 2 to 100g/l. The solids content may be determined by density measurements or ICP (inductively coupled plasma) or by Coriolis meters and refers to the slurried particles. Dissolved compounds such as, but not limited to Na_2SO_4 are neglected in this context.

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In one embodiment of the present invention, step (b) – as well as step (c) – is performed under an inert atmosphere, for example nitrogen or a rare gas such as argon. Oxygen-depleted air, for example with up to 2% by weight of O₂, is feasible as well, especially when TM does not contain manganese. Due to the strong alkalinity of solution (β), CO₂ is not a suitable inert atmosphere.

In step (c), slurry from step (b) is transferred into a continuously or preferably batch-wise operated stirred tank reactor wherein a solution (α) and a solution (β) and, if applicable, a solution (γ) are combined.

In step (c), the pH value of the liquid phase of the slurry is in the range of from 9.6 to 11.6, preferably in the range from 9.8 to 11.2, more preferably in the range from 10.0 to 10.8. The pH value is determined at 23°C. A pH value lower than in step (b) may be effected by reducing the ratio of hydroxide to transition metals of solution (α), or by reducing the amount of solution or even terminating the addition of solution (γ).

Solution (α) and a solution (β) and, if applicable, solution (γ) in step (c) are defined as above. They may have the same composition as their equivalents in step (b) or different – but in the framework of the definition as set out above, for example, one of them contains a water-soluble salt of nickel and at least one of cobalt and manganese. In such cases, they are also referred to as solutions (α') and a solution (β') and, if applicable, solution (γ'), respectively. Preferably, however, the compositions of solutions (α) in steps (b) and (c) are identical in composition.

Even more preferably, the compositions of solutions (α) in steps (b) and (c) are identical as well as the compositions of solutions (β).

In one embodiment, wherein step (c) is performed in a batch-wise operated stirred tank reactor, the composition of solution (α) – or (α'), as the case may be – varies in the course of step (c), for example the concentrations of nickel and cobalt or manganese. In another embodiment of the present invention, the composition of solution (α) – or (α'), as the case may be – remains constant.

In one embodiment of the present invention, the duration of step (c) is in the range of from 30 minutes to 80 hours, preferably in the range from 10 to 70 hours, more preferred in the range of 15 to 60 hours.

In one embodiment of the present invention, step (c) is performed at a temperature in the range from 10 to 85°C, preferably at temperatures in the range from 20 to 60°C.

In one embodiment of the present invention, step (c) is performed at constant pressure, for example at ambient pressure. In other embodiments, step (b) is performed at elevated pressure, for example up to 50 bar.

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In one embodiment of the present invention, the inventive process is carried out in a cascade of at least two stirred tank reactors of which the first stirred tank reactor is equipped with an overflow system through which slurry is removed from the first stirred tank reactor and transferred to the second stirred tank reactor, directly or indirectly.

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In a preferred embodiment, slurry is removed from the continuous stirred tank reactor in which step (b) is carried out and transferred to a stirred storage vessel where the slurry is stored under stirring for a time period of from 15 minutes to 24 hours, preferably from 30 minutes to 10 hours, before being transferred to the second stirred tank reactor. Said operation is also referred to as storage step. In the course of the storage step, neither solution (α) nor solution (β) nor solution (γ) is added. Said storage is preferably under inert gas, *vide supra*.

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In one embodiment of the present invention, the temperature during the storage step is in the range of from 20 to 70°C, preferably 30 to 60°C.

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In one embodiment of the present invention, the pH value of the slurry in the storage vessel is in the range of from 10.0 to 13.0 determined at 23°C, preferably from 12.0 to 12.5.

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In one embodiment of the present invention, at the same time in the range of from 5 to 30 vol-%, preferably 10 to 20 vol-% of slurry are in the storage vessel and 70 to 95 vol-%, preferably 80 to 90 vol-% of slurry are in the tank reactors wherein steps (b) and (c) are performed. In this context, the amount of slurry being located in any piping or related part is neglected.

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In one embodiment of the present invention, the slurry in the storage vessel is occasionally stirred, for example with an average energy input of from 0.2 to 1 W/l. Said occasional stirring is useful for avoiding sedimentation of the solids of the slurry.

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By performing step (c), solid particles of a hydroxide or oxyhydroxide are created, said solid particles being slurried. Thus, a slurry is obtained. Preferably, said slurry has a solids content in the range of from 200 to 1,200 g/l.

In one embodiment of the present invention, a clarifier or at least one candle filter is used to mother liquor withdrawal. Such candle filter(s) is/are connected to the stirred vessel in a way that mother liquor may be removed easily but the solids are held back in the stirred vessel.

- 5 In step (d), the addition of solution (α) to slurry from step (c) is terminated but the addition of solution (β) is continued to adjust the pH value to 12.0 to 14.0. Optionally, addition of solution (γ) may be continued or resumed or performed for the first time. Preferably, in step (d) solely solution (α) is added to slurry from step (c).
- 10 In one embodiment of the present invention, the temperature in step (d) is in the range of from 30 to 95°C. Preferably, during step (d) any heating is set off. More preferably, during step (d) the temperature is brought to ambient temperature or to a temperature of at least 5°C lower than in step (c).
- 15 It is preferred to stir the slurry from step (c) during step (d), and it is preferred to continue stirring after the pH adjustment in accordance to step (d), for example over a period of time in the range of from 1 minute to 24 hours, preferably 5 minutes to 12 hours and even more preferably 15 minutes to 6 hours.
- 20 In one embodiment of the present invention, the pH value in step (d) is adjusted to be at least 1 unit higher than in step (c), preferably at least 1.5 units. The difference does not exceed 4.4 units. If the pH value difference exceeded more than 4.5 units, for example 5 units, this only being possible by lowering the pH value in step (c) more pronouncedly, the solubility of the hydroxides of nickel and transition metals other than nickel becomes too high.
- 25 In one embodiment of the present invention, the pH value in step (d) is adjusted to be at least 0.5 units, preferably at least one unit higher than in step (b).
- 30 In one embodiment of the present invention, the removal of mother liquor is continued during step (d). In an alternative embodiment, mother liquor is removed during steps (b) and (c) – or solely during step (c) – but not during step (d).
- 35 In one embodiment of the present invention, step (d) is performed in a separate vessel connected through an overflow system to the vessel in which step (c) is performed. In an alternative embodiment, steps (b) to (d) are performed in the same vessel, for example a stirred tank reactor.

In one embodiment of the present invention, step (d) is performed in the absence of oxygen. That means that step (d) is performed under an atmosphere of nitrogen or of a rare gas such as argon. In the context of the present invention, oxygen-depleted air with an oxygen content below 1.0 vol-% is considered to be oxygen-free.

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In step (e), the particulate (oxy)hydroxide of TM generated in the previous steps is removed by a solid/liquid separation method, followed by drying.

In such a step (e), the particles from step (d) are separated from the liquid phase by a solid-liquid separation method, preferably by filtration or in a centrifuge. The liquid phase may also be termed mother liquor. Filtration may be performed, e.g., on a belt filter or in a filter press.

10

In order to remove mother liquor, it is preferred to wash the filter cake, for example with water or with alkali metal hydroxide or alkali metal carbonate solution.

15

Filtration may be supported by suction or by pressure.

The solid/liquid separation step (e) may be performed at any temperature at which water is in the liquid state, for example 5 to 95°C, preferred is 20 to 60°C.

20

Step (e) includes drying the solid material. Step (e) includes a thermal treatment of the solid, for example in a drying oven, in a rotary kiln or in a flash calciner.

25

By performing the solid-liquid separation part of step (e), a solid material is obtained which is a particulate (oxy)hydroxide or oxide of TM. Said material usually has a high water content, for example 1 to 30% by weight, and may be dried, e.g. at air, at a temperature in the range of from 80 to 150°C, or at reduced pressure ("*in vacuo*"), to a moisture content in the range of from 100 to 5,000 ppm, ppm being ppm by weight. The water content may be determined by drying *in vacuo* at a temperature of 100°C until the weight is remaining unchanged. The moisture content may be determined by Karl-Fischer titration.

30

Upon drying, some hydroxyl groups may be removed as water, and an oxyhydroxide is obtained. In embodiments where drying is performed under air, a partial oxidation may take place, leading to an oxyhydroxide of TM as well.

35

The duration of drying may be in the range of from 30 minutes to 12 hours.

In one embodiment of step (e), the wet solid material (filter cake) is introduced into a rotary kiln by a chute or a vibrating chute, by a spiral conveyor or a screw conveyor, preferably by a screw conveyor with a single screw or multiple screws.

- 5 In one embodiment of the present invention, step (e) is followed by a thermal treatment at a temperature in the range of from 250 to 500°C in the absence of a source of lithium. Such thermal treatment may be performed under an atmosphere of nitrogen, of air or of oxygen or of oxygen-enriched air. Such thermal treatment may be performed in a rotary kiln or in a moving bed or fixed bed or in a fluidized bed.

10

A further aspect of the present invention refers to particulate (oxy)hydroxides or oxides of TM, hereinafter also referred to as inventive (oxy)hydroxides or inventive precursors. Inventive precursors are advantageously made according to the inventive process.

- 15 Inventive precursors are (oxy)hydroxides of or oxides TM wherein TM comprises nickel and one transition metal selected from Co and Mn and at least one further element selected from Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta. Preferably, TM is a combination according to formula (I), *vide supra*.

- 20 Inventive precursors as (oxy)hydroxides or oxides have a sulfate content in the range of from 0.01 to 0.75% by weight, determined by catalytic S-combustion, preferred are 0.1 to 0.5 % by weight, and a content of at least one of from Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta in the range of from 0.01 to 1.5% by weight, and sulfate and the at least one of Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta are uniformly dispersed within the primary particles of inventive precursor.

- 25 Preferably, the total content of Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta is in the range of from 0.05 to 1.0% by weight. Even more preferred are 0.05 to 1.0 % of a combination of Al, W, Mg and Nb or of Ti, Zr, Al and Mg. The sulfate is preferably uniformly dispersed over the diameter of the precursor particles.

- 30 Inventive precursors have an average particle diameter (D50) in the range of from 3 to 20 µm, preferably 5 to 15 µm and more preferred 6 to 12 µm, determined by dynamic light scattering.

In one embodiment of the present invention, inventive precursors are selected from oxyhydroxides and oxides with an average oxidation state of TM in the range of from + 2.1 to + 2.6, de-

- 35 terminated by iodometric titration.

In one embodiment of the present invention, inventive precursors are comprised of secondary particles comprising asymmetric plate-like shaped primary particles that have a thickness of 20 to 200 nm and a length of 50 to 500 nm.

5 In one embodiment of the present invention, the primary particles are essentially radially aligned. The portion of radially aligned primary particles may be determined, e.g., by SEM (Scanning Electron Microscopy) of a cross-section of at least arbitrarily selected 5 secondary particles.

10 “Essentially radially alignment” does not require a perfect radial orientation but includes that in an SEM analysis, a deviation to a perfectly radial orientation is at most 5 degrees.

Inventive precursors as oxides of TM have a moisture content in the range of from 100 to 10,000 ppm by weight, preferably 250 to 8,000 ppm and more preferably 300 to 5,000 ppm. The
15 moisture content may be determined by Karl-Fischer-titration.

Inventive precursors as (oxy)hydroxides and inventive oxides are preferably obtained according to the inventive process. Inventive precursors are excellent starting materials for cathode active materials which are suitable for producing batteries with a high volumetric energy density due to
20 the low content of inactive impurities and an excellent cycling stability due to mitigation of parasitic side reactions of impurities inside the electrochemical cell. An undesired lithium consumption during calcination can be avoided.

A further aspect of the present invention is related to the use of inventive precursors for making
25 cathode active materials, for example for lithium-ion batteries. A further aspect of the present invention is a process of making a cathode active material for a lithium-ion battery by using an inventive precursor, hereinafter also referred to as inventive calcination. Such inventive calcination may be performed by mixing with a source of lithium, e.g., LiOH or Li₂O₂ or Li₂CO₃, followed by calcination, for example at a temperature in the range of from 600 to 1000°C. Especially in
30 embodiments wherein TM of inventive (oxy)hydroxides corresponds to formula (I), said calcination is preferably performed in an atmosphere of oxygen or oxygen-enriched air, for example with at least 60 vol-% of oxygen, preferably 80 vol-% of oxygen and more preferably at least 90 vol-% oxygen. In embodiments wherein TM of inventive (oxy)hydroxides corresponds to formula (II), said calcination may be performed in air atmosphere.

35 Examples of suitable set-ups for said calcination are rotary kilns, roller hearth kilns, and pusher kilns.

By performing a calcination in the above way, the essentially radial alignment of primary particles is – e.g., to at least 80%, preferably to at least 90% – retained, and cathode active materials with excellent capacity retention are obtained.

- 5 Specifically, the inventive calcination comprises the step of mixing an inventive precursor – as (oxy)hydroxide or oxide – with a source of lithium and, optionally, with an oxide or (oxy)hydroxide of at least one of Nb, Al, Ti or Zr, and thermally treating the resultant mixture at a temperature in the range of from 650 to 1000°C in one or more steps.

- 10 In one embodiment of the present invention, the mixing has a duration of 10 minutes to 2 hours.

- Mixing of precursor, source of lithium compound and oxide or hydroxide of aluminum or Zr or Ti or Nb or Ta may be performed all in one or in sub-steps, for example by first mixing source of lithium compound and said oxide or hydroxide of aluminum and then combining such mixture
15 with the precursor, or by first mixing precursor and source of lithium and then adding said oxide or hydroxide of aluminum, or by first mixing said oxide or hydroxide of aluminum and precursor and then adding source of lithium. It is preferred to first mix precursor and source of lithium compound and to then add said oxide or hydroxide of aluminum.

- 20 Although it is possible to add an organic solvent, for example glycerol or glycol, or water in for the mixing it is preferred to perform such mixing in the dry state, that is without addition of water or of an organic solvent.

- Then, said mixture is subjected to heat treatment at a temperature in the range of from 650 to
25 1000°C, preferably 650 to 850°C.

- In one embodiment of the present invention, the mixture of precursor and source of lithium and oxide or hydroxide of aluminum or Zr or Ti or Nb or Ta and, optionally, solvent(s), is heated to 700 to 1000 °C with a heating rate of 0.1 to 10 °C/min.

- 30 In one embodiment of the present invention, the temperature is ramped up before reaching the desired temperature of from 700 to 1000°C, preferably 750 to 900°C. For example, first the mixture of precursor and source of lithium and oxide or hydroxide of Al is heated to a temperature to 350 to 550°C and then held constant for a time of 10 min to 4 hours, and then it is raised to
35 650°C up to 1000°C, preferably 650 to 850°C.

In embodiments wherein for mixing at least one solvent has been used, as part of the thermal treatment, such solvent(s) are removed, for example by filtration, evaporation or distilling of such solvent(s). Preferred are evaporation and distillation.

- 5 In one embodiment of the present invention, the thermal treatment is performed in a roller hearth kiln, a pusher kiln or a rotary kiln or a combination of at least two of the foregoing. Rotary kilns have the advantage of a very good homogenization of the material made therein. In roller hearth kilns and in pusher kilns, different reaction conditions with respect to different steps may be set quite easily. In lab scale trials, box-type and tubular furnaces and split tube furnaces are
10 feasible as well.

- In one embodiment of the present invention, the inventive calcination is performed in an oxygen-containing atmosphere, for example in a nitrogen-air mixture, in a rare gas-oxygen mixture, in air, in oxygen or in oxygen-enriched air. In a preferred embodiment, the atmosphere in the
15 inventive calcination is selected from air, oxygen and oxygen-enriched air. Oxygen-enriched air may be, for example, a 50:50 by volume mix of air and oxygen. Other options are 1:2 by volume mixtures of air and oxygen, 1:3 by volume mixtures of air and oxygen, 2:1 by volume mixtures of air and oxygen, and 3:1 by volume mixtures of air and oxygen.

- 20 In one embodiment of the present invention, the inventive calcination is performed under a forced flow of gas, for example air, oxygen and oxygen-enriched air. Such stream of gas may be termed a forced gas flow. Such stream of gas may have a specific flow rate in the range of from 0.5 to 15 m³/h·kg material according to general formula $\text{Li}_{1+x}\text{TM}_{1-x}\text{O}_2$. The volume is determined under normal conditions: 298 Kelvin and 1 atmosphere. Said forced flow of gas is useful
25 for removal of gaseous cleavage products such as water and carbon dioxide.

- In one embodiment of the present invention, the inventive calcination has a duration in the range of from one hour to 30 hours. Preferred are 10 to 24 hours. The cooling time is neglected in this context.

- 30 After thermal treatment, the cathode active material so obtained is cooled down before further processing. Additional – optional – steps before further processing the resultant electrode active materials are sieving and de-agglomeration steps.

- 35 By performing the inventive calcination process, cathode active materials with excellent properties are available through a straightforward process. Preferably, the electrode active materials so obtained have a specific surface (BET) in the range of from 0.1 to 0.8 m²/g, determined according to DIN-ISO 9277:2003-05.

A further aspect of the present invention relates to cathode active materials, hereinafter also referred to as inventive cathode active materials. They are preferably made according to the inventive calcination.

5

Inventive cathode active material are particulate materials according to the general formula $\text{Li}_{1+x}\text{TM}_{1-x}\text{O}_2$ wherein x is in the range of from zero to 0.05 and TM comprises nickel and one transition metal selected from Co and Mn and at least one further element selected from Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta wherein said cathode active material has a sulfate content in the range of from 0.01 to 0.75% by weight, preferred are 0.1 to 0.5 % by weight, and a content of at least one of Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta in the range of from 0.01 to 1.5% by weight. Sulfate and the at least one of Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta uniformly dispersed within the primary particles of said cathode active material, and wherein said cathode active material has an average diameter (D50) in the range of from 3 to 20 μm .

15

In one embodiment of the present invention, inventive cathode active materials have a content of residual lithium compounds in the range of from 0.3 to 1.0 % by weight, wherein said residual lithium compounds are selected from lithium oxide, lithium hydroxide, lithium carbonate and lithium sulfate. Lithium oxide, hydroxide and carbonate may be detected by titration.

20

In one embodiment of the present invention, it can be detected that especially Al or Zr or Ti or Mg or Ca or Si is uniformly distributed in cathode active material obtained according to the inventive process, without accumulations.

25 Preferably, inventive cathode active materials are comprised from secondary particles that are comprised from primary particles.

In one embodiment of the present invention, the average primary particle size of inventive cathode active materials is 100 to 500 nm, determined from SEM images.

30

In one embodiment of the present invention, inventive cathode active materials have an a-lattice parameter in the range of from 2.873 to 2.875 Ångstrom, determined by X-Ray diffraction and Rietveld refinement of X-ray diffractograms

35 In one embodiment of the present invention, inventive cathode active materials have a BET-surface in the range of from 0.1 0.1 to 0.8 m^2/g , determined according to DIN-ISO 9277:2003-05. Outgassing temperature was 200°C.

A further aspect of the present invention refers to electrodes and specifically to cathodes, hereinafter also referred to as inventive cathodes. Inventive cathodes comprise

- (A) at least one inventive cathode active material,
- (B) carbon in electrically conductive form,
- 5 (C) at least one binder.

In a preferred embodiment of the present invention, inventive cathodes contain

- (A) 80 to 99 % by weight inventive cathode active material,
 - (B) 0.5 to 19.5 % by weight of carbon,
 - 10 (C) 0.5 to 9.5 % by weight of binder polymer,
- percentages referring to the sum of (A), (B) and (C).

Cathodes according to the present invention contain carbon in electrically conductive modification, in brief also referred to as carbon (B). Carbon (B) can be selected from soot, active carbon, carbon nanotubes, graphene, and graphite. Carbon (B) can be added as such during preparation of electrode materials according to the invention.

Electrodes according to the present invention can comprise further components. They can comprise a current collector (D), such as, but not limited to, an aluminum foil. They further comprise a binder polymer (C), hereinafter also referred to as binder (C). Current collector (D) is not further described here.

Suitable binders (C) are preferably selected from organic (co)polymers. Suitable (co)polymers, i.e., homopolymers or copolymers, can be selected, for example, from (co)polymers obtainable by anionic, catalytic or free-radical (co)polymerization, especially from polyethylene, polyacrylonitrile, polybutadiene, polystyrene, and copolymers of at least two comonomers selected from ethylene, propylene, styrene, (meth)acrylonitrile and 1,3-butadiene. Polypropylene is also suitable. Polyisoprene and polyacrylates are additionally suitable. Particular preference is given to polyacrylonitrile.

In the context of the present invention, polyacrylonitrile is understood to mean not only polyacrylonitrile homopolymers but also copolymers of acrylonitrile with 1,3-butadiene or styrene. Preference is given to polyacrylonitrile homopolymers.

In the context of the present invention, polyethylene is not only understood to mean homopolyethylene, but also copolymers of ethylene which comprise at least 50 mol% of copolymerized ethylene and up to 50 mol% of at least one further comonomer, for example α -olefins such as propylene, butylene (1-butene), 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-pentene, and

also isobutene, vinylaromatics, for example styrene, and also (meth)acrylic acid, vinyl acetate, vinyl propionate, C₁-C₁₀-alkyl esters of (meth)acrylic acid, especially methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, 2-ethylhexyl acrylate, n-butyl methacrylate, 2-ethylhexyl methacrylate, and also maleic acid, maleic anhydride and itaconic anhydride. Polyethylene may be HDPE or LDPE.

In the context of the present invention, polypropylene is not only understood to mean homopolypropylene, but also copolymers of propylene which comprise at least 50 mol% of copolymerized propylene and up to 50 mol% of at least one further comonomer, for example ethylene and α -olefins such as butylene, 1-hexene, 1-octene, 1-decene, 1-dodecene and 1-pentene. Polypropylene is preferably isotactic or essentially isotactic polypropylene.

In the context of the present invention, polystyrene is not only understood to mean homopolymers of styrene, but also copolymers with acrylonitrile, 1,3-butadiene, (meth)acrylic acid, C₁-C₁₀-alkyl esters of (meth)acrylic acid, divinylbenzene, especially 1,3-divinylbenzene, 1,2-diphenylethylene and α -methylstyrene.

Another preferred binder (C) is polybutadiene.

Other suitable binders (C) are selected from polyethylene oxide (PEO), cellulose, carboxymethylcellulose, polyimides and polyvinyl alcohol.

In one embodiment of the present invention, binder (C) is selected from those (co)polymers which have an average molecular weight M_w in the range from 50,000 to 1,000,000 g/mol, preferably to 500,000 g/mol.

Binder (C) may be cross-linked or non-cross-linked (co)polymers.

In a particularly preferred embodiment of the present invention, binder (C) is selected from halogenated (co)polymers, especially from fluorinated (co)polymers. Halogenated or fluorinated (co)polymers are understood to mean those (co)polymers which comprise at least one (co)polymerized (co)monomer which has at least one halogen atom or at least one fluorine atom per molecule, more preferably at least two halogen atoms or at least two fluorine atoms per molecule. Examples are polyvinyl chloride, polyvinylidene chloride, polytetrafluoroethylene, polyvinylidene fluoride (PVdF), tetrafluoroethylene-hexafluoropropylene copolymers, vinylidene fluoride-hexafluoropropylene copolymers (PVdF-HFP), vinylidene fluoride-tetrafluoroethylene copolymers, perfluoroalkyl vinyl ether copolymers, ethylene-tetrafluoroethylene copolymers,

vinylidene fluoride-chlorotrifluoroethylene copolymers and ethylene-chlorofluoroethylene copolymers.

5 Suitable binders (C) are especially polyvinyl alcohol and halogenated (co)polymers, for example polyvinyl chloride or polyvinylidene chloride, especially fluorinated (co)polymers such as polyvinyl fluoride and especially polyvinylidene fluoride and polytetrafluoroethylene.

A further aspect of the present invention is an electrochemical cell, containing
(A) a cathode comprising inventive electrode active material (A), carbon (B), and binder (C),
10 (B) an anode, and
(C) at least one electrolyte.

Embodiments of cathode (1) have been described above in detail.

15 Anode (2) may contain at least one anode active material, such as carbon (graphite), TiO_2 , lithium titanium oxide, silicon or tin. Anode (2) may additionally contain a current collector, for example a metal foil such as a copper foil.

Electrolyte (3) may comprise at least one non-aqueous solvent, at least one electrolyte salt and,
20 optionally, additives.

Non-aqueous solvents for electrolyte (3) can be liquid or solid at room temperature and is preferably selected from among polymers, cyclic or acyclic ethers, cyclic and acyclic acetals and cyclic or acyclic organic carbonates.
25

Examples of suitable polymers are, in particular, polyalkylene glycols, preferably poly- C_1 - C_4 -alkylene glycols and in particular polyethylene glycols. Polyethylene glycols can here comprise up to 20 mol% of one or more C_1 - C_4 -alkylene glycols. Polyalkylene glycols are preferably polyalkylene glycols having two methyl or ethyl end caps.
30

The molecular weight M_w of suitable polyalkylene glycols and in particular suitable polyethylene glycols can be at least 400 g/mol.

The molecular weight M_w of suitable polyalkylene glycols and in particular suitable polyethylene glycols can be up to 5,000,000 g/mol, preferably up to 2,000,000 g/mol.
35

Examples of suitable acyclic ethers are, for example, diisopropyl ether, di-n-butyl ether, 1,2-dimethoxyethane, 1,2-diethoxyethane, with preference being given to 1,2-dimethoxyethane.

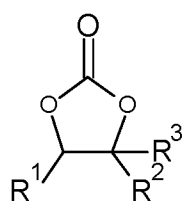
Examples of suitable cyclic ethers are tetrahydrofuran and 1,4-dioxane.

Examples of suitable acyclic acetals are, for example, dimethoxymethane, diethoxymethane,
5 1,1-dimethoxyethane and 1,1-diethoxyethane.

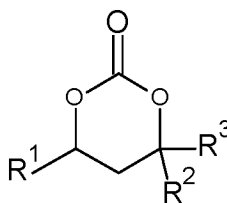
Examples of suitable cyclic acetals are 1,3-dioxane and, in particular, 1,3-dioxolane.

Examples of suitable acyclic organic carbonates are dimethyl carbonate, ethyl methyl carbonate
10 and diethyl carbonate.

Examples of suitable cyclic organic carbonates are compounds of the general formulae (II) and
(III)



(II)

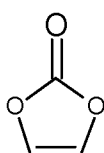


(III)

15 where R¹, R² and R³ can be identical or different and are selected from among hydrogen and C₁-C₄-alkyl, for example methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl and tert-butyl, with R² and R³ preferably not both being tert-butyl.

20 In particularly preferred embodiments, R¹ is methyl and R² and R³ are each hydrogen, or R¹, R² and R³ are each hydrogen.

Another preferred cyclic organic carbonate is vinylene carbonate, formula (IV).



(IV)

The solvent or solvents is/are preferably used in the water-free state, i.e. with a water content in the range from 1 ppm to 0.1% by weight, which can be determined, for example, by Karl-Fischer titration.

- 5 Electrolyte (3) further comprises at least one electrolyte salt. Suitable electrolyte salts are, in particular, lithium salts. Examples of suitable lithium salts are LiPF_6 , LiBF_4 , LiClO_4 , LiAsF_6 , LiCF_3SO_3 , $\text{LiC}(\text{C}_n\text{F}_{2n+1}\text{SO}_2)_3$, lithium imides such as $\text{LiN}(\text{C}_n\text{F}_{2n+1}\text{SO}_2)_2$, where n is an integer in the range from 1 to 20, $\text{LiN}(\text{SO}_2\text{F})_2$, Li_2SiF_6 , LiSbF_6 , LiAlCl_4 and salts of the general formula $(\text{C}_n\text{F}_{2n+1}\text{SO}_2)_t\text{YLi}$, where m is defined as follows:
- 10 $t = 1$, when Y is selected from among oxygen and sulfur,
 $t = 2$, when Y is selected from among nitrogen and phosphorus, and
 $t = 3$, when Y is selected from among carbon and silicon.

- Preferred electrolyte salts are selected from among $\text{LiC}(\text{CF}_3\text{SO}_2)_3$, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, LiPF_6 , LiBF_4 ,
15 LiClO_4 , with particular preference being given to LiPF_6 and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$.

- In a preferred embodiment of the present invention, electrolyte (3) contains at least one flame retardant. Useful flame retardants may be selected from trialkyl phosphates, said alkyl being different or identical, triaryl phosphates, alkyl dialkyl phosphonates, and halogenated trialkyl
20 phosphates. Preferred are tri- C_1 - C_4 -alkyl phosphates, said C_1 - C_4 -alkyls being different or identical, tribenzyl phosphate, triphenyl phosphate, C_1 - C_4 -alkyl di- C_1 - C_4 -alkyl phosphonates, and fluorinated tri- C_1 - C_4 -alkyl phosphates,

- In a preferred embodiment, electrolyte (3) comprises at least one flame retardant selected from
25 trimethyl phosphate, $\text{CH}_3\text{-P}(\text{O})(\text{OCH}_3)_2$, triphenylphosphate, and tris-(2,2,2-trifluoroethyl)-phosphate.

- Electrolyte (3) may contain 1 to 10% by weight of flame retardant, based on the total amount of electrolyte.
30

- In an embodiment of the present invention, batteries according to the invention comprise one or more separators (4) by means of which the electrodes are mechanically separated. Suitable separators (4) are polymer films, in particular porous polymer films, which are unreactive toward metallic lithium. Particularly suitable materials for separators (4) are polyolefins, in particular
35 film-forming porous polyethylene and film-forming porous polypropylene.

Separators (4) composed of polyolefin, in particular polyethylene or polypropylene, can have a porosity in the range from 35 to 50%. Suitable pore diameters are, for example, in the range from 30 to 500 nm.

- 5 In another embodiment of the present invention, separators (4) can be selected from among PET nonwovens filled with inorganic particles. Such separators can have a porosity in the range from 40 to 55%. Suitable pore diameters are, for example, in the range from 80 to 750 nm.

Batteries according to the invention can further comprise a housing which can have any shape,
10 for example cuboidal or the shape of a cylindrical disk. In one variant, a metal foil configured as a pouch is used as housing.

Batteries according to the invention provide a very good discharge and cycling behavior, in particular at high temperatures (45 °C or higher, for example up to 60°C) in particular with respect
15 to the capacity loss.

Batteries according to the invention can comprise two or more electrochemical cells that combined with one another, for example can be connected in series or connected in parallel. Connection in series is preferred. In batteries according to the present invention, at least one of the
20 electrochemical cells contains at least one electrode according to the invention. Preferably, in electrochemical cells according to the present invention, the majority of the electrochemical cells contain an electrode according to the present invention. Even more preferably, in batteries according to the present invention all the electrochemical cells contain electrodes according to
the present invention.

25

The present invention further provides for the use of batteries according to the invention in appliances, in particular in mobile appliances. Examples of mobile appliances are vehicles, for example automobiles, bicycles, aircraft or water vehicles such as boats or ships. Other examples of mobile appliances are those which move manually, for example computers, especially
30 laptops, telephones or electric hand tools, for example in the building sector, especially drills, battery-powered screwdrivers or battery-powered staplers.

The present invention is further illustrated by working examples.

35 Nickel sulfate was generated as follows:

Discharged end-of-life lithium-ion batteries were shredded, crushed and milled until a black powder was obtained. The current collectors from the electrodes were removed by sieving, and

metallic iron was removed by using magnetic separation. The resulting black mass was subjected to an acid leaching with concentrated sulfuric acid and a reducing agent at a pH value of below 2.0 until all metals were dissolved. By adjusting the pH-value of the resulting solution to 3, the remaining iron, aluminum and copper impurities were depleted by precipitation and subsequent filtration. For further purification of the metal solution, manganese and cobalt were recovered as aqueous sulfates by organic solvent extraction with kerosine as organic solvent and Di-(2-ethylhexyl) phosphoric acid as extractant. This resulted in the following impurity profile in the recovered NiSO_4 : 5.0 wt% Na_2SO_4 , 0.12 wt% $\text{Al}_2(\text{SO}_4)_3$, 0.07 wt% TiOSO_4 , 0.10 wt% ZrSO_4 and 0.23 wt% MgSO_4 .

The following aqueous solutions were provided, step (a.1):

Solution (α .1): NiSO_4 as synthesized above, commercially available CoSO_4 and MnSO_4 (both commercially available battery grade) dissolved in deionized water (molar ratio 91:4.5:4.5, total transition metal concentration: 1.45 mol/kg)

Solution (β .1): 25wt% NaOH dissolved in deionized water

Solution (γ .1): 25wt% ammonia in deionized water

I.1 Synthesis of an inventive precursor P-CAM.1

A 3.0 l stirred vessel equipped with baffles and a cross-arm stirrer, and three dosing tubes, one for an aqueous solution (α .1), one for solution (β .1) and one for solution (γ .1), was charged with 2.5 l of deionized water and the temperature of the vessel was set to 55°C. The feed for the metal sulfate solution was separated from both other tubes by 8 cm each, while the tube for ammonia was separated by 2.5 cm from the tube for the NaOH solution. All tubes had an outer diameter of 6 mm, an inner diameter of 2 mm and were located in the vessel so that the corresponding outlet was approximately 5 cm below the liquid level. The vessel had a constant nitrogen overflow during all reactions.

The stirrer element was operated at 1100 rpm. Aqueous solution (α .1), (β .1) and (γ .1) were simultaneously introduced into the vessel through the corresponding tubes. The molar ratio between ammonia and transition metal was adjusted to 0.25. Initially, the sum of volume flows was set to adjust the residence time to 12.5 hours for 1 hour reaction time and was then ramped up to 5 hours over 3 hours linearly and remained constant at a residence time of 5 hours thereafter. The flow rate of solution (β .1) was adjusted by a pH regulation circuit to keep the pH value in the stirred vessel at a constant value of 12.5.

Step (c.1): After 10 hours of reaction time, the pH-value in the stirred vessel was lowered by 1 unit to a constant pH-value of 11.5 by reducing the feed of (β .1). The pH-value and particle size

of growing (oxy-)hydroxide particles were carefully controlled by sampling reaction slurry. Throughout the reaction mother liquor was withdrawn applying a settler system.

Step (d.1): As soon as a particle diameter of the 14 μm was reached, the addition of solution (α .1) was terminated, and by continuing the addition of solution (β .1), the pH-value was adjusted to 12.7 under stirring for another 5 minutes.

Step (e.1): The resulting slurry was filtered, washed with deionized water and an aqueous solution of sodium hydroxide (1kg of 25 wt% aqueous sodium hydroxide solution per kg of solid hydroxide and dried at 120 °C for 12 hours to obtain the inventive precursor P-CAM.1. P-CAM.1 had an average particle diameter (D50) of 13.9 μm , a value of (D90-D10)/D50 of 0.4, a BET surface of 14.3 m^2/g , and a sulfate-content of 0.66 wt%. P-CAM.1 had an Al-content of 0.29 wt%, a Ti-content of 0.33 wt%, a Zr-content of 0.41 wt% and a Mg-content of 1.20 wt%. The sulfate was uniformly dispersed within the primary particles of P-CAM.1, ditto Al, Zr, Ti, and Mg.

I.2: Synthesis of a comparative precursor C-P-CAM.2

The above protocol was repeated but step (d.1) was omitted.

Step (e.1): The resulting slurry was filtered, washed with deionized water and an aqueous solution of sodium hydroxide (1kg of 25 wt% aqueous sodium hydroxide solution per kg of solid hydroxide and dried at 120 °C for 12 hours to obtain the comparative precursor C-P-CAM.2. C-P-CAM.2 had an average particle diameter (D50) of 14.0 μm , a value of (D90-D10)/D50 of 0.4, a BET surface of 14.2 m^2/g , and residual sulfate-content of 1.0 wt%. The Al-content was 0.35 wt%, the Ti-content was 0.27 wt%, the Zr-content was 0.40 wt% and the Mg-content was 1.00 wt%. The sulfate was uniformly dispersed within the primary particles of P-CAM.1, ditto Al, Zr, Ti, and Mg.

I.3 Manufacture of the inventive cathode active materials CAM.1, and of the comparative cathode active materials C-CAM.2:

The respective precursor was thermally treated at about 450 C for one hour. The respective pre-calcined material was mixed with $\text{LiOH}\cdot\text{H}_2\text{O}$, Al_2O_3 and $\text{Zr}(\text{OH})_4$ in molar ratio of $\text{Li}:(\text{Ni}+\text{Co}+\text{Mn})$ of 1.04:1, $\text{Al}:(\text{Ni}+\text{Co}+\text{Mn})$ of 0.006:1, $\text{Zr}:(\text{Ni}+\text{Co}+\text{Mn})$ of 0.003:1, poured into a alumina crucible and heated at 765 C for 8 hours under oxygen atmosphere (10 exchanges/h), heating rate of 3 C/min. The resultant cathode active material was cooled to ambient temperature at a cooling rate of 10 C / min, washed with H_2O in H_2O :cathode active material ratio of 1:2 and dried at 300 °C for two hours. It was subsequently sieved using a mesh size of 30 μm to

obtain the inventive cathode active material CAM.1 from inventive precursor P-CAM.1 and the comparative cathode active material C-CAM.2 from the precursor C-P-CAM.2.

5 In CAM.1, the sulfate content was about 0.6% by weight, uniformly dispersed within the primary particles of CAM.1 ditto Al, Ti, and Mg.

In C-CAM.2, the sulfate content was higher than 0.75% by weight, uniformly dispersed within the primary particles of CAM.1, ditto Al, Ti, and Mg.

10 II. Testing of Cathode Active Material

II.1 Cathode manufacture

Positive electrode: PVDF binder (polyvinylidene difluoride, Solef® 5130) was dissolved in NMP (Merck) to produce a 7.5 wt.% solution. For electrode preparation, binder solution (2.5 wt.%),
15 and carbon black (Li 400, 2.5 wt.-%) were suspended in NMP. After mixing using a planetary centrifugal mixer (ARE-250, Thinky Corp., Japan), either inventive CAM.1 or C-CAM.2 (95 wt.%) was added and the suspension was stirred again to obtain a lump-free slurry. The solids content of the slurry was adjusted to 65%. The slurry was coated onto Al foil using a KTF-S roll-to-roll coater (Mathis AG). Prior to use, all electrodes were calendared. The thickness of cathode material was 85 µm, corresponding to 21 mg/cm². All electrodes were dried at 120°C for 7 hours
20 before battery assembly.

II.2 Electrolyte Manufacture

25 A base electrolyte composition EL base 1 was made containing 12.0 wt% of LiPF₆, 44.0 wt% of ethylene carbonate (EC), and 44.0 wt% of di-ethyl carbonate (DMC) (EL base 1), based on the total weight of EL base 1.

II.3 Test cell Manufacture – coin type half cells

30 Coin-type half cells (20 mm in diameter and 3.2 mm in thickness) comprising a cathode prepared as described under II.1 as working electrode and lithium metal as counter electrode, respectively, were assembled and sealed in an Ar-filled glove box. In addition, the cathode and anode and a separator were superposed in order of cathode // separator // Li foil to produce a
35 half coin cell. Thereafter, 0.15 mL of the EL base 1 which is described above (II.2) were introduced into the coin cell.

II.4 Evaluation of cell performance

The initial performance, C-rate performance and cycling performance were measured as fol-

5 lows: Coin half cells according to II.3 were tested in a voltage range between 4.3 V to 2.7 V at room temperature. For the initial cycles, the initial lithiation was conducted in the CC-CV mode, i.e., a constant current (CC) of 0.04 C was applied until reaching 4.3V, followed by the CV step until the current dropped to 0.01 C. After 10 min resting time, reductive lithiation was carried out at constant current of 0.04 C up to 2.7 V. For the C-rate test charge and discharge rates were
10 adjusted accordingly. For the cycling test, the constant current was chosen to be 0.33 C until 56 cycles were reached.

After 56 cycles tested against a graphite anode, CAM.1 shows superior properties compared to C-CAM.2.

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Patent Claims

1. Process for making a particulate (oxy)hydroxide or oxide of TM wherein TM comprises nickel and one transition metal selected from Co and Mn and at least one further element selected from Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta and wherein said process comprises the steps of:

(a) Providing an aqueous solution (α) containing sulfates of Ni and of at least one transition metal selected from Co and Mn, and a water-soluble compound of at least one further element selected from Ca, Si, Ti, Zr, Mo, W, Al, Mg, Nb, and Ta, and an aqueous solution (β) containing an alkali metal hydroxide and, optionally, an aqueous solution (γ) containing ammonia,

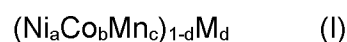
(b) combining solution (α) and solution (β) and, if applicable, solution (γ) at a pH value in the range of from 12.5 to 14.0 in a stirred tank reactor, thereby creating particles of a hydroxide containing nickel, said particles being slurried,

(c) adding solution (α) and solution (β) and, if applicable, a solution (γ) to slurry from step (b) at a pH value in the range of from 9.6 to 11.6 in a stirred tank reactor, thereby growing particles of hydroxide of TM,

(d) terminating the addition of solution (α) but continuing the addition of solution (β) and, if applicable, of solution (γ), to adjust the pH value to 12.0 to 14.0, and

(e) removing the particulate hydroxide of TM by a solid/liquid separation method, followed by drying.

2. Process according to claim 1 wherein TM is a combination of metals according to general formula (I)



with

a being in the range of from 0.6 to 0.95,

b being in the range of from 0.025 to 0.2,

c being in the range of from zero to 0.2, and

d being in the range of from 0.02 to 0.1,

M is selected from Mg, Al, Ca, Si, Ti, Zr, Mo, W, Nb, and Ta,

$$a + b + c = 1.$$

- 5 3. Process according to claim 1 or 2 wherein the nickel sulfate is at least partially made by recycling of lithium-ion batteries.
4. Process according to any of the preceding claims wherein step (d) is performed in the absence of oxygen.
- 10 5. Process according to any of the preceding claims wherein the temperature in step (d) is in the range of from 30 to 95°C.
6. Process according to any of the preceding claims wherein the pH value in step (d) is adjusted to be at least 1 unit higher than in step (c).
- 15 7. Process according to any of the preceding claims wherein the pH value in step (d) is adjusted to be at least 1 unit higher than in step (b).
- 20 8. Process according to any of the preceding claims wherein the pH value in step (c) is lowered by reducing the addition of solution (β) until the desired pH-value is obtained.
9. Process of making an oxide precursor, comprising the steps (a) to (e) according to claims 1 to 9, followed by a thermal treatment at a temperature in the range of from 250 to 500°C in the absence of a source of lithium.
- 25 10. Particulate (oxy)hydroxide of TM wherein TM comprises nickel and one transition metal selected from Co and Mn and at least one further element selected from Ca, Si, Ti, Zr, Mo, W, Al, Mg, Nb, and Ta wherein said (oxy)hydroxide has a sulfate content in the range of from 0.01 to 0.75% by weight and a content of at least one of Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta in the range of from 0.01 to 1.5% by weight, and wherein sulfate and the at least one of Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta are uniformly dispersed within the primary particles of said (oxy)hydroxide, and wherein said particulate (oxy)hydroxide has an average diameter (D50) in the range of from 3 to 20 μm.
- 30 11. Particulate (oxy)hydroxide according to claim 11 comprising secondary particles comprising asymmetric plate-like shaped primary particles that have a thickness of 20 to 200 nm and a length of 50 to 500 nm.
- 35

12. Particulate oxide of TM wherein TM comprises nickel and one transition metal selected from Co and Mn and at least one further element selected from Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta wherein said (oxy)hydroxide has a sulfate content in the range of from 0.01 to 0.75% by weight and a content of at least one of Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta in the range of from 0.01 to 1.5% by weight, and wherein sulfate and the at least one of Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta are uniformly dispersed within the primary particles of said oxide and an average diameter (D50) in the range of from 3 to 20 μm , and wherein said particulate oxide of TM has a moisture content in the range of from 100 to 10,000 ppm by weight.
13. Process of making a cathode active material for a lithium-ion battery comprising the step of mixing a particulate (oxy)hydroxide according to claim 11 or 12 or a particulate oxide according to claim 13 with a source of lithium and, optionally, with an oxide or (oxy)hydroxide of at least one of Nb, Al, Ti or Zr, and thermally treating the resultant mixture at a temperature in the range of from 650 to 1000°C in one or more steps.
14. Cathode active material according to the general formula $\text{Li}_{1+x}\text{TM}_{1-x}\text{O}_2$ wherein x is in the range of from zero to 0.05 and TM comprises nickel and one transition metal selected from Co and Mn and at least one further element selected from Ca, Si, Ti, Zr, Mo, W, Al, Mg, Nb, and Ta wherein said cathode active material has a sulfate content in the range of from 0.01 to 0.75% by weight and a content of at least one of Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta in the range of from 0.01 to 1.5% by weight, and wherein sulfate and the at least one of Ti, Zr, Ca, Si, Mo, W, Al, Mg, Nb, and Ta are uniformly dispersed within the primary particles of said cathode active material, and an average diameter (D50) in the range of from 3 to 20 μm .
15. Cathode active material according to claim 14 having a content of residual lithium compounds in the range of from 0.3 to 1.0 % by weight, wherein said residual lithium compounds are selected from lithium oxide, lithium hydroxide, lithium carbonate and lithium sulfate.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/067376

A. CLASSIFICATION OF SUBJECT MATTER

INV. C01G53/00

ADD.

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)

C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data

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Y	US 2013/108926 A1 (KIM YONG-SEON [KR] ET AL) 2 May 2013 (2013-05-02) paragraph [0126] - paragraph [0133] -----	1 - 15
Y	US 2023/212028 A1 (BERGNER BENJAMIN JOHANNES HERBERT [DE] ET AL) 6 July 2023 (2023-07-06) the whole document -----	1 - 15
X	EP 3 093 272 A1 (BASF SE [DE]) 16 November 2016 (2016-11-16) -----	10, 11, 13, 14
Y	paragraph [0133] - paragraph [0140] -----	1 - 15
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search

30 August 2024

Date of mailing of the international search report

11/09/2024

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/067376

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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