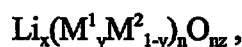


Process for preparing lithium transition metallates

The present invention relates to a process for preparing lithium transition metallates of the general formula

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wherein

10 M^1 represents nickel, cobalt or manganese,

M^2 represents a transition metal which is different from M^1 and is chromium, cobalt, iron, manganese, molybdenum and/or aluminium,

15 n is 2 if M^1 is manganese, and n is 1 if M^1 is nickel or cobalt, wherein

x has a value from 0.9 to 1.2,

y has a value between 0.5 and 1 and

20

z has a value between 1.9 and 2.1.

These types of lithium transition metallates are used as electrode materials, in particular as cathode materials for non-aqueous lithium storage battery systems, so-called lithium ion batteries.

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A number of proposals have already been made relating to methods of preparation of these types of lithium transition metallates, but these are mostly unsuitable for large-scale production or lead to products which have imperfect electrochemical properties.

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The use of LiCoO_2 has recently gained acceptance, but this is extremely expensive due to the limited availability, and thus high price, of cobalt and is therefore not suitable for mass production (e.g. to provide the power for electrically operated vehicles). Therefore intensive efforts have already been made to replace some or all of the

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LiCoO_2 with, for example, LiNiO_2 and/or LiMn_2O_4 as a cathode material.

Synthesis of the corresponding cobalt compound LiCoO_2 is generally regarded as a non-critical procedure. Due to the thermal stability of LiCoO_2 , it is even possible, with this system, to react cobalt carbonate and lithium carbonate, as reaction components, directly at relatively high temperatures without troublesome concentrations of carbonate being left in the final product.

The transfer of this method to LiNiO_2 has been possible only at temperatures of 800 to 900°C. These high calcination temperatures, however, lead to partly decomposed lithium nickelates with relatively low storage capacities and/or unsatisfactory resistance to cyclic operation.

For this reason, carbonate-free mixtures are proposed for preparing LiNiO_2 , in which, in most cases, β -nickel hydroxide is favoured as the nickel component, such as is described, for example in US-A 5 591 548, EP 0 701 293, J. Power Sources 54 (95) 209-213, 54 (95) 329-333 and 54 (95) 522-524. Moreover, the use of nickel oxide was also recommended in JP-A 7 105 950 and that of oxynickel hydroxide NiOOH in DE-A 196 16 861.

According to US-A 4 567 031, the intimate mixture is prepared by co-precipitation of soluble lithium and transition metal salts from solution, drying the solution and calcining. Relatively finely divided crystals of the lithium transition metallate are obtained in this way at comparatively low calcining temperatures and within comparatively short times. The allocation of lithium and transition metal ions to particular layers in the crystal lattice, however, is greatly distorted so that, to a large extent, lithium ions occupy nickel layer lattice positions and vice versa. These types of crystals have unsatisfactory properties with regard to their use as electrodes in rechargeable batteries. Other processes (EP-A 205 856, EP-A 243 926, EP-A 345 707) start with solid, finely divided carbonates, oxides, peroxides or hydroxides of the initial metals. The intimate mixture is prepared by joint milling of the starting metals. The formation of lithium transition metallates takes place by solid diffusion during calcination. Solid diffusion requires comparatively high temperatures and comparatively long calcining times and does not generally lead to phase-pure lithium metallates with outstanding electronic properties. Extensive observations appear to prove that, in the case of the nickel system, decomposition of LiNiO_2 with the production of Li_2O and NiO is initiated during prolonged thermal treatment at temperatures above about 700°C.

Therefore, in order to intensify the intimate mixing procedure, it has already been proposed, according to EP-A 468 942, starting the preparation of lithium nickelate with powdered nickel oxide or hydroxide, suspending the powder in a saturated lithium hydroxide solution and extracting the water from the suspension by spray drying. This should lead to a reduction in the calcining time and calcining temperature. Due to the relatively low solubility of lithium hydroxide in water, however, the homogeneity of this mixture is limited.

- 10 US-A 5 591 548 proposes milling a powdered oxygen-containing transition metal compound with lithium nitrate and then calcining under an inert gas. The advantage of this process is the low melting point of lithium nitrate, 264°C, which means that intimate mixing takes place after heating to, for example, 300°C in the form of a suspension of transition metal particles in molten lithium nitrate, which favours
15 reaction with the solid.

The disadvantage of this process is that, during calcination, the gases released (H₂O, NO_x, O₂) do not escape, or escape only very slowly, from the viscous molten suspension so that the intimate contact required for the solid reaction and diffusion is
20 hindered and on the other hand only a few suspended particles are present due to concentration inhomogeneities in the geometric spacing. Therefore, interruptions in the calcining process and intermediate milling to homogenise the reaction material are required.

- 25 According to the invention, it is now proposed that calcination be performed for at least some of the time under an at least partial vacuum. This produces a significant reduction in reaction times and temperatures required.

The invention therefore provides a process for preparing lithium transition metallates
30 of the general formula



wherein

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M¹ represents nickel, cobalt or manganese,

M^2 represents a transition metal which is different from M^1 and is chromium, cobalt, iron, manganese, molybdenum and/or aluminium,

5 n is 2 if M^1 is manganese, and n is 1 if M^1 is nickel or cobalt, wherein

x has a value from 0.9 to 1.2,

y has a value between 0.5 and 1.0 and

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z has a value between 1.9 and 2.1,

by preparing an intimate mixture of finely divided, oxygen-containing compounds of the transition metals and one or more oxygen-containing lithium compounds and
15 calcining the mixture in a reactor, which is characterised in that calcination takes place for at least some of the time under an absolute pressure of less than 0.5 bar absolute.

At least one of the lithium compounds preferably has a melting point of less than 600°C, particularly preferably at least 90 % of the lithium compounds used.

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Calcination is preferably performed for at least some of the time under a partial vacuum corresponding to a pressure of 0.01 to 0.4 bar absolute, particularly preferably at a pressure of 0.01 to 0.2 bar absolute.

25 Furthermore, it is also preferred that calcination be initially started at atmospheric pressure so that the molten lithium compound becomes supersaturated with dissolved gases resulting from the evolution of gases during reaction and still sub-stable bubble nuclei with diameters in the range of a few micrometres under atmospheric pressure are produced. This may take place, in industrial-scale batches, over a period of 2 to 12
30 hours, in the event that oxides are used as the transition metal compounds, or also over a longer period of time. The reactor is preferably evacuated, optionally also stepwise, only after this initial calcination stage under atmospheric pressure, so that, on the one hand, the volume of the bubble nuclei already present increases due to pressure reduction and, on the other hand, supersaturation of the molten material with dissolved
35 gases and thus the diffusion pressure of the dissolved molecules in the direction of the gas bubbles is increased. Gas bubbles enlarged in this way, which have several times the volume of the suspended solid particles, come into contact with each other,

coagulate and rise in the molten suspension until they are emitted into the reactor atmosphere at the surface of the suspension. The movement produced in this way in localised areas of the molten suspension leads to a degree of homogenisation of the reaction mixture which can only be produced, according to the prior art, by cooling the
5 reaction mixture, milling and replacing in the reactor for further heat treatment.

If the gas release reaction has substantially ended, for example more than 99 % of the releasable gases has been released, further calcination is preferably continued, according to the invention, at atmospheric pressure. The reaction is perfected during
10 this third calcination stage by solid diffusion and possible lattice defects, which may have been caused by mechanical stresses under the partial vacuum, are rectified. The reaction product is present, in this third stage, as porous, largely open-pored "cakes".

If required, the third stage may be interrupted by a homogenising intermediate milling
15 stage. However, this is not generally required if oxygen-containing transition metal compounds with a large surface area, if possible exceeding 50 m²/g, were used during the preliminary preparation stages using the process described here. In this case, the reaction mixture retains its homogeneous character over all the stages.

20 According to the invention, a purge gas is passed through the reactor in order rapidly to remove the gases released during the reaction, preferably in all three calcination stages but in particular during the vacuum calcination stage. To avoid temperature differences across the reactor, the purge gas stream is preferably introduced in such a way that a low purge gas flow, for example less than 1 cm/sec, with respect to standard
25 conditions, is produced in the reactor.

The transition from stage to stage may be performed smoothly and be regulated, for example, in accordance with the composition of the reaction gases.

30 The reaction-accelerating and homogenising effect of applying a vacuum according to the invention can be amplified by applying the vacuum in a pulsed manner, for example with a cycle of 1 to 15 minutes, in particular with a cycle of 5 to 15 minutes. The pressure variations due to pulsed application of a vacuum cause a "breathing" effect in the gas bubbles enclosed in the molten suspension and thus movement and
35 homogenisation in localised regions in the reaction mixture. Pulsed application of a vacuum is preferably produced by using an internal pressure controlled valve on the vacuum pump with simultaneous introduction of the purge gas.

Preferred oxygen-containing lithium compounds with a melting point below 600°C are lithium hydroxide with a melting point of 450°C, lithium nitrate with a melting point of 264°C, mixtures of lithium hydroxide and lithium nitrate or lithium nitrate hydrates.

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Preferred oxygen-containing transition metal compounds according to the invention are hydroxides, since these provide a ready-made rhombohedral lattice with layered atomic positions into which the lithium ions can diffuse, after the elimination of water from the hydroxide crystals, with the production of largely element-pure layers. Due to their low reactivity, transition metal oxides are less preferred. However, their use is not excluded within the scope of the invention, in particular when oxides with very large specific surface areas are used. Furthermore, carbonates, hydroxycarbonates and nitrates, optionally also containing water of crystallisation, are suitable according to the invention.

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Preferred transition metals M^1 are nickel and manganese, in particular in the form of their hydroxides, especially those with a BET specific surface area of more than 5 m²/g, in particular more than 20 m²/g, quite specifically more than 50 m²/g.

20 In the event that M^1 is Ni, β -nickel hydroxide, prepared according to US 5 391 265/DE 42 29 295, is particularly preferred as a reaction component, since this has a BET surface area of 65 to 80 m²/g and is able to absorb the concentrated lithium solution completely.

25 When using oxides or hydroxides with a much smaller surface area, e.g. spherical β -nickel hydroxide with a surface area of less than 5 m²/g, some of the nickel oxide formed during the solid reaction settles out of the molten lithium nitrate or lithium hydroxide. The reaction mixture becomes inhomogeneous and phase-pure lithium metallates cannot be obtained without a homogenising, intermediate milling stage.

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The powdered lithium and transition metal compounds are milled together in a manner known per se before use in the reactor and preferably compressed to form tablets in order to avoid dust and segregation. This also, on the one hand, increases the density, i.e. shortens the diffusion paths and, on the other hand, produces an effective gas-permeable bed. Intimate mixing is preferably achieved, instead of using a milling procedure, by suspending the powdered transition metal compound in a concentrated

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solution of the lithium compound followed by removal of water and then the production of tablets or pellets.

5 A LiNO_3 solution or a molten lithium nitrate hydrate salt with a LiNO_3 content of 50 to 80 % is preferably used. The calculated amounts of transition metal compounds are stirred into this and the mixture is dried or spray dried to produce pellets at 120 to 200°C, for example in a heated mixer, while subjected to motion. Complete drying can be recognised, inter alia, by the fact that no lithium nitrate "bloom" is produced during subsequent heating in the reactor.

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The process which is particularly preferred according to the invention uses lithium hydroxide, lithium hydroxide hydrate, lithium oxide or lithium carbonate, or mixtures thereof, as the starting materials for the lithium component. The starting materials are carefully introduced into preferably concentrated nitric acid. Nitric acid is used here in
15 slightly more than stoichiometric amounts in order to reliably drive out any residual amounts of carbonate which may be present.

In practice the preferred procedure is to introduce the lithium starting material into concentrated nitric acid until the pH of the solution exceeds 7. The mixture is then
20 acidified to pH 3.0 by adding nitric acid. Furthermore, the solution obtained is preferably evaporated at 120 to 170°C, optionally under a partial vacuum, wherein it is attempted to obtain a LiNO_3 content of 50 to 80 % in the solution or molten salt. Then the calculated amounts of transition metal compounds are introduced and the mixture is dried or spray dried to produce pellets at 120 to 200°C while subjected to motion.

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Since, inter alia, nitrous gases are produced during calcination of this starting mixture, these have to be washed out of the vent gas and preferably converted directly into concentrated nitric acid. This nitric acid is then used again in accordance with the invention to prepare fresh lithium nitrate solution in the context of a complete
30 recycling process.

The process for preparing an intimate mixture according to the invention is also of great advantage when conditions different from those according to the invention are used.

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The calcination temperatures during the preparation of lithium nickelate, optionally modified by a concentration of M^2 , are preferably between 550 and 700°C. In the case of the preferred three-stage calcination, the calcination temperature is preferably 580 to 680°C, particularly preferably 600 to 650°C, wherein the temperature is increased in particular by a total of 10 to 30°C over the course of the entire reaction. In the case of preparing lithium manganate, the preferred temperatures are 50 to 100°C above the temperatures cited for lithium nickelate.

Calcination may be performed in a static bed, preferably with a bed depth of less than 100 mm. A moving bed, e.g. a rotary tubular furnace, may also be advantageously used for the calcination process.

Selection of the purge and transport gases depends on the reaction components used: if M^{2+} compounds are intended to react with non-oxidising lithium compounds, e.g. lithium hydroxide or lithium carbonate, the use of an oxygen-containing purge gas is absolutely necessary. N_2/O_2 mixtures or Ar/O_2 mixtures are preferably used in this case, wherein the proportion of O_2 is 20 to 80 %, in particular 30 to 50 %. As an alternative, the use of air, preferably low- CO_2 air, or a mixture of air and oxygen is possible.

When using lithium nitrate, the oxygen required to oxidise M^{2+} to M^{3+} is formed in sufficient amounts by the decomposition of NO_x produced during the reaction, so no further oxygen needs to be supplied. In this case, argon, nitrogen and/or water vapour are preferably used as purge gases in the first and second stages. For the third reaction stage (under atmospheric pressure), a certain concentration of O_2 is again required in the purge gas. It is expressly recommended that water vapour is not used as a purge gas in the third stage.

Although the invention has been described with reference to particular advantages relating to the use of low-melting lithium compounds, a person skilled in the art can easily recognise that calcination under reduced pressure is also advantageous when using non-melting reaction partners, e.g. a mixture of oxides and/or carbonates, due to the effective removal of gaseous elimination products.

Examples

Example 1

- 5 1.02 mol. $\text{LiOH}\cdot\text{H}_2\text{O}$ were carefully dissolved in 1.03 mol. concentrated HNO_3 .
1.00 mol. spherical $\beta\text{-Ni}(\text{OH})_2$, which had been prepared in accordance with the
example given in DE 4 342 620 C1 (18.5 m^2/g) BET, was stirred into this solution.
The resulting suspension was then dried at 150°C and homogenised.
- 10 The reaction mixture was heated for 8 hours at 320°C under nitrogen and then milled
and homogenised.

- The mixture was then heated again slowly (rate of heating up: 2°C/min) and finally
calcined for 24 hours at 610°C in an atmosphere of 90 % Ar/10 % O_2 , cooled and then
- 15 milled and homogenised.

The material was then heated once more for 12 hours at 670°C under oxygen.

- The X-ray diffraction spectrum shows a phase-pure LiNiO_2 (figure 1).
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Example 2

- One mol. spherical nickel oxide (NiO), produced by the calcination at 280°C of
spherical nickel hydroxide $\text{Ni}(\text{OH})_2$ which had been prepared in accordance with the
- 25 example given in DE 4 342 620 C1, was mixed with 1.05 mol $\text{LiOH}\cdot\text{H}_2\text{O}$ and
intensively milled in a ball mill. The mixture was calcined for 24 hours at 500°C under
50 % Ar/50 % O_2 and then milled and homogenised. It was then calcined again for 24
hours at 680°C under 50 % Ar/50 % O_2 and the resulting product was milled.
- 30 The X-ray diffraction spectrum shows that a phase-pure LiNiO_2 was still not produced
under these conditions. This was obtained only following aftertreatment for 24 hours at
700°C under oxygen.

Example 3

One mol. spherical nickel oxide (NiO) in accordance with example 2 was impregnated with 1.05 mol. LiOH·H₂O, which had previously been dissolved in boiling water, dried
5 at 150°C and homogenised. The mixture was thermally treated in the same way as described in example 2 with the result that phase-pure LiNiO₂ was produced after calcination for 24 hours at 680°C. Further heat treatment was not required.

Example 4

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101.0 mol. LiOH·H₂O were carefully dissolved in 102.0 mol. concentrated HNO₃. Then this solution was evaporated down at 140°C to a density of 1.50 g/ml. 100.0 mol. of normal nickel hydroxide (prepared in accordance with US 5 391 265 / DE 42 39 295, BET 73.4 m²/g) were stirred into the hot solution or molten salt. The suspension
15 was dried in a heated mixer at 150°C and pelletised.

10 kg of the mixture prepared in this way were heated to 600°C in a gas-tight tubular furnace under 100 l/h of N₂ and held at this temperature for 6 hours.

20 Then the temperature was increased to 650°C and 100 l/h of N₂ were passed into the furnace as purge gas.

When processing comparable batches using small amounts (0.2 to 1.0 kg) the reaction, visible due to the emission of NO_x, had completely finished after about 12 to 36 h, but
25 with this 10 kg batch it was shown that even after 4 days (96 h) NO_x was still being continuously evolved, i.e. the reaction had still not finished. Only after a further 50 h at a reaction temperature increased to 685°C had the reaction obviously terminated, i.e. no more NO_x emissions could be seen. The mixture was then aftertreated for a further 6 hours at 640°C under 50 l/h of N₂ and 50 l/h of O₂.

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The resulting lithium nickelate still contained 0.43 % NO₃ and a second phase (Li₂O) was detectable in the X-ray diffraction spectrum, this being due to partial decomposition of LiNiO₂ during the extremely long reaction time combined with the relatively high reaction temperature.

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Example 5

10 kg of an intimate preliminary mixture prepared in the same way as in example 4 were first further processed at 600°C for 6 h at atmospheric pressure under an atmosphere of 100 l/h of N₂ and 20 l/h of O₂.

Then the temperature was increased to 640°C and the pressure within the furnace was first reduced to 0.5 bar and then, after 30 minutes, reduced to 0.08 bar. At the same time 100 l/h of N₂ and 20 l/h of O₂ were supplied via a capillary from the "rear face" of the furnace.

After about 16 h, visible emissions of NO_x were no longer detectable and the vacuum pump was switched off.

After a further 4 h of heat treatment at 640°C at atmospheric pressure (50 l/h of N₂ plus 50 l/h of O₂), the reaction had finished completely.

The resulting lithium nickelate contained only 18 ppm of nitrate and the X-ray diffraction spectrum (figure 2) showed that the product was a phase-pure lithium nickelate.

In comparison with example 4, the reaction time was a total of 70 % shorter and the product was not subjected, at any time, to temperatures higher than 640°C.

Example 6

The test conditions in example 5 were repeated, wherein, however, no oxygen at all was supplied during the first calcination stage (6 h/600°C) and the second calcination stage (16 h/640°C/partial vacuum).

The result was identical to that obtained in example 1, i.e. a phase-pure LiNiO₂ which contained only 16 ppm of nitrate was obtained.

Example 7

Example 6 was repeated, but using a "pulsed vacuum" in the second reaction stage. This was achieved by activating an automatically operated cut-off valve installed in the vacuum pipe in such a way that the vacuum pipe was sealed when the pressure
5 dropped below 0.08 bar absolute (measured inside the furnace chamber) and opened again when the pressure reached 0.5 bar.

The pressure build-up inside the (vacuum-tight!) furnace chamber in this case took
10 place on the one hand due to the continuous emission of reaction gases from the reaction mixture and on the other hand due to a steady flow of purge gas (N_2), as a result of which a pulse frequency of about 8 min was set up.

Since no more NO_x production could be detected after about 12 hours, the pulsed
15 vacuum was switched off after a total of 13 hours and the product was aftertreated in the way described in example 5.

The result was identical to that obtained in example 5 and example 6: a phase-pure $LiNiO_2$ was obtained, but with an even shorter reaction time. The nitrate content was
20 determined as 15 ppm.

Claims

1. A process for preparing lithium transition metallates of the general formula



wherein

- 10 M^1 represents nickel, cobalt or manganese,
- M^2 represents chromium, cobalt, iron, manganese, molybdenum or aluminium and is not the same as M^1 ,
- 15 n is 2 if M^1 is manganese, otherwise 1,
- x is a number between 0.9 and 1.2,
- y is a number between 0.5 and 1.0 and
- 20 z is a number between 1.9 and 2.1,

25 by preparing an intimate solid mixture of oxygen-containing compounds of the transition metals and oxygen-containing lithium compounds and calcining the mixture in a reactor, characterised in that calcination takes place for at least some of the time under a pressure of less than 0.5 bar absolute.

2. A process according to Claim 1, characterised in that compounds with a melting point below 600°C are used as lithium compounds.
- 30 3. A process according to Claim 1 or 2, characterised in that calcination takes place for at least some of the time, under a partial vacuum corresponding to a pressure of 0.01 to 0.4 bar absolute.
- 35 4. A process according to one of Claims 1 to 3, characterised in that calcination is performed in several stages, wherein atmospheric pressure is used in the first stage, a partial vacuum is used in the second stage and atmospheric pressure is used in the third stage.



5. A process according to one of Claims 1 to 4, characterised in that the partial vacuum is pulsed with a cycle of 1 to 15 minutes.
- 5 6. A process according to one of Claims 1 to 5, characterised in that a purge gas is passed through the reactor during calcination.
7. A process according to one of Claims 1 to 6, characterised in that the intimate mixture is prepared by impregnating sparingly soluble transition metal compounds with highly concentrated lithium nitrate solution followed by a drying procedure.
- 10 8. A process according to one of Claims 4 to 6, characterised in that inert gases (N_2 , Ar, He), water vapour, low- CO_2 air and/or oxygen are used as purge gases during the first and second reaction stages.
- 15 9. A process according to one of Claims 4 to 7, characterised in that oxygen, an inert gas and/or air are used as purge gases during the third reaction stage.
- 20 10. A process according to one of Claims 1 to 9, characterised in that calcination is performed in a moving bed.
- 25 11. A process for preparing a preliminary mixture suitable for producing lithium transition metallates, consisting of an oxygen-containing lithium component and oxygen-containing transition metal compounds, characterised in that sparingly soluble transition metal compounds are impregnated with highly concentrated lithium salt solutions and then dried.
- 30 12. A process according to Claim 11, characterised in that drying takes place in a spray dryer or a heated mixer.
13. A process according to Claim 11 or 12, characterised in that the intimate mixture consists of pellets or micropellets.
- 35 14. A process according to one of Claims 11 to 13, characterised in that lithium nitrate solutions or molten salts of lithium nitrate hydrates are used as highly concentrated lithium salt solutions.



15. A process according to Claim 14, characterised in that the highly concentrated lithium salt solutions are obtained by dissolving lithium carbonate and/or lithium hydroxide in concentrated nitric acid and then evaporating down the reaction solution.
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16. A process according to one of Claims 1 to 15, characterised in that transition metal compounds are used which are either oxidic or else eliminate water during decomposition.
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17. A process according to one of Claims 1 to 16, characterised in that the transition metal compounds have a BET specific surface area of more than 10 m²/g, preferably more than 50 m²/g.
- 15 18. A process according to Claims 7 and 15, characterised in that the NO_x released during calcination is converted into nitric acid and concentrated and used to dissolve lithium carbonate and/or lithium hydroxide.

