

Powdered lithium oxide, process for its preparation
and its use

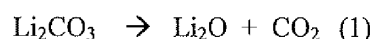
The invention relates to powdered, surface-rich lithium oxide, an economical process for producing the lithium oxide from lithium peroxide, and the use of the lithium oxide for the production of overlithiated lithium metal oxides. Overlithiated lithium metal oxides are used as cathode additives for the purpose of prelithiation for lithium ion batteries.

State of the art

Lithium oxide is currently used as a raw material for the production of glasses, glass ceramics, ceramics as well as positive electrodes of lithium batteries. Furthermore, it can be used for the production of lithium hydroxide. Of particular importance is the use of Li_2O for the production of overlithiated metal oxides, which can alternatively be referred to as lithium-rich metal oxides. These are those lithium-containing oxide compounds that have an increased lithium content compared to the LIB cathode materials used as standard and can make this excess content available during the first charge/discharge cycle to compensate for irreversible lithium losses on the anode side. Examples of overlithiated metal compounds are: Li_5FeO_4 , Li_2NiO_2 , Li_6CoO_4 , or an overlithiated manganese-containing spinel compound, especially $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ or $\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, where $x = > 0$ to 1.

Lithium oxide can be produced by combustion of lithium metal in an oxygen-containing atmosphere. This process is uneconomical because it starts from metallic lithium, which in turn is produced via energy-consuming fused-salt electrolysis.

Furthermore, lithium oxide can be obtained starting from the lithium base chemical lithium carbonate. The process according to



requires very high temperatures of about 900-1000°C, preferably under reduced pressure. Due to intermediate melting of lithium carbonate, the oxide is usually formed in lumpy form, which must be ground before further use (D.S. Appleton, R.B. Poeppel in: Advances in Ceramics, Vol. 25, "Fabrication and properties of lithium ceramics," ed. I.J. Hastings and G.W. Hollenberg, 1989, 111-116). The strong corrosive effect of molten lithium salts at such high temperatures inevitably causes the introduction of undesirable impurities into the thermolysis product and the corrosion-induced destruction of the crucible materials used.

At a very low pressure of $< 10^{-5}$ Torr, thermal decomposition can also occur below the Li_2CO_3 melting point of 720°C (T. Takahashi, H. Watanabe, Fusion Eng. Design 8 (1989)

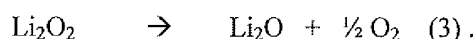
399-405). However, such low pressures are not economically achievable in engineered apparatus.

The admixture of elemental carbon, such as carbon black, serves to accelerate lithium carbonate decomposition (J.-W. Kim, H.-G. Lee, Metallurgical Mater. Trans. B, 32B (2001) 17-24). This carbothermal decomposition does not require a vacuum but occurs under Ar flow, and it proceeds rapidly at temperatures above about 720°C (i.e., the melting point temperature of lithium carbonate) according to the following reaction in alumina crucibles:



A disadvantage is the strong corrosive effect of the carbonate melt on the used container material alumina. The calcination product is thereby contaminated by aluminum.

Li₂O can further be produced by thermal decomposition of lithium peroxide, Li₂O₂:



This process has the advantage that no melting or sintering phases are passed through and the Li₂O can be obtained directly in powder form. The calcination process starting from lithium peroxide is also characterized by lower energy costs, and corrosion of container materials is not expected due to mild calcination temperatures and the avoidance of melting phenomena.

P. Pierron, Bull. France Chim. 1939, 235-238, states that a pure white lithium oxide can be obtained by heating lithium peroxide to 300°C in a Pyrex tube. Details such as thermolysis time are not documented. In our own experiments, it was found that times of at least 20 hours are necessary to achieve > 90% conversion to lithium oxide at 300°C.

US-A-3 321 277 teaches to decompose granular porous Li₂O₂ at a temperature between 225 and 450°C to obtain granular Li₂O suitable for CO₂ absorption. In the example, calcination takes 22 hours and 47 minutes under a stream of argon at a temperature of 386°C.

US-A-4 732 751 describes a process for producing high-purity Li₂O by decomposition of Li₂O₂ in an inert atmosphere at temperatures of initially 350 to 450°C, followed by a calcination process under mild vacuum at 900°C.

KR 20200051931 teaches the use of Li₂O with primary particle sizes $D_{50} \leq 5 \mu\text{m}$ and secondary particle sizes D_{50} between 10 and 100 μm for the production of Li₂NiO₂, where the lithium oxide is produced by thermal decomposition of Li₂O₂ in the temperature range 400 - 600°C. In the example, the Li₂O is obtained by heat treatment at 420°C for 3 hours.

KR 20210079844 teaches the preparation of a finely divided grade of lithium peroxide (particle size 1-130 μm , preferably 5-50 μm) and its use for the preparation of lithium oxide. Calcination is carried out at a minimum of 300°C, preferably at 350-650°C. In the experiment, a temperature of 425°C is described.

CN 109336139 relates to a process for the preparation of high-purity nanometer lithium oxide, characterized in that lithium peroxide is decomposed to lithium oxide at temperatures of initially 350-500°C, then further calcined at 600-800°C and then ground to the desired fineness by means of a ball mill.

The preparation of overlithiated nickel oxide, Li_2NiO_2 , from nickel oxide and Li_2O , the latter obtained by thermal decomposition of Li_2O_2 , is described in a publication by J. Kim et al. (Molecules 2019, 24, 4624). The Li_2O_2 calcination process is studied in the temperature range between 350 and 600°C. A Li_2O reaction product calcined at 450°C was used to prepare Li_2NiO_2 . According to the cited literature (K. Kang et al., Chem. Mater. 2009, 16, 2685-2690), the mixture of NiO and Li_2O was ground in a ball mill under argon for one day and then the homogenized mixture was thermolyzed at 650°C under Ar atmosphere for 24 hours (Kang) or 12 hours (Kim) to give the final product Li_2NiO_2 .

The known processes for the production of Li_2O from Li_2O_2 have the disadvantage that they either require unattractively long reaction times for commercial reasons (at least 20 hours at 300°C) or yield granular Li_2O or/and require a relatively high temperature of at least 350°C. Temperatures $\geq 350^\circ\text{C}$ are not achievable in classical oil-fired reactors, but require furnace technologies. Furthermore, pyrolysis temperatures of 350°C and above result in Li_2O with low surface area, which is detrimental for solid/solid conversions such as in the preparation of overlithiated metal oxide compounds, for example Li_2NiO_2 , from transition metal oxides and Li_2O . To achieve complete conversion of transition metal oxides with Li_2O at acceptable reaction times (< 12 -24 hours), the materials must be intensively pre-painted. This process requires very long meals (24 hours) when using conventional Li_2O , for example, prepared by Li_2O_2 thermolysis $\geq 350^\circ\text{C}$. This causes high costs and, in addition, the input of impurities due to abrasion phenomena scales with the grinding time.

Object

The invention is based on the object of providing a process that enables the production of a powdery lithium oxide with a high specific surface area and low density, which can be ground with the lowest possible energy input and can be advantageously converted into corresponding lithium metal oxides when mixed with transition metal oxides, for example nickel oxide.

Description of the invention

It was surprisingly found that the calcination temperature has a significant effect on the morphology of the lithium oxide formed from lithium peroxide. This is shown in the following tabular overview:

calcination temperature (°C)	calcination duration (hours)	spec. surface (m ² /g)	bulk density (g/mL)	remarks
285	30	14.7	0.1	free flowing
325	5	13.5	0.12	free flowing
350	2	8	0.15	free flowing
380	2	0.3	0.5	free flowing
425	2	0.4	0.7	free flowing
450	2	0.23	0.7	free flowing

A lithium peroxide with a specific surface area between 15 and 20 m²/g and a peroxide content of at least 97% (remainder to 100% consists essentially of LiOH and Li₂CO₃) was used for the experiments. All experiments were performed under inert gas atmosphere consisting of nitrogen, i.e. excluding air, respectively O₂, CO₂ and H₂O.

It can be seen that up to a temperature in the range of 325°C, a product quality with high specific surface area (≥ 10 m²/g) is obtained. When reaching and exceeding about 350°C, the specific surface area decreases sharply. At the same time, the bulk density becomes larger.

The Li₂O variant with a higher surface area is easier to grind and can therefore be brought more quickly and with less energy input into the particle size range required for conversion with finely divided metal oxides, i.e. particle sizes < 20 µm, preferably < 10 µm.

The lithium peroxide used for the process according to the invention has a Li₂O₂ content (by weight) of at least 95%, preferably at least 97% and particularly preferably at least 98%, measured by manganometric titration. The balance to 100% consists essentially of LiOH and Li₂CO₃. From impure lithium peroxide grades, a surface-rich lithium oxide is also formed when the mild calcination temperatures are applied, but this generally contains undesirable granular components and the contents of carbonate and hydroxide remaining in the Li₂O interfere with its use in the preparation of the overlithiated lithium transition metal oxides.

According to BET determination, the specific surface area of the lithium peroxide used is 5 to 30 m²/g, preferably 10 to 30 m²/g more preferably 15 to 20 m²/g.

The calcination is carried out under exclusion of ambient air, especially under exclusion of compounds reactive to lithium oxide and/or lithium peroxide. These are water (moisture), CO₂ and other air trace components. Therefore, calcination is preferably carried out either under inert gas (argon, helium, nitrogen) or in vacuum (< 10 mbar). Furthermore, synthetic, dry and CO₂-free air can be used. Because of the mild reaction temperatures, there are no special requirements for the container material, i.e. most heat-resistant materials, metals as well as glasses (e.g. borosilicate glass, quartz glass) and ceramics (aluminum oxide, porcelains, etc.) can be used.

Calcination is carried out either statically, i.e. the Li₂O₂ starting material is placed in crucibles and calcined in furnaces, or under mixing conditions, i.e. in stirred tank reactors, rotary tubes, or heatable mixing units (e.g. vertical or horizontal dryers, tumble dryers and the like). Fluidized bed reactors can also be used.

The calcination temperature is in the range between 280 and 370°C, preferably 300 and 350°C, more preferably 310 to 350°C, particularly preferably 310 to 340°C. The calcination time to achieve complete conversion depends on the temperature used. Calcination is carried out until the lithium peroxide residue content is a maximum of 5, preferably a maximum of 2, particularly preferably a maximum of 1 wt%. This is achieved by calcination durations of between 1 and 30, in particular 1 to 20, preferably 1 to 10 hours.

The specific surface area of the powdered lithium oxide is at least 5 m²/g, preferably at least 8 m²/g and particularly preferably at least 10 m²/g. It is measured by gas adsorption, a method known as "BET measurement", named after the developers Stephen Brunauer, Paul Hugh Emmett and Edward Teller, according to the standard specification ASTM D6556. In the present case, the adsorption gas is nitrogen.

The powdered lithium oxide has a bulk density of max. 0.3 g/mL, preferably max. 0.2 g/mL, more preferably max. 0.15 g/mL. The bulk density is determined according to the EN ISO 60 standard.

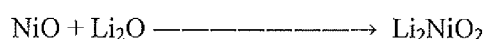
The high surface area lithium oxide according to the invention is preferably used for the preparation of overlithiated metal compounds, the overlithiated metal compounds preferably consisting of: Li₅FeO₄, Li₂NiO₂, Li₆CoO₄, or an overlithiated manganese-containing spinel compound, in particular Li_{1+x}Mn₂O₄ or Li_{1+x}Ni_{0.5}Mn_{1.5}O₄, where x > 0 to 1. For this purpose, the surface-rich lithium oxide is reacted with the corresponding transition metal hydroxide or transition metal oxide or a mixture of different transition metal hydroxides or oxides.

Generally, the surface-rich lithium oxide is first intensively mixed and/or ground with the transition metal salt. Preferably, the mixture is ground in grinding media mills using hard grinding media such as balls, rods and the like consisting of metals (steels or nickel-based alloys) or hard ceramics (metal oxides, metal carbides, metal nitrides, etc.). The Vickers hardness of the grinding vessels and grinding media is at least 400, preferably at least 600. Materials made of stainless steels or metal oxides, for example aluminum oxide or zirconium oxide, are particularly preferred. Ball, rod or hammer mills can be used.

The subsequent reaction of the mixture of surface-rich lithium oxide and transition metal oxide or hydroxide to the overlithiated metal oxide is usually carried out in the absence of oxygen, i.e. in a reducing atmosphere, or in vacuo at pressures between 0.01 and 50 mbar at temperatures between 400 and 900°C. The reducing atmosphere consists of nitrogen or nitrogen compounds. The reducing atmosphere consists of nitrogen or a noble gas, preferably argon or helium. With regard to the atmosphere, however, there are exceptions, namely when the oxidation state of the transition metal in the starting oxide or hydroxide is lower than in the final product to be produced. In this case, an oxidizing atmosphere is necessary, at least temporarily. This will be explained with reference to some characteristic conversions.

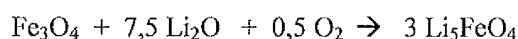
For example, overlithiated lithium nickel oxide (Li_2NiO_2) is produced according to the state of the art (G. Cedar, Chem. Mater. 2004, 2685) by reacting lithium oxide with nickel oxide in an inert (i.e., reducing, oxygen-free) atmosphere:

1. ball mill



2. 650°C/24h-Ar

For this purpose, nickel oxide is first ground with the surface-rich lithium oxide in a ball mill and calcined under an inert argon atmosphere for 1 - 24 hours at about 650°C. Overlithiated lithium cobalt oxide Li_6CoO_4 is prepared by a solid/solid reaction by reacting CoO and Li_2O at 900°C under a nitrogen atmosphere (Yingying Zhou, dissertation 2021, <https://doi.org/10.14989/doctor.k22548>). Li_5FeO_4 is prepared from Li_2O and Fe_3O_4 at 500 or 800°C is prepared under air atmosphere (M.V. Blanco et al., Chem. Eng. J. 354, 2018, 370-7) according to:



Fe_3O_4 contains two iron species, one with +2 oxidation state, the other with +3 oxidation state. To convert the +2 state to +3, the reaction is run at least temporarily under oxidizing conditions. In contrast, the same overlithiated metal compound is synthesized from a ground

mixture of Fe_2O_3 (oxidation state of iron +3) and Li_2O by heating to first 450°C , then 750°C under inert conditions (W.M. Dose et al., J. Electrochem. Soc. 2020, 167 160543):



Overlithiated spinels such as $\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ are prepared by reacting the corresponding normal cathode material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with lithium oxide at 600°C under reducing conditions (G. Gabrielli et al., J. Power Sources, 351, 2017, 35).

Examples

Example 1. Preparation of surface-rich Li_2O from Li_2O_2 according to the invention.

In an Ar-filled glove box, 15.0 g of lithium peroxide (peroxide content 97.9%) was filled into a ceramic vessel consisting of alumina ceramic and placed in a hinged tube furnace with a borosilicate reaction tube under exclusion of air. A furnace temperature of 325°C was set under slight nitrogen overflow and held at this temperature for 5 hours.

Yield: 9.5 g of white fine powder (97% of theory).

Specific surface area: $13.5 \text{ m}^2/\text{g}$

Bulk density: 0.12 g/mL

Li_2O content: 98.6 wt% (acidimetric titration)

Peroxide content: undetectable ($< 0.5 \text{ wt\%}$)

Example 2. Preparation of Li_2NiO_2 from surface-rich Li_2O and NiO according to the invention.

In an Ar-filled glove box, 1.49 g (50 mmol) of lithium oxide (from Example 1) and 3.73 g (50 mmol) of nickel-(II)-oxide (nanopowder from Sigma-Aldrich, 99.8% purity based on trace metal impurities) were mixed in an agate mortar and ground using a pestle.

This mixture was then filled into a crucible consisting of alumina and placed in a hinged tube furnace with the air largely excluded. The heated, nitrogen-permeated furnace tube was made of Inconel 601.

The ground mixture was calcined at a furnace temperature of 650°C for 10 hours.

After cooling to RT, the crucible was introduced into an Ar-filled glove box under exclusion of air.

Yield: 5.1 g (98% of theory).

XRD: nearly phase-pure Li_2NiO_2 (Immm structure); traces (< 1 %) of NiO.

Claims

1. Process for the preparation of powdered lithium oxide Li_2O having a specific surface area according to BET of at least $5 \text{ m}^2/\text{g}$ and a bulk density of at most 0.3 g/ml characterized in that powdered lithium peroxide Li_2O_2 with a minimum content of Li_2O_2 of 95 wt.%, is calcined at temperatures of 280 to 370°C under inert gas conditions or in vacuo at pressures $< 10 \text{ mbar}$ until the reaction according to
$$\text{Li}_2\text{O}_2 \rightarrow \text{Li}_2\text{O} + \frac{1}{2} \text{O}_2$$
to lithium oxide Li_2O has taken place to at least 95%, based on the weight of the calcined reaction product.
2. Process according to claim 1, characterized in that the Li_2O_2 residual content after calcination is at most 2% by weight, preferably at most 1% by weight, based on the weight of the calcined reaction product.
3. Process according to claim 1 or 2, characterized in that the inert gas is selected from nitrogen, argon, helium or dry, CO_2 -free air.
4. Process according to any one of claims 1 to 3, characterized in that the calcination period is 1 to 30, in particular 1 to 20, preferably 1 to 10 hours.
5. Process according to any one of claims 1 to 4, characterized in that the powdered lithium peroxide has a Li_2O_2 content of at least 97 wt.%, preferably at least 98 wt.%.
6. Process according to any one of claims 1 to 5, characterized in that the calcination temperature is 300 to 350°C , preferably 310 to 350°C , in particular 310 to 340°C .
7. Process according to any one of claims 1 to 6, characterized in that the specific surface area of the lithium peroxide used according to BET is 5 to $30 \text{ m}^2/\text{g}$, preferably 10 to $30 \text{ m}^2/\text{g}$ more preferably 15 to $20 \text{ m}^2/\text{g}$.
8. Powdered lithium oxide Li_2O , characterized in that it has a specific surface area according to BET of at least $5 \text{ m}^2/\text{g}$ and a bulk density of at most 0.3 g/ml .

9. Powdered lithium oxide according to claim 8, characterized in that it has a specific surface area according to BET of at least 8, preferably at least 10 m²/g, more preferably at least 12 m²/g, still more preferably at least 15 m²/g.
10. Powdered lithium oxide according to claim 8 or 9, characterized in that it has a bulk density of at most 0.2 g/mL, preferably at most 0.12 g/mL.
11. Process for the preparation of overlithiated metal oxides, characterized in that one or more oxidic transition metal salt(s) is/are intensively mixed and/or ground with the powdered lithium oxide Li₂O according to one of claims 8 to 10 or prepared according to one of claims 1 to 7 and then reacted in a calcination process at a temperature in the range of 400 to 900°C under inert gas or in vacuum at < 50 mbar to give the overlithiated metal oxides.
12. Process according to claim 11, characterized in that the oxidic transition metal salt or salts are selected from the substance groups of transition metal oxides or transition metal hydroxides.
13. Process according to claim 11 or 12, characterized in that the oxidic transition metal salts are selected from nickel, manganese, cobalt or iron oxides, preferably from NiO, CoO, Fe₂O₃, Fe₃O₄ and FeO, particularly preferably from NiO, CoO and Fe₂O₃ or the corresponding hydroxide compounds.
14. Process according to one of claims 11 to 13, characterized in that the calcination is carried out under reducing conditions, in particular an oxygen-free atmosphere or in a vacuum at 0.01 to 50 mbar, in the case of identical transition metal oxidation stages in the raw material as in the end product.
15. Process according to any one of claims 11 to 14, characterized in that the reducing atmosphere is selected from nitrogen, argon and helium.
16. Process according to any of claims 11 to 15, characterized in that the overlithiated metal oxides are selected from Li₅FeO₄, Li₂NiO₂, Li₆CoO₄ or an overlithiated manganese-containing spinel compound, in particular Li_{1+x}Mn₂O₄ or Li_{1+x}Ni_{0.5}Mn_{1.5}O₄, where x = > 0 to 1.

17. Use of a lithium oxide according to any one of claims 8 to 10 or a lithium oxide prepared by the process according to any one of claims 1 to 7 for the preparation of overlithiated metal oxides, in particular selected from Li_5FeO_4 , Li_2NiO_2 , Li_6CoO_4 , or an overlithiated manganese-containing spinel compound, preferably $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ or $\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, where $x = > 0$ to 1, characterized in that one or more oxidic transition metal salt(s) is/are intensively mixed and/or ground with the lithium oxide and then reacted in a calcination process under reducing atmosphere or in vacuum from 0.01 to 50 mbar to the overlithiated metal oxides.