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(54) Titre : PROCEDE DESTINE A LA PREPARATION D'OXYDE DE LITHIUM
(54) Title: METHOD FOR PRODUCING LITHIUM OXIDE

(57) Abrégé/Abstract:

The invention relates to a new method for producing lithium oxide and the use thereof, wherein lithium carbonate is converted with elementary carbon or a carbon source forming elementary carbon under the reaction conditions in a temperature range from 720 to 1200°C and wherein the conversion takes place largely with the exclusion of oxygen (i.e. in a vacuum or in a gas atmosphere inert with respect to carbon, for example containing N_2, Ar or other noble gases) and the conversion is further carried out in containers, the product-contacting surfaces of which are corrosion-resistant with respect to the reactants and products. The lithium oxide obtained according to the method is used either for producing pure lithium hydroxide solutions or for producing glass, glass ceramics or crystal ceramics, for example lithium ion-conducting ceramics.

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Erklärungen gemäß Regel 4.17:

— *hinsichtlich der Berechtigung des Anmelders, ein Patent zu beantragen und zu erhalten (Regel 4.17 Ziffer ii)*

— *Erfindererklärung (Regel 4.17 Ziffer iv)*

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— *mit internationalem Recherchenbericht (Artikel 21 Absatz 3)*

(54) Title: METHOD FOR PRODUCING LITHIUM OXIDE

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON LITHIUMOXID

(57) Abstract: The invention relates to a new method for producing lithium oxide and the use thereof, wherein lithium carbonate is converted with elementary carbon or a carbon source forming elementary carbon under the reaction conditions in a temperature range from 720 to 1200°C and wherein the conversion takes place largely with the exclusion of oxygen (i.e. in a vacuum or in a gas atmosphere inert with respect to carbon, for example containing N_2, Ar or other noble gases) and the conversion is further carried out in containers, the product-contacting surfaces of which are corrosion-resistant with respect to the reactants and products. The lithium oxide obtained according to the method is used either for producing pure lithium hydroxide solutions or for producing glass, glass ceramics or crystal ceramics, for example lithium ion-conducting ceramics.

(57) Zusammenfassung: Die Erfindung betrifft ein neues Verfahren zur Herstellung von Lithiumoxid und dessen Verwendung, wobei Lithiumkarbonat mit elementarem Kohlenstoff oder einer unter den Reaktionsbedingungen elementaren Kohlenstoff bildenden Kohlenstoffquelle im Temperaturbereich von 720 bis 1200°C umgesetzt wird und wobei die Umsetzung unter weitgehendem Ausschluß von Sauerstoff (d.h. im Vakuum oder unter gegenüber Kohlenstoff inerter Gasatmosphäre, beispielsweise enthaltend N_2, Ar oder andere Edelgase) stattfindet und die Umsetzung weiterhin in Behältnissen vorgenommen wird, deren produktberührende Oberflächen gegenüber den Reaktanden und Produkten korrosionsstabil sind. Das verfahrensgemäß erhaltene Lithiumoxid wird entweder für die Herstellung reiner Lithiumhydroxidlösungen oder für die Herstellung von Gläsern, Glaskeramiken oder kristallinen Keramiken, beispielsweise lithiumionen-leitfähigen Keramiken, verwendet.

Method for Producing Lithium Oxide

The invention relates to an economical method for the production of powdered lithium oxide and its use.

Lithium oxide is currently used as raw material for the Production of glasses, glass-ceramics, ceramics and positive electrodes of lithium batteries. Further, it can be used for the production of lithium hydroxide.

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

Li_2O may further be produced by thermal decomposition of lithium peroxide, Li_2O_2, at 300-400 °C. Also, this process is economically disadvantageous, since it is a two-step process and needs lithium hydroxide and the hazardous oxidizing agent hydrogen peroxide as starting compounds.

Finally, processes are known that start from the Lithium base chemical lithium carbonate. By thermal decomposition at about 1000 °C, i. e. of molten lithium carbonate, in platinum crucibles at a pressure of max. 2000 µmHg the oxide in lumpy form arises according to

$Li_2CO_3 \rightarrow Li_2O + CO_2$ (1)

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). At a very low pressure of $< 10^{-5}$ Torr, the thermal decomposition can also take place below the melting point of Li_2CO_3 of 720 °C (T. Takahashi, H. Watanabe, Fusion Eng. Design 8 (1989) 399-405). However, such low pressures cannot be reached economically in technical apparatuses.

Furthermore, it is known to reduce lithium carbonate in the temperature range 400-725 °C by means of hydrogen gas according to

$Li_2CO_3 + H_2 \rightarrow Li_2O + H_2O + CO$ (2)

(JP2014047117A). This method has safety-related disadvantages, due to the use of explosive hydrogen gas at high temperatures.

Finally, carbon black can be used as a reducing agent for lithium carbonate (J.-W. Kim, H.-G. Lee, Metallurgical Mat. Trans. B, 32B (2001) 17-24). The carbothermic decomposition does not require a vacuum but takes place under an argon gas stream and is rapid at temperatures above about 720 °C according to the following reaction in alumina crucibles:

$Li_2CO_3 + C \rightarrow Li_2O + 2CO$ (3)

The disadvantage here is the strong corrosion effect of the carbonate melt on the alumina used as container material, as was found out in our own experiments (see Comparative Examples). The crucible mass is removed by formation of $LiAlO_2$. There is no passivation of the crucible wall. Lithium oxide becomes recurrently contaminated by $LiAlO_2$. For this reason, the alumina crucibles cannot be used for the production of high purity lithium oxide. The carbothermal decomposition using coke, charcoal, activated carbon, sugar, synthetic graphite and the like can also take place at temperatures above 500 °C, but below 720 °C, i. e. while avoiding the melting of lithium carbonate (JP2012121780A). In this case relative long reaction times are to be expected. Similarly, lithium carbonate embedded in a polymer resin can be reduced in the temperature range between 600 and 700 °C to granular lithium oxide (JP11209122A). The disadvantages are the long reaction times of at least 6 hours and the fact that the oxide is obtained in granulated form. For the further use, e. g. for the production of electrode materials for lithium batteries, the product must then be ground up beforehand.

It is the object of the invention to provide a simple and single-stage method using the basic raw material lithium carbonate by means of which a powdered lithium oxide can be produced in high purity under economical, simple reaction conditions.

According to the invention the object is achieved by a method in which lithium carbonate is reacted with elemental carbon or a carbon source forming elemental carbon under the reaction conditions in the temperature range of 720 to 1200 °C, wherein the reaction takes place under substantial exclusion of oxygen and the reaction is carried out in containers whose product-contacting surfaces are corrosion resistant to the reactants and products. The reaction is carried out either under reduced pressure, for example "technical vacuum" (i. e. in the pressure range from 0.1 to 50 mbar) or under gas atmosphere inert or substantially inert to carbon at pressures of about 0.5 to 2 bar. Preferably nitrogen or noble gases (preferably argon) or mixtures of inert gases may be used as inert gas atmosphere.

To obtain a satisfactory reaction rate also from a commercial point of view, the reaction takes place above the melting temperature of lithium carbonate, that is above about 720-730 °C. Preferably, the reaction temperature is in the range between 800 and 950 °C. Under these conditions, typically, reaction times of less than 5 h, preferably less than 3 h are observed. At 900 °C, the reaction time is about 30 minutes according to thermogravimetric analyses. The elemental carbon is used in powdery form. Commercially available carbon black or activated carbon, for example furnace carbon blacks (carbon blacks for car tires) such as Carbon Black N220 and N110, gas carbon blacks like Timcal C45, Conductive Carbon Black or thermal carbon blacks like N990 Thermal Carbon Black are preferably used. These carbons may contain up to 1 wt.% sulfur and up to 2 wt.% silicon. Commercially available, inexpensive carbon blacks produced from petroleum for car tires are also particularly suitable with the following impurity profile: 2300 ppm Na, 1900 ppm S, 200 ppm Ca, 100 ppm Fe, about 1 wt.% Si. It was surprisingly found that the contaminants mentioned can be largely separated in the inventive preparation of aqueous lithium hydroxide solutions by a simple solid/liquid separation method, that is for example, by filtration or centrifugation.

Instead of elemental carbon, an organic, carbon-containing material can be used as a reducing agent. Organic materials coke under the above stated, non-oxidizing (exclusion of oxygen) high temperature conditions completely to elemental carbon and volatile by-products. The elementary carbon, whether used as such or formed under reaction conditions by thermal decomposition of organic materials (coking) is used in the stoichiometric molar ratio of lithium carbonate to carbon of 1 : 0.5 to 1 : 1.5.

It has surprisingly been found that the reaction product lithium oxide, although formed from molten lithium carbonate, is obtained as a flowable powder. For further use it is not necessary therefore to transfer the reaction product by crushing or grinding in a manageable form.

To avoid contaminants in the product, as well as from a cost perspective, it is necessary that the reaction is carried out in reaction vessels whose product-contacted surfaces are largely inert against the reactants as well as the reaction products and long-term corrosion resistant. For example, glassy carbon, lithium aluminate or carbon coated ceramics, for example, C@quartz may be used as such resistant construction materials. Furthermore, tantalum has a moderate stability. It was again surprisingly observed that glassy carbon crucibles are corrosion stable against lithium carbonate melt and the lithium oxide formed. This was not to be expected, since it is known that carbon at high temperatures reduces lithium carbonate with lithium oxide formation and thereby is consumed according to Eq. 3. In own experiments it was found that metallic materials are generally unusable. For example, titanium crucibles crumble already after single use. Tantalum, on the other hand, has limited stability.

In the simplest case, the reaction can be carried out under static conditions, i. e. without stirring and without moving. Preferably, the reaction is carried out in a moving bed reactor. For this purpose, the reaction mixture is brought in a rotary tube or in a circulating fluidized bed reactor to the necessary temperature and reacted accordingly to the product lithium oxide. Under homogenizing conditions it is possible to further increase the reaction rate.

It is also possible to liquefy the mixture of carbon and lithium carbonate in an externally cooled reaction space by inductive heating and thus to react the two reactants. Due to the external cooling a layer of frozen melt forms so that the molten reaction mixture, which is continuously pumped or pushed through the reaction vessel, does not come into contact with the container material (for example, copper). This procedure is known by the term "skull technique".

The lithium oxide-containing reaction mixture according to the invention can be used, for example, for the production of pure lithium hydroxide solution by dissolving the reaction product in Water. The amount of water should be chosen so that the reaction product lithium hydroxide (LiOH) has a concentration of at least 8 wt.%. Preferably, the LiOH concentration is at least 9 wt.%. Any excess carbon is insoluble in water, so it can be easily removed by filtration or centrifugation. It was surprisingly observed that more contaminants such as the silicon introduced via the carbon source or sulfur, are converted into water-insoluble products, so that these also can be separated by a simple solid/liquid separation method. In this way a pure lithium hydroxide solution is obtained from which pure, solid lithium hydroxide or lithium hydroxide monohydrate can be produced by a known method. The purity of the 10% solution of LiOH produced by the method according to the invention is preferably at least 99.8%. The concentrations of the contaminants silicon and sulfur which were introduced mainly via the carbon source are preferably not more than 0.05 and 0.1 wt.%, respectively, based on LiOH contained. The contaminants can be further depleted in the subsequent crystallization of LiOH x H_2O. The lithium oxide according to the invention can be used for the production of cathode materials (positive electrode materials) for lithium batteries and for the production of glasses, glass ceramics or crystalline ceramics. Very particularly preferred is the use for lithium-conductive glasses, glass ceramics or ceramics. Such materials, for example LLZO (lithium lanthanum zirconium oxide with garnet structure), have a lithium conductivity of at least 10^{-5} S/cm at room temperature (RT).

Example 1: Production of lithium oxide by carbothermal decomposition of lithium carbonate in glassy carbon crucible

8.6 g of Li_2CO_3 (116 mmol) together with 1.4 g of C (Carbon Black N220, 116 mmol C) were filled into a bottle with ISO thread, mixed on the dolly and filled into a crucible made of glassy carbon, the bed height was 0.75 cm.
The crucible was flushed in a quartz glass tube continuously with 50 l of N_2/h and heated to 900 °C in a tube furnace. After 4 hours, cooling was started.

The product obtained was: 3.4 g (100% of theory) of weakly gray powder. The total base (acidimetric titration) gave the following result: 66.1 mmol OH^-/g, corresponding to 98.8% Li_2O. The following contaminants were determined by means of ICP (Inductively Coupled

Plasma): 0.50 wt.% Si; 0.35 wt.% S; 0.03 wt.% Na; 0.03 wt.% Ca; 0.005 wt.% Al
Total Organic Carbon (TOC): 0.1 wt.% C and
XRD: only reflections for Li_2O.
Particle size distribution (measurement with Mastersizer 3000 from Malvern Instruments):
D_{10} = 30 µm
D_{50} = 69 µm
D_{90} = 163 µm

No measurable mass change of the crucible was observed, the weight difference was < 0.01 g. The same crucible was used for a further 10 experiments without any microstructural destruction or weight change being observed.

Example 2: Production of a pure aqueous lithium hydroxide solution from lithium oxide

2.1 g of the product from Example 1 were dissolved in 31.0 g of water and insoluble residue was filtered off. The clear, colorless filtrate was analyzed:
Total base (acidimetric titration). 4.25 mmol/g corresponding to 10.2 wt.% LiOH (97% of theory)
Carbonate titration: 0.15 wt.% Li_2CO_3.

The following contaminants were found by ICP analysis of the solution:
8 ppm Fe; Na, K < 10 ppm; 60 ppm S; 14 ppm Si
The purity of the lithium hydroxide formed is about 99.9% (based on LiOH-solid contained).

Extrapolated to the lithium oxide used, the main contaminants were thus depleted as follows:
Si: 96%
S: 73%

Comparative Example 1: Production of lithium oxide by carbothermal decomposition of lithium carbonate in the Alox crucible

As in Example 1, a mixture of 8.6 g of lithium carbonate powder and 1.6 g of carbon black, type N220 was reacted at 900 °C to form lithium oxide in a crucible made of Al_2O_3.
The reaction product contained 0.34 wt.% Al. In comparison, the product produced in the glassy carbon crucible only 0.005 wt.% Al. 0.05 wt.% crucible mass was removed by corrosion. In subsequent experiments similar removal rates were observed. Thus, there is no passivation of the surface.

Comparative Example 2: Production of lithium oxide by carbothermal decomposition of lithium carbonate in the Ti-lined crucible

A titanium foil was placed at the bottom of glassy carbon crucible and a homogenized reaction mixture consisting of 8.6 g of lithium carbonate and 1.6 g of carbon black, type N220, was added on top. The reaction mixture was reacted to form lithium oxide under the same conditions as described in Example 1.
The foil became white and brittle during the course of the reaction. It already disintegrated at slight mechanical stress and could not be completely separated from the Li_2O formed.

Claims

1. A method for the production of powdered lithium oxide from lithium carbonate and elemental carbon or a carbon source forming elemental carbon under the reaction conditions in the temperature range of 720 to 1200 °C, characterized in that the reaction takes place under substantial exclusion of oxygen and the reaction is carried out in containers whose product-contacting surfaces are corrosion resistant to the reactants and products.

2. The method according to claim 1, characterized in that the elemental carbon is reacted in the stoichiometric ratio of the lithium carbonate to the carbon of 1 : 0.5 to 1 : 1.5.

3. The method according to any one of claims 1 to 2, characterized in that the elemental carbon is used in the form of carbon black or activated carbon having a sulfur content of up to 1 weight percent and a silicon content up to 2 weight percent.

4. The method according to any one of claims 1 to 3, characterized in that organic materials or organic material mixtures selected from the group consisting of sugar, methane, starch, cellulose, paraffin wax or petroleum are used as a source of elemental carbon.

5. The method according to any one of claims 1 to 4, characterized in that the reaction is carried out in reaction vessels whose product-contacted surfaces are consisting of glassy carbon, lithium aluminate or carbon-coated ceramic or C-coated quartz.

6. The method according to claim 5, characterized in that the reaction is carried out in reaction vessels whose product-contacted reaction vessel walls consist of a solidified molten salt.

7. The method according to any one of claims 1 to 6, characterized in that the reaction temperature is in the range between 800 and 950 °C.

8. The method according to any one of claims 1 to 7, characterized in that the reaction is carried out in the pressure range of 0.01 to 2 bar.

9. The method according to any one of claims 1 to 8, characterized in that the reaction is carried out in a moving bed reactor.

10. The method according to claim 9, characterized in that the reaction is carried out in a rotary reactor or in a circulating fluidized bed reactor.

11. The use of lithium oxide obtained according to any one of claims 1 to 10 for the production of pure lithium hydroxide solution by dissolving the reaction product in water, the amount of water being chosen so that the reaction product lithium hydroxide LiOH has a concentration of at least 8 wt.% and that the insoluble constituents are removed by filtration or centrifugation.

12. The use of lithium oxide obtained according to any one of claims 1 to 10 for the production of cathode materials for lithium batteries.

13. The use of lithium oxide obtained according to any one of claims 1 to 10 for the production of glasses, glass ceramics or crystalline ceramics.

14. The use of lithium oxide according to claim 13, characterized in that the glasses, glass ceramics or ceramics have a lithium conductivity of at least 10^{-5} S/cm at room temperature.