

Production of Lithium Oxide by Decomposition Lithium Carbonate in the Flow of a Heat Carrier

M. G. Ktalkherman, V. A. Emelkin, and B. A. Pozdnyakov

Institute of Theoretical and Applied Mechanics, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia

e-mail: ktalkherman@itam.nsc.ru

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Abstract—Decomposition of lithium carbonate with formation of lithium oxide in the flow of a high-temperature heat carrier studied. Atmospheric-pressure air was used as the heat transfer medium. The results of measurements show that the proposed method for producing lithium oxide is promising. In experiments, the lithium carbonate conversion into lithium oxide exceeds 70% perpass. A physical model for the process of lithium carbonate dissociation at high temperatures is considered.

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Lithium oxide is part of the composition of materials for electrodes in lithium batteries and tritium-producing materials in thermonuclear reactors. Different methods for producing lithium oxide are described in monographs [1, 2]: direct metal oxidation and heating of lithium carbonate, nitrate, or hydroxide in the flow of dry hydrogen at a temperature higher than 1070 K. The majority of works considered in [1, 2] are laboratory studies. Specific methods for producing lithium oxide from lithium peroxide and hydroxide that are proposed for practical use are given in a number of publications (see, for example, [3–5]). Thermal decomposition processes considered in these studies are carried out in inert gases at moderately high temperatures and low pressure and consist of several stages.

In addition to the above methods, of interest is the process of producing lithium oxide directly from the feedstock of the lithium industry—lithium carbonate—by means of its thermal dissociation according to the reaction $\text{Li}_2\text{CO}_3 = \text{Li}_2\text{O} + \text{CO}_2$.

Despite the apparent simplicity, the implementation of this process is associated with overcoming certain difficulties. Since the reaction is accompanied by CO_2 release from the reaction mass, this process is diffusive-kinetic. The diffusion of the gas and its release from the reaction mass are hindered by agglomeration of particles of Li_2CO_3 powder upon reaching the melting point, as well as by a low pressure of CO_2 saturated vapor (about 4 Torr at a melting point of about 1000 K). In addition, since the melting point of lithium oxide that forms during the reaction is very high (≈ 1700 K), the reaction product (Li_2O) is in the solid phase at lower temperatures of the process, which also impedes the release of CO_2 . Therefore, on a laboratory scale, the process of lithium carbonate decomposition is fre-

quently studied in vacuum furnaces at relatively low temperatures. In this case, the duration of the process is tens of hours.

Among the studies in this area, of greatest interest is a method for producing granules of sintered lithium oxide, the authors of which propose it for industrial-scale production [6]. In brief, the technique is as follows. First, according to a special procedure, conglomerates of spherical particles are prepared from powdered Li_2CO_3 , which are then placed into a vacuum furnace, where a pressure of 10–4 Torr is maintained. The process of dissociation occurs for 60 h at a temperature of 930 K. The final product—spherical granules of lithium oxide—is obtained after the sintering of particles at a temperature of 1370 K.

A fundamentally different method of thermal decomposition of lithium carbonate is proposed in [7]. Its distinctive features are the high temperature of the process (above the melting point of lithium oxide) and the absence of the need to maintain vacuum (pressure $p = 0.1$ MPa). The process of decomposition is carried out in the dynamic regime.

The method is as follows. Powdered Li_2CO_3 is introduced into the flow of an inert (with respect to the feedstock and reaction products) gas heated to a high temperature. The gas-dispersed mixture fed into a vertical reactor. With the use of a swirler, powder particles are thrown onto the heated wall of the reactor, made of graphite, in which a film of the melt is formed that drains into a collector under gravity and a frictional force from the flow. As the film drains, the reaction of Li_2CO_3 decomposition with carbon dioxide release into the flow occurs in the film.

The important result of the studies is the possibility of implementing high-temperature decomposition of

Li_2CO_3 set in experiments (with a high yield of Li_2O) at atmospheric pressure, which was established experimentally. For this, the temperature of the process must be maintained at a high level. It is known [1] that CO_2 saturation pressure in Li_2CO_3 dissociation increases sharply with a rise in temperature (from 4 Torr at $T \approx 1000$ K to 10^5 Pa at $T = 1540$ K). Therefore, under conditions of experiments [6], the influence of the partial pressure of CO_2 on the course of the process was eliminated.

This study deals with another variant of the high-temperature method for producing lithium oxide: dissociation of Li_2CO_3 particles in the flow of a heat transfer medium. In contrast to [7], air is used as the heat carrier instead of nitrogen.

To conduct studies, an experimental setup was designed and manufactured. The main elements of the setup are as follows: a plasmatron with a unit for powder introduction, a reactor, a collector, and systems for feeding the powder and air supplied to the plasmatron and powder transportation.

A V-shaped plasmatron was used for heating the heat transfer medium. The angle between the anode and cathode axes was 60° . The diameter of the plasmatron jet at the outlet was 35 mm. In the housing of the plasmatron, two holes were drilled at an angle of 140° to introduce the powder with the transport gas. The intersection point of the axes of these holes was located 15 mm below the intersection point of the axes of the working gas jets.

The plasmatron was fastened to the vertically installed reactor. Figure 1 shows a diagram of the reactor. The reactor consists of a water-cooled section with a diameter of 140 mm and a length of 900 mm and an extending uncooled tube, both of them made of stainless steel. A collector with a sleeve for air supply for quenching the reaction products is connected to the reactor. The gas is withdrawn from the collector through a filter (a wire mesh made of stainless steel with a mesh size of $56 \mu\text{m}$). The total length of the reactor from the jet entrance to the collector bottom is 1500 mm.

During experiments, the power of the plasmatron, air flowrate for the plasmatron and for transportation, and powder mass flow were measured. Heat fluxes into the housing of the plasmatron and the walls of the reactor were determined by calorimetry.

The fractional composition of commercial lithium carbonate used in the experiments (white powder susceptible to adhesion) was characterized by considerable nonuniformity. Since dry sieving was impossible because of the adhesion of particles, sieving was conducted in ethanol using sieves with nominal mesh sizes of 80, 160, 280, 480, and 590 μm . After ethanol evaporation, the fractions were weighed using a VLR-200 analytical balance to an accuracy of 0.00015 g. Figure 2 presents the mass particle size distribution. It can be seen that the composition of the powder has a wide spectrum of particles, with

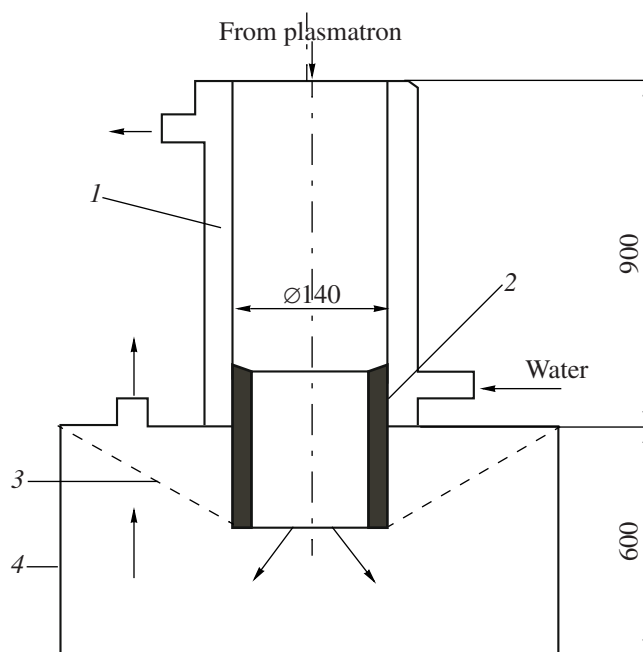


Fig. 1. Diagram of the reactor: (1) housing of the reactor, (2) extension pipe, (3) filter, and (4) collector.

more than 80% of the mass due to particles with sizes of over 80 μm . The weighted-average particle size d_{43} is 390 μm . The fraction of particles smaller than 80 μm was analyzed using a Malvern-3600E automatic granulometer [8]. According to the results of measurements, approximately 80% of the mass of this fraction falls within a particle size of 5–55 μm .

The sequence of operations in performing experiments was as follows. At a small flow rate of air, the plasmatron was switched on, and its power and the air flow rate were then brought to the given values. In most experiments, air for quenching the reaction products was not supplied. Over several minutes, the setup operated in the wall-warm-up mode. Stabilization of the temperature regime of the walls was judged from the

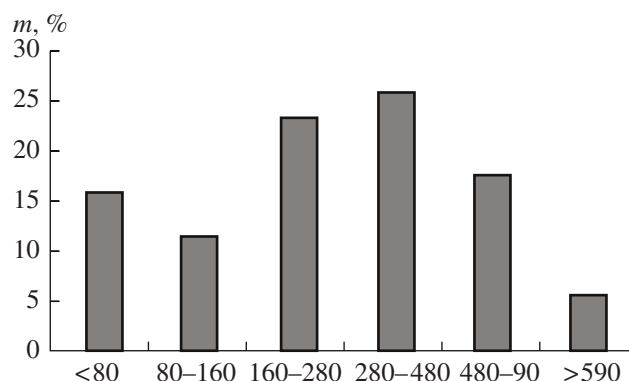


Fig. 2. Fractional composition of powdered Li_2CO_3 .

cooling-water temperature at the outlet of the reactor housing and the plasmatron cooling circuit. Then, powdered lithium carbonate was fed to the reactor. The duration of the working stage was 3–4 min. After the supply of powder was stopped and the plasmatron was switched off, cold air was blown through the setup.

Reaction products as a finely divided powder were deposited on the walls of the lower section of the reactor and in part on the wall of the filter. The powder was easily separated from metal surfaces and was subsequently used for determining the lithium oxide content.

The concentration of lithium oxide ($C_{\text{Li}_2\text{O}}$) in the reaction product was determined from the density of the aqueous solution of the product ρ measured by areometers. In this case, known data on the density of LiOH solutions were used [9]. These data were recalculated as the dependence $\rho(C_{\text{Li}_2\text{O}})$. From the value of ρ , the mass of dissolved lithium oxide was determined: $M_{\text{Li}_2\text{O}} = C_{\text{Li}_2\text{O}} V$, where V is the volume of the solution. Then, the mass of the deposit (lithium carbonate that was not decomposed) was calculated: $\Delta M_{\text{Li}_2\text{O}} = M_{\text{Li}_2\text{CO}_3}^0 - M_{\text{Li}_2\text{O}}$, where $M_{\text{Li}_2\text{CO}_3}^0$ is the initial mass of the powder. From this quantity of Li_2CO_3 in the case of its complete conversion to Li_2O , it is possible to produce lithium oxide in amounts of $\Delta M_{\text{Li}_2\text{O}} = M_{\text{Li}_2\text{CO}_3}^0 \rho_{\text{Li}_2\text{O}} / \mu_{\text{Li}_2\text{CO}_3}$, where μ is the molecular mass. Ultimately, the lithium carbonate conversion to lithium oxide is determined by the parameter

$$\eta = M_{\text{Li}_2\text{O}} / (M_{\text{Li}_2\text{O}} + \Delta M_{\text{Li}_2\text{O}}).$$

In a series of experiments, the flow rates of the media and the power of the plasmatron were almost unchanged: the flow rate of air supplied to the plasmatron was 6 g/s, the flow rate of air supplied for powder transportation was 2 g/s, the flow rate of the powder was 0.9–1 g/s, and the power of the plasmatron was 90–100 kW.

The power of the plasmatron was chosen so that, taking into account heat loss and energy consumption for powder decomposition, the temperature of the flow along the entire length of the reactor remained higher than the melting point of lithium oxide $T_m = 1726$ K. In this case, we proceeded from the following considerations. First, a high temperature of the heat carrier ensures intensive heat transfer to the a particle, which leads to an increase in the rates of its heating and the reaction. On the other hand, it can be assumed that the outer layer of the particle will decompose in the first place. Lithium oxide that forms here must be in the liquid, rather than solid, state, which should facilitate the diffusion of carbon dioxide that forms during the reaction from the inner space to the gas flow (the issue of the diffusion restriction of the process due to a low CO_2

pressure saturation during Li_2CO_3 decomposition will be discussed below).

Thermodynamic calculations were performed using the TERRA program [10]. From the results of calculations, the heat content of the gas-dispersed mixture at the outlet of the reactor taking into account heat losses (≈ 1500 kJ/kg) and the weighted-average value of the equilibrium temperature of the mixture ($T_{\text{eq}} \approx 2200$ K) were determined. This calculated temperature is in agreement with the experimental values of η and the equality of the temperatures of the gaseous and solid phases. Since the relative powder content of the mixture was small, the temperature of the gas had to be close to the calculated value, and the temperature of particles in the flow had to be lower because of phase changes.

In the first two experiments performed under the above conditions, the lithium carbonate conversion to lithium oxide was small: $\eta = 0.2$. We suppose that such a result is due to the fact that large fractions are predominant in the composition of the powder (see Fig. 1). Therefore, particles do not have time to decompose during the residence time in the reactor. The validity of this assumption is qualitatively confirmed by the results of calculating the residence time of particles in the reactor and the time of their heating up to the melting point of lithium carbonate. Clearly, the heat-up stage is only the initial stage of the process; however, in the literature, there are no data on the particularities of the complex diffusive-kinetic process of Li_2CO_3 dissociation. Therefore, the calculated time of heat-up is the lower estimate of the necessary residence time.

Calculations of the residence time for the conditions of our experiments were performed using the equation of motion of a spherical particle in the flow of air. The drag coefficient of a particle was calculated by the Stokes formula $C_d = 24/\text{Re}_d$ since the Reynolds number was small ($\text{Re}_d = 1.2$ at $d = 500$ μm).

The time of particle heat-up to the melting point was determined from the solution of the problem of non-steady-state heat conduction for a sphere placed into a gas flow at a constant temperature [11]. The heat transfer coefficient was calculated by the criterion equation for the case of steady-state flow past spherical particles [11]. The temperature of the gas was taken to be 2200 K. The thermophysical properties of a particle were considered to be temperature-independent. The specific heat of Li_2CO_3 is given in [12]. The thermal conductivity of Li_2CO_3 is unknown to us. On the basis of data on the thermal conductivity of certain lithium compounds given in [13], we took a value of $\lambda_{\text{Li}_2\text{CO}_3} = 5$ W/(m K). The uncertainty in the value of $\lambda_{\text{Li}_2\text{CO}_3}$ affects only slightly the results of calculations: a twofold decrease in the specified value reduces the time of heat-up by 17%.

Figure 3 shows the residence time of particles in the reactor t_r and the time of their warm-up to the melting point T_m as a function of the particle diameter d . The

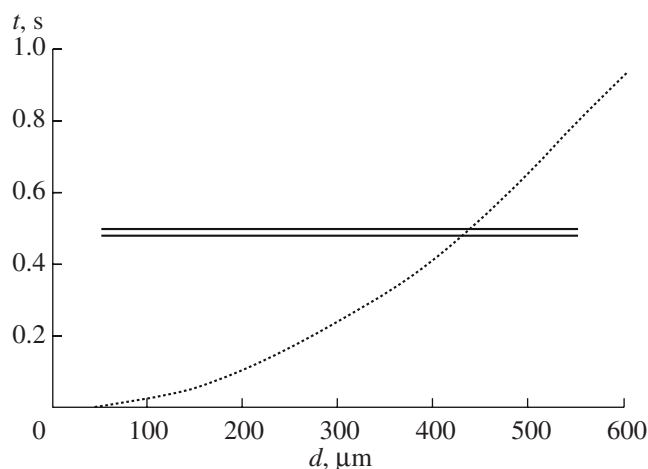


Fig. 3. Residence time of particles in the reactor t_r and the time of their heating to the melting point t_m at the length of the reactor $L = 1.5$ m and $T = 2000$ K.

values of t_r depend little on the particle diameter d and lie between two closely located lines. On the other hand, the dependence $t_m(d)$ is very strong. Both dependences intersect at $d \approx 435$ μm . Therefore, such particles or larger ones, the content of which in the original powder is rather high (see Fig. 1), have time only to warm up to the state of the beginning of decomposition during the residence time in the reactor. It is evident that, under the given conditions of the experiments, medium-sized particles also do not have time to completely decompose in the reactor.

Taking into account data in Fig. 3, we decided to perform experiments with smaller particles. For these experiments, the original powder was milled and sieved. In this way, powders with maximum particle sizes of $d_{\text{max}} = 250$, 100, and 63 μm were prepared. The fractional composition of these powders was not determined.

Figure 4 presents the results of experiments with these batches of samples that were performed under the above conditions. The rightmost point represents the original powder of Li_2CO_3 ($d_{43} = 390$ μm); the remaining points represent the powders screened through sieves with mesh sizes of 250, 100, and 63 μm . The data in Fig. 4 show the important role of the particle sizes in Li_2CO_3 decomposition. More precisely, the matter concerns the choice of the necessary residence time for particles of a certain size. In the given case, the dependence $\eta(d_{\text{max}})$ corresponds to a value of $t_r \approx 0.5$ s. A high degree of conversion of small Li_2CO_3 particles should also be noted. The highest value in the given experiments $\eta = 0.78$ corresponds to the particle diameter $d_{\text{max}} = 63$ μm .

Since, as follows from Fig. 4, Li_2CO_3 decomposition under conditions of the present experiments is not completed ($\eta < 1$), there is some interest in the equilibrium state of the given system. Appropriate calculations were performed using the TERRA program. Figure 5 shows

the transformation of the composition of the original gas-dispersed mixture in the temperature range $T = 1000$ – 2300 K at a pressure of $p = 0.1$ MPa and ratio of the gas and solid phases that is relevant to the conditions of experiments.

The data in Fig. 5 indicate one of the possible causes of disagreement between the reaction product mass obtained after an experiment and the calculated amount determined from the quantity of consumed powder taking into account the Li_2CO_3 conversion to Li_2O . In all experiments, the mass of the product was significantly less than the calculated value. According to a thermodynamic calculation, at high temperatures, a considerable portion of lithium oxide is in the gaseous state. Therefore, a portion of the reaction product can be carried outside the setup by the flow. Evidently, the data in Fig. 5 correspond to the equilibrium state, which, as follows from the results of measuring the conversion, is

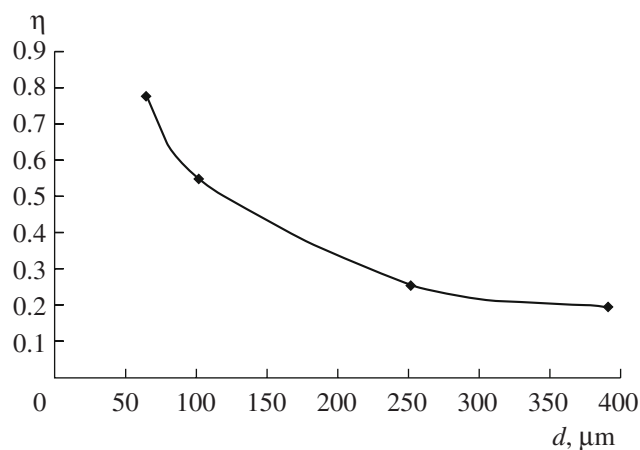


Fig. 4. Degree of conversion of lithium carbonate particles to lithium oxide.

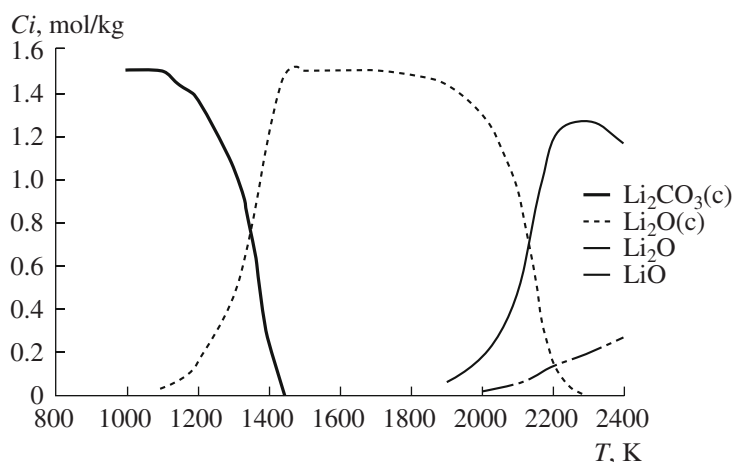


Fig. 5. Equilibrium composition of the reaction products at $P = 0.1$ MPa and when the ratio of air and Li_2CO_3 flow rates is 8 : 1.

not attained. Nevertheless, the influence of this factor on the results of experiments cannot be ignored.

Another, and apparently the main, cause of the noted disagreement is illustrated by the results of particle-size analysis of the produced powder, which was performed using a Malvern 3600E granulometer (Fig. 6). From comparison of Figs. 6 and 2, it is seen that the degree of dispersion of the reaction product differs considerably from the degree of dispersion of powdered Li_2CO_3 . Almost 90% of the product powder is smaller than $80\text{ }\mu\text{m}$, and the particle size distribution in Fig. 6 corresponds to this fraction. The mass of particles with sizes of up to $5\text{ }\mu\text{m}$ exceeds 80%. The mass fraction of particles with sizes of up to $2\text{ }\mu\text{m}$ is also large.

On the basis of the data in Figs. 6 and 2 and the results of experiments, the possible mechanism of Li_2CO_3 decomposition in a high-temperature flow of the heat carrier can be assumed. At a temperature of $T \geq 2000\text{ K}$, sublimation of the substance of particles into the external environment occurs. Probably, this substance is partially decomposed lithium carbonate. Its further reaction occurs in the gas phase. In this case,

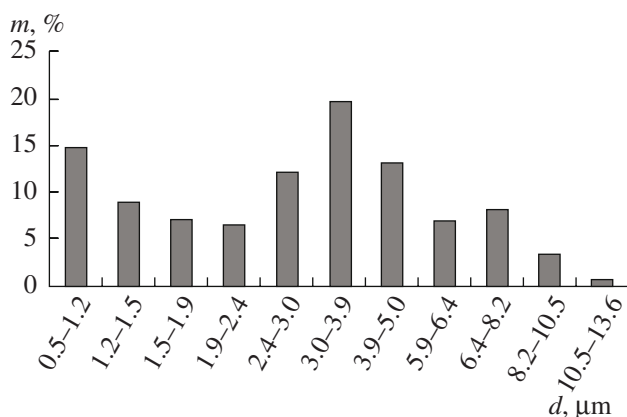


Fig. 6. Fractional composition of the reaction product.

the largest particles do not have time to react completely under conditions of the given experiments. In this context, it can be assumed that the experimental values of η are the lower limit of the actual value, since completely reacted particles are carried outside the setup, not being retained on the filter.

Since thermal decomposition of Li_2CO_3 is accompanied by CO_2 formation, it is necessary to take into account the influence of the saturation pressure P_s of carbon dioxide on the course of the process. It is known (see, for example, [2]) that, at the melting point of Li_2CO_3 , the value of P_s is 4 Torr, which prevents the achievement of a high value of lithium carbonate decomposition. With a rise in the temperature of the process, the saturation pressure of CO_2 increases and reaches 0.1 MPa at $T = 1540\text{ K}$. In our experiments, the temperature was even higher; therefore, the value of P_s did not affect the course of the process, and a high degree of conversion was achieved at atmospheric pressure in the reactor.

Thus, the main results of the study are as follows:

1. The process of high-temperature decomposition of lithium carbonate particles in the flow of the heat carrier is realized for the first time.
2. The important result of the study is the possibility of carrying out Li_2CO_3 dissociation (with a high yield of Li_2O) at atmospheric pressure in the reactor, which was established experimentally.
3. It seems that complete conversion of lithium carbonate to lithium oxide can be achieved by optimizing the design of the setup and operating parameters, which will allow this method to be realized in practice.

NOTATION

C_d —drag coefficient;

$C_{\text{Li}_2\text{O}}$ —concentration of Li_2O in the solution, g/l;

d —powder particle size, μm ;
 G —flow rate, g/s;
 m —mass percentage of the powder of the i th fraction, %;
 M —mass, g;
 p —pressure, MPa;
 T —temperature, K;
 t —time, s;
 λ —thermal conductivity, W/(m K);
 η —lithium carbonate conversion to lithium oxide;
 Re_d —Reynolds number.

SUBSCRIPTS AND SUPERSSCRIPTS

eq—equilibrium;
 m—melting;
 max—maximum;
 r—residence.

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