Problem of the lithium peroxide thermal stability

R A Nefedov¹*, Yu A Ferapontov¹ and N P Kozlova²
¹Tambov State Technical University, 106, Sovetskaya Str., Tambov, Russia
²JSC Corporation “Roskhimzashchita”, 19, Morshanskoe Highway, Tambov, Russia

*E-mail: klorik@mail.ru

Abstract. The behavior of lithium peroxide and lithium peroxide monohydrate samples under heating in atmospheric air was studied by the method of thermogravimetric analysis (TGA) and differential thermal analysis (DTA). It was found that in the temperature range of 32°С to 82°С the interaction of lithium peroxides and steam with the formation of lithium peroxide monohydrate occurs, which was confirmed chemically and by X-ray Single-qualitative analysis. It was experimentally found that lithium peroxide starts to decompose into the lithium oxide and oxygen in the temperature range of 340 ÷ 348°С. It was established that the resulting thermal decomposition of lithium oxide, lithium peroxide at the temperature of 422 °C melts with lithium carbonate eutectically. The manifestation of polymorphism was not marked(seen or noticed) under the heating of studied samples of lithium peroxide and lithium peroxide monohydrate in the temperature range of 25 °C ÷ 34 °C.

1. Introduction
Lithium peroxide (Li₂O₂) is a compound that contains 34.87% of active oxygen which is released in contact with water or steam. According to this criterion, Li₂O₂ concedes only to hydrogen peroxide and sodium superoxide from all of the peroxide compounds which are stable under normal conditions, and its stoichiometric capacity for carbon dioxide (488 l / kg) is the maximum total number used for chemisorbents in this purpose. Therefore, it is widely used as a component of chemical products applied for the regeneration of the air in the life-support systems (LSS), which is forced to work in the conditions isolated from the environment [1 - 4]. Not only detailed knowledge of the mechanisms of interaction of chemisorbents with water vapor and carbon dioxide, the main kinetic parameters of these processes, but also the knowledge of factors that may affect these parameters is required to make a right choice of chemical composition of chemisorbents, construction systems of LSS etc. Furthermore the goal of that choice is to increase the efficiency of LSS systems and create more comfortable conditions for the user. Previously mentioned factors include phase transitions, polymorphic transformations and others phenomena that occur in chemisorbents during the thermal exposure. However, there is not enough information about the problem of lithium peroxide. Moreover, any information on it is quite contradictory. Authors [5 - 6] report about the presence of irreversible exothermic effect on the DTA curve at about 225 °C, which they interpret as a polymorphic transformation of α-Li₂O₂ to β-Li₂O₂ that was accompanied by an increase in the reactivity of the sample, confirming the results of X-ray diffraction. At the same time, authors [7 - 8] did not confirm this information in later works. Therefore, it was significant scientific and practical interest to study the behavior of various samples of lithium peroxide at the thermal exposure in air, at the conditions, the occurrence of which is possible in the life - support systems.
2. Experimental part

Different samples of lithium peroxide were taken for this study. They were obtained at the temperature of 33 °C by reaction of solid lithium hydroxide and 50% hydrogen peroxide aqueous solution of “puriss. spec.” marks at a molar ratio LiOH/H2O2 = 1.85, compartment of intermediate adduct of lithium peroxide monohydrate (Li2O2·H2O) by filtration and its subsequent dehydration by heating in a muffle furnace at the temperature of 80 °C for 4 hours (sample #1), extended exposure (about three days) at a room temperature over a layer of zeolite (sample #2) [9] and dehydration in the ultra high frequency (UHF) (sample #3) [10 - 16]. Time of dehydration in the UHF was between 7 and 12 seconds, depending on the sample’s weight. In cases of dehydration of Li2O2·H2O in the UHF and thermal treatment in the muffle furnace processes were carried out in the current of dry decarbonized air in order to intensify dehydration (accompanied by an increase in the content of the target product) and prevent the formation of lithium carbonate. After exposure at the previously mentioned temperature, resulting from the interaction of the system for 2 hours required to achieve the equilibrium between the phases, solid phase (Li2O2·H2O) was separated by filtration, washed with distilled water and dried at a room temperature over a layer of adsorbent until the full removal of chemically unbound water [14, 16 - 17]. The temperature during the experiments was maintained with a water bath up to ±0.2 °C.

In order to determine the chemical composition, samples were analyzed for the content of active oxygen, lithium hydroxide and lithium carbonate. Determining the content of active oxygen, studied samples were preliminary stabilized with boric acid, followed by permanganometric titration [18]. Analyzing of the LiOH content, samples were boiled with water for 15 - 20 minutes to break down peroxide compounds, and then titrated 0.1N H2SO4 by phenolphthalein. Determination of lithium carbonate was performed by the method of Fresenius [19].

Compositions of the samples that were determined by chemical analysis and confirmed by data of X-ray qualitative diffraction are presented in Table 1. X-ray diffraction analysis was carried out on a DRON-6 with the filtered Cu Kα-radiation (λ = 1.54051 Å). Scan step 0.05°, scanning range of 20° ≤ 2θ ≤ 120°, 3 seconds exposure at each point. In addition, Table 1 shows the dispersion characteristics of the studied samples, evaluated by a specially developed method of determining particle’s size of peroxide products based on their inertial separation [20].

### Table 1. The chemical composition of the samples

| Sample number | Method of production | The median particle diameter, d<sub>m</sub>, μm | Chemical composition, wt% |
|---------------|----------------------|---------------------------------------------|---------------------------|
|               |                      | Li₂O₂ | LiOH | Li₂CO₃ | H₂O |
| 1             | thermal dehydration  | Li₂O₂·H₂O | 23.4 | 97.7 | 0.4 | 1.4 | 0.5 |
| 2             | dehydration Li₂O₂·H₂O over a dehumidifier | 23.2 | 98.0 | 0.3 | 1.3 | 0.4 |
| 3             | dehydration Li₂O₂·H₂O in the UHF | 18.7 | 97.8 | 0.3 | 1.5 | 0.4 |
| 4             | initial Li₂O₂·H₂O | 21.6 | 70.3 | 0.4 | 1.3 | 28.0 |

Thermogravimetric and differential thermal analysis of the samples was carried out under non-isothermal conditions at a research complex TAG - 24 of "Setaram" company (France). Investigated samples were of 70 ÷ 80 mg. Temperature was recorded with an accuracy of 0.01°C changes in the sample’s weight were recorded with an accuracy of 0.01 mg. Studied samples were placed in a corundum crucible. A platinum - platinum-rhodium thermocouple, placed in the volume of the tested sample and calibrated on common reference points, were used to measure the temperature. Study was
carried out in air at atmospheric pressure with a heating rate of \( 5 \div 10 \) degrees per minute. Mentioned heating rate provides the identity of temperatures throughout the whole volume of the tested sample during the experiment.

When the heating rate of the sample is less than 5 °C / min and above 12 °C / min, there is a significant deviation of the curve, changes in the temperature \( T \) from a straight line, leading to a significant error in the calculations of kinetic parameters of the studied process. This experimental fact is explained by a violation of temperatures’ equality of external and internal layers of weighted quantity of tested samples, caused by insufficient thermal conductivity of lithium peroxide and lithium peroxide monohydrate [21, 22].

3. Results and discussion
During the experiments, it was found that the nature of the TGA and DTA curves of lithium peroxide samples obtained by various methods is similar. Therefore, not to make this text complicated with the same results, we decided to report only the results of the thermal tests of sample # 3 from Table 1 (figure 1).

![Figure 1. Complex thermal analysis of Li₂O₂](image)

All the samples of lithium peroxide obtained by various methods showed exothermal effect on the DTA curves at the temperature range from of 32 °C to 82 °C accompanied by an increase in weight of the samples and related to the interaction of lithium peroxide with water vapor with the formation of lithium peroxide monohydrate. That fact was mentioned by authors [23 - 24], who studied the interaction of lithium peroxide and water vapor. To validate the assumption that was made about the nature of the exothermic effect, parent drug Li₂O₂ was heated in air at a temperature of 450 °C and a relative humidity \( \varphi = 96 \% \) for 1 hour and then exposed to qualitative XRF analysis. The appearance of new reflexes on the diffractogram (at an angle of slip \( 2 \Theta = 35.09 \) - reflex corresponding to the interplanar spacing \( d = 2.543 \ \AA \), at an angle of slip \( 2 \Theta = 30.48 \) - reflex corresponding to the interplanar spacing \( d = 2.90 \ \AA \), at an angle of slip \( 2 \Theta = 40.75 \) - reflex corresponding to the interplanar spacing \( d = 2.20 \ \AA \)) clearly indicates the appearance of a new phase composition Li₂O₂·H₂O in the tested sample [16, 25]. It should be noted that during this exothermic effect weight of samples #1 and #2 increases by approximately 1.7 %, while there is an increase in the weight of the tested sample №3 for 2.4% on the TGA curve. Peak on the DTA curve for sample №3 has more expressed nature than the peaks in the DTA curves for samples #1 and 2. This difference in the behavior of lithium peroxide samples, obtained in different ways, is due to differences in the surface area of the tested samples in other words because of the kinetics of the interaction between lithium peroxide and water vapor. Then, all Li₂O₂ samples have endothermic effect that has a maximum at a temperature of 106 °C, leading to a
decrease in the mass of the tested samples for about 2.9%. Following large endothermic effect on the DTA curves, starts at a temperature 348 °C, 344 °C and 341 °C with peaks at temperatures of 369 °C, 373 °C and 374 °C for samples № 1 - № 3, respectively. In addition, this effect is accompanied by a decrease in the weight of all tested samples by approximately 34%, corresponding to the decomposition of the lithium peroxide to lithium oxide and oxygen (stoichiometric content of active oxygen in the tested samples is about 34.6%). This assumption was confirmed by chemical and qualitative XRF analyzes that showed that original samples of lithium peroxide warmed at 390 °C (at a temperature slightly above this effect) for 3 hours contain only lithium oxide and lithium carbonate, but not the original Li₂O₂. Obtained results are in better agreement with the results of authors [7, 26], indicating the decomposition temperature lithium peroxide at 350 °C than with the results of authors [5, 6, 8], observing the beginning of decomposition of lithium at 315 °C. Finally, all tested samples clearly expressed endothermic effect on the DTA curves that has a maximum at 424 °C altogether with the corresponding eutectic melting of system Li₂O - Li₂CO₃, visually observable, that also was noted in [7 - 8].

Figure 2 shows the results of lithium peroxide monohydrate thermal analysis (sample #4).

![Complex thermal analysis of Li₂O₂·H₂O](image)

**Figure 2.** Complex thermal analysis of Li₂O₂·H₂O

During the process of lithium peroxide decomposition the mass of the tested sample is reduced by 24.1% due to the evolved oxygen (theoretical content of active oxygen in the tested sample was 24.5%). Data obtained on lithium peroxide monohydrate dehydration temperature and decomposition temperatures of lithium peroxide produced, as a result of this process, is similar to the results obtained T. A. Dobrynina [25]. However, as for samples of lithium peroxide, there are no effects on the DTA curve at the temperature range of 200 °C – 240 °C that allow argument about existence of polymorphic transformations, which contradicts with the data of the author [25]. This author registered a weak exothermic effect on the DTA curve at the temperature of 225 °C, which was interpreted as a manifestation of polymorphism - the transition α-Li₂O₂ in β-Li₂O₂. Last endothermic effect starting at 424 °C with a maximum at 436 °C corresponds to the eutectic melting of Li₂O - Li₂CO₃.

Carrying out thermal analysis in atmospheric air at the temperature range from of 25 °C to 340 °C lithium peroxide samples obtained by different ways with different chemical and dispersion composition as well as lithium peroxide monohydrate, we didn’t find data indicating the manifestation of polymorphism in the tested samples, not only due to a change in the crystal lattice, but also to the transition from a nonequilibrium state to an equilibrium. Obtained experimental results do not confirm authors [5, 6, 25], who told about the existence of two polymorphic modifications of lithium peroxide.

4. Conclusion
The behavior of lithium peroxide samples, obtained by different methods, under the heating of atmospheric air was studied by the method of thermogravimetric and differential thermal analysis. The interaction of lithium peroxide with water vapor, forming lithium peroxide monohydrate at the temperature range from 32 °C to 82 °C was confirmed by the methods of thermal, chemical and qualitative XRF analysis. It was determined that temperatures of decomposition of lithium peroxide into lithium oxide and oxygen, obtained by different ways, are at the range from 340 °C to 348 °C. It was found that the resulting thermal decomposition of lithium oxide, lithium peroxide melts with lithium carbonate eutectically at 422 °C. There were not any signs of polymorphism in all tested samples of lithium peroxide during the experiments.

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