

Thermal Analysis of Lithium Peroxide Prepared by Various Methods

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Abstract—Behavior of lithium peroxide samples at heating in air was studied by the methods of thermogravimetric analysis (TGA) and differential thermal analysis (DTA). In the temperature range from 32 to 82°C all the studied samples we found to react with water vapor forming lithium peroxide monohydrate as confirmed by the methods of chemical analysis and of qualitative X-ray phase analysis. It was found experimentally that in the temperature range from 340 to 348°C lithium peroxide began to decompose into lithium oxide and oxygen, the starting temperature depended on the method of preparation of lithium peroxide. For all the studied samples polymorphism in the temperature range from 25 to 340°C was not detected.

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Lithium peroxide (Li_2O_2) is a compound whose composition includes 34.87% of active oxygen that is liberated in the reaction with water vapor or carbon dioxide. By the content of active oxygen, that is, the oxygen that could be liberated in the course of chemical processes, Li_2O_2 is more rich than any other compound stable under ambient conditions, except hydrogen peroxide and sodium superperoxide, and its stoichiometric capacity on carbon dioxide (488 l kg^{-1}) is maximal in the series of all chemisorbents used for the carbon dioxide conversion. Therefore lithium peroxide is used widely enough as a component of chemical compositions of the systems of human survival (HSS) when people should exist and work isolated from external environment [1–3]. For a proper choice of chemical composition of chemisorbents in designing the HSS systems, increasing the HSS performance and creation of more comfortable conditions for the users of the system not only detailed knowledge is needed of the reaction of these chemisorbents with water vapor and carbon dioxide, but also of the basic kinetic parameters of these processes and factors that can affect these parameters. A scope of such factors embrace phase transitions, polymorphic transformations, and other phenomena proceeding in chemisorbents at heating. However, for lithium peroxide there are no sufficient data in literature concerning this problem while the published

data are fairly contradictory. In [4, 5] had been reported on irreversible exothermic effect on the DTA curve at the temperature near 225°C that had been considered as polymorphic transformation of $\alpha\text{-Li}_2\text{O}_2$ into $\beta\text{-Li}_2\text{O}_2$ with increase in reactivity of the sample, and this conclusion had been confirmed by the data of X-ray phase analysis, but in more recent publications [6, 7] this was not confirmed.

Therefore it is significant from scientific and practical viewpoints to explore behavior of various samples of lithium peroxide exposed to heating in air, that is, under conditions that can appear at the application of human survival systems.

In the course of the experiments we established that TGA and DTA curves are of the same character for all samples of lithium peroxide, therefore Fig. 1 shows the results of thermal study for one sample (no. 3, see the table).

In all samples of lithium peroxide obtained by different procedures on the DT curves in the range from 32 to 82°C an exothermic effect was observed with simultaneous increase in weight that was assigned to the reaction of lithium peroxide with water vapor leading to the formation of lithium peroxide monohydrate, as had been mentioned in [8, 9] where the reaction between lithium peroxide and water vapor had been studied. To verify the validity of our assumption concerning the nature of the exothermic

Chemical composition of studied samples^a

Sample no.	Method of preparation	Average particle diameter d_m , μm	Chemical composition, wt %			
			Li_2O_2	LiOH	Li_2CO_3	H_2O
1	Thermal dehydration of $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$	23.4	97.7	0.4	1.4	0.5
2	Dehydration of $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$ over dryer	23.2	98.0	0.3	1.3	0.4
3	Dehydration of $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$ in superhigh frequency field	18.7	97.8	0.3	1.5	0.4
4	Parent $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$	–	70.3	0.4	1.3	28.0

^aDispersion characteristics of lithium peroxide monohydrate were not measured.

effect we heated the initial sample of Li_2O_2 in air to 45°C at the relative humidity $\varphi = 96\%$ for 1 h and then the sample was examined by qualitative X-ray phase analysis. The appearance in the diffractogram of new reflexes (at sliding angle $2\theta = 35.09^\circ$, the reflex corresponding to interplane distance $d = 2.543 \text{ \AA}$, at sliding angle $2\theta = 30.48^\circ$, the reflex corresponding to interplane distance $d = 2.90 \text{ \AA}$, and at sliding angle $2\theta = 40.75^\circ$, the reflex corresponding to interplane distance $d = 2.20 \text{ \AA}$) proves undoubtedly the appearance in the studied sample of a new phase with the composition $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$ [14, 20]. Note that in the time when this exothermic effect was observed the weights of samples no. 1 and no. 2 increased by approximately 1.7 %, while for the sample no. 3 on TGA curve increase in weight by 2.4 % was seen and a more pronounced peak on DTA curve. This difference in behavior of the samples of lithium peroxide prepared by different methods was attributable to the difference in the surface area of the samples, that is, to the kinetics of the process of lithium peroxide interaction with water vapor. Then for all Li_2O_2 samples an endothermic

effect occurs with the maximum at 106°C that leads to a decrease in the sample weight approximately by 2.9%. This effect corresponds to the dehydration of the samples. The following large endothermic effect on the DTA curves started at the temperatures 348, 344, and 341°C and had maxima at 369, 373, and 374°C for the samples nos. 1–3 respectively and was accompanied by the weight decrease by approximately 34%. These effects correspond to decomposition of lithium peroxide into lithium oxide and oxygen (stoichiometric content of active oxygen in the studied samples was approximately 34.6%). This assumption is confirmed by chemical analysis and qualitative X-ray phase analysis showing that the samples of lithium peroxide after heating at 390°C (that is, at the temperature slightly above the considered effect) for 3 h contained only lithium oxide and carbonate while the parent Li_2O_2 was totally absent. The results obtained are in better agreement with the results of [6, 12] where the temperature of the start of lithium peroxide decomposition was reported as 350°C rather than with the results published in [4, 5, 7] where the beginning of decomposition of lithium peroxide was registered at 315°C . Finally, on all DTA curves of the studied samples was clearly seen an endothermic effect with a maximum at 424°C that corresponded to eutectic melting of $\text{Li}_2\text{O} - \text{Li}_2\text{CO}_3$ system observable visually, that also was noted in [6, 7].

Thermal analysis of lithium peroxide monohydrate (sample no. 4) is shown in Fig. 2.

The DTA curve shows three endothermic effects, two of which with decrease in weight. The first effect beginning at 92°C with maximum at 105°C and accompanied with the sample weight loss by 27.6% corresponded to the dehydration of this compound (theoretical water content in the sample was 28.0%).

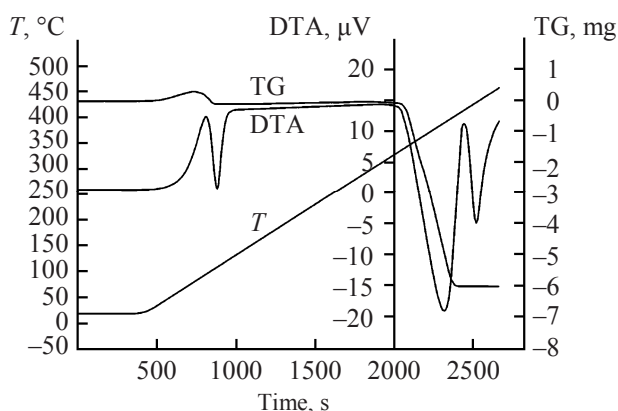


Fig. 1. Complex thermal analysis of Li_2O_2 .

The second endothermic effect beginning at 340°C with a maximum at 374°C corresponded to the decomposition of Li_2O_2 formed after dehydration of $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$. At the decomposition the sample weight loss was 24.1% due to the evolution of oxygen from the peroxide (theoretical content of active oxygen in the studied sample was 24.5%). The data obtained on the temperatures of lithium peroxide monohydrate dehydration and dehydrated lithium peroxide decomposition are consistent with the results in [11]. However, like the case of the samples of lithium peroxide, on the DTA curve are absent effects in the range 200–240°C that should suggest the occurrence of polymorphous transformations. This fact contradicts to the data of [11] where on the DTA curve a weak exothermic effect has been registered at 225°C that was interpreted as revealing polymorphism, that is, transformation of $\alpha\text{-Li}_2\text{O}_2$ into $\beta\text{-Li}_2\text{O}_2$. The last endothermic effects that begins at 424°C and shows a maximum at 436°C corresponds to the melting of $\text{Li}_2\text{O}\text{-Li}_2\text{CO}_3$ eutectic.

While performing the thermal analysis in air in the temperature range from 25 to 340°C on the lithium peroxide samples prepared by different methods, with different chemical and dispersion compositions, and on lithium peroxide monohydrate we did not find any data indicating polymorphism in the studied samples either due to the change in the crystal lattice or due to the transition from non-equilibrium state to the equilibrium one. The experimental results obtained by us do not confirm reports [4, 5, 11] about existence of lithium peroxide in two polymorphic states.

EXPERIMENTAL

For examination were taken various samples of lithium peroxide formed in the reaction at 33°C of solid lithium hydroxide and 50% aqueous hydrogen peroxide at the molar ratio $\text{LiOH}/\text{H}_2\text{O}_2 = 1.85$. The intermediate adduct, lithium peroxide monohydrate ($\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$) was isolated by filtration and then it was dehydrated either by heating in a muffle furnace at 80°C for 4 h (sample no. 1), or by prolonged exposure (ca. 3 days) at room temperature over zeolite layer (sample no. 2) or by exposure to a superhigh frequency field for 7 to 12 s depending on the sample weight (sample no. 3) [8–14]. To avoid formation of lithium carbide at the dehydration of $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$ in superhigh frequency field or in muffle furnace the process was carried out in the flow of dry and decarbonized air. Besides, we explored behavior of lithium peroxide

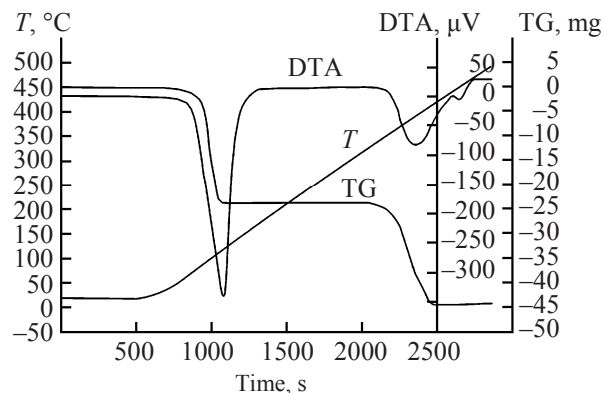


Fig. 2. Complex thermal analysis of $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}$.

monohydrate at the thermal exposure (sample no. 4). Compositions of the examined samples determined by the chemical analysis [15–21] and confirmed by the data of qualitative X-ray phase analysis are shown in the table. The X-ray phase analysis was carried out on a DRON-5 diffractometer with filtered $\text{CuK}\alpha$ -radiation ($\lambda = 1.54051 \text{ \AA}$). Scan increment 0.05° , scan range $20^\circ \leq 2\theta \leq 120^\circ$, exposition 3 sec in each point. The table also contains dispersion characteristics of the examined samples estimated by means of specially developed method of measuring particle size of the peroxide substances based on their inertial separation [17].

Thermogravimetry and differential thermal analysis of the samples were carried out under nonisothermal conditions on an instrumental complex TAG-24 of “Setaram” company (France). For the investigation were taken samples with the weight $\sim 30 \text{ mg}$. Temperature was registered with an accuracy 0.01°C , change in the sample weight was measured with an accuracy 0.01 mg. The examined samples were placed in a corundum crucible. The measurements were carried out in air at ordinary pressure, heating rate 5 degrees per minute. Temperature was measured by platinum–platinum–rhodium thermocouple that has been graduated on the commonly used reference points.

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