Mechanochemical Synthesis of Superfine Lithium Gamma-Monoaluminate

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Abstract

An influence of the conditions of the mechanical activation of aluminium hydroxide and lithium carbonate mixture in the planetary type activator APF and of the conditions of subsequent thermal treatment upon the phase composition, morphology and dispersity level of lithium gamma-monoaluminate (γ–LiAlO$_2$) is considered. Potentialities are demonstrated concerning the use of the γ–LiAlO$_2$ synthesized for obtaining the matrix electrolyte for a fuel element with molten carbonate electrolyte as well as within a separator for thermal lithium batteries.

Key words: mechanical activation, aluminium hydroxide, lithium carbonate, lithium gamma-monoaluminate, fuel element with molten carbonate electrolyte

INTRODUCTION

Superfine lithium gamma-monoaluminate, γ-LiAlO$_2$, is used as a material for producing tritium [1], as a component in the composition of matrix electrolyte for a fuel cell with molten carbonate electrolyte [2], as a separator material in thermal lithium batteries, as well as for modifying the conduction of lithium polymeric electrolytes [3]. The most known methods of synthesizing γ-LiAlO$_2$ are presented by a ceramic-based method [4, 5] and a sol-gel technique [6–9]. The ceramic method is easy to realize, however the γ-LiAlO$_2$ formed often has a low specific surface area insufficient for using the material in the aluminate electrolyte matrix. The sol-gel technique allows one to obtain γ-LiAlO$_2$ with a sufficiently high (510 m^2/g) surface area; however, this method involves expensive synthetic organic compounds of aluminium and lithium. Moreover, the sol-gel method is rather complicated in realization, being at the same time not environmentally safe. In this respect, the development of novel, technologically simple and environmentally safe methods

for the synthesis of superfine lithium gamma-monoaluminate is of undoubted interest.

The authors of [10, 11] demonstrated the potentiality of synthesizing superfine γ-LiAlO$_2$ by means of the mechanical activation of lithium carbonate and aluminium trihydroxide mixture of in a laboratory planetary type activator AGO-2 with the subsequent heat treatment of the activation products in ambient air.

The aim of the present work consisted in revealing the potentialities and conditions for the mechanochemical synthesis of superfine lithium gamma-monoaluminate using enlarged mechanochemical activators, as well as determining the possibility of using it in order to obtain a matrix electrolyte for fuel cells and as a separator material in thermal batteries.

EXPERIMENTAL

As starting substances, we used pure grade lithium carbonate and aluminium trihydroxide (gibbsite). The activation was carried out with the use of an APF planetary type activator (de-

veloped at the ISSCM of the SB RAS, Novosibirsk). The capacity of cylinders was equal to 600 mL, the number of cylinders being 4 pcs; the activation time ranged from 3 to 10 min, the mass of ball load in the experiments amounted to 500 g, the weighed sample portion was equal to 50 g, the diameter of steel balls being of 8 mm.

The heat treatment of the mechanically activated mixture was carried out in ambient air within the temperature range of 700–900 °C. In order to study the products formed by means of mechanochemical synthesis we used the methods of XRD, TGA and DSC. For structural and morphological characterizing the synthesized lithium gamma-monoaluminate we used XRD phase analysis, measured the specific surface area, investigated the particle size distribution. The XRD profiles were registered with the use of a DRON-4 diffractometer at a rate of 2°/min within the angle range $2\theta = 10$–60°, CuK$_\alpha$ radiation. The XRD profiles were processed with the use of a Microcal Origin 6.0 package. For studying the microstructure of lithium aluminate we determined the size of coherent scattering regions (CSR) and the level of microdeformation using Powder Cell-2.4 software. For the calculation, we used XRD profiles registered at a rate of 1°/min. The specific surface area of the samples was measured according to the BET method in the course of nitrogen thermal desorption employing a Sorbtometer unit (Katakon Co., Russia). The thermal analysis was performed using an STS 449S Jupiter derivatograph (Netzsch, Germany), an air atmosphere, the heating rate amounting to 10 °C/min. For measuring the dispersion level of lithium monoaluminate we used a Microsizer 201A laser particle dispersiometer (Russia); as a dispersion medium we chose ethyl alcohol.

RESULTS AND DISCUSSION

Synthesis of lithium gamma-monoaluminate

The mechanical treatment of the mixture of aluminium hydroxide and lithium carbonate during 3 min results in a significant decrease of the intensity of aluminium trihydroxide reflexes, whereas the intensity of lithium car-
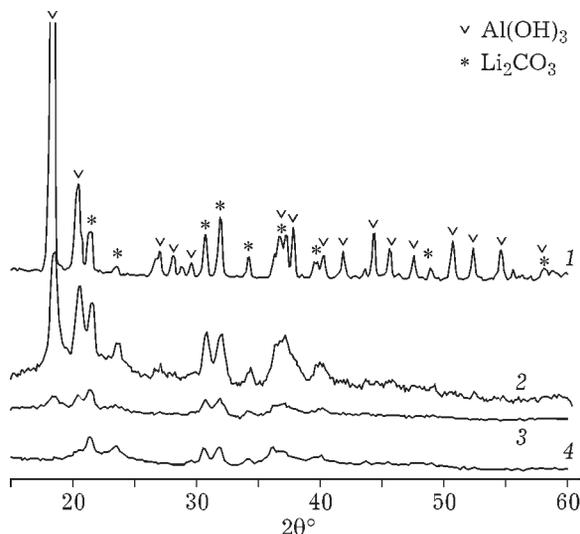
Fig. 1. XRD profiles for the products of the mechanical activation of mixture Al(OH)$_3$ + Li$_2$CO$_3$ at different values of the activation time in the APF activator, min: 0 (*1*), 3 (*2*) 5 (*3*), 10 (*4*).

bonate reflexes remain intact. The increase in the activation time up to 5 min promotes further reducing the intensity of aluminium hydroxide reflexes, as well as a significant decrease in the intensity of lithium carbonate reflexes (Fig. 1). The activation during 10 min results in almost complete disappearance of all the aluminium trihydroxide reflexes against the background of remaining some reflexes of lithium carbonate.

The DTA curve (Fig. 2) for the mixture mechanically activated during 5 min exhibit two
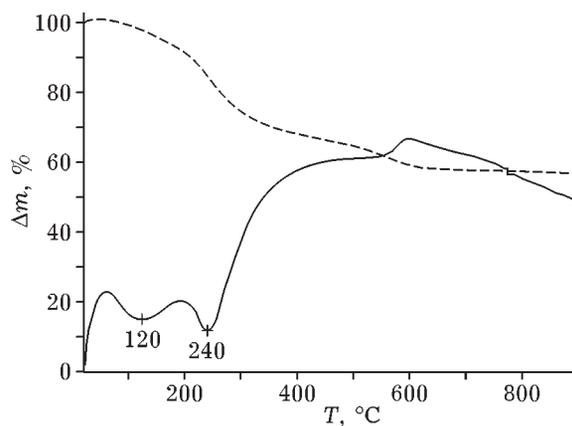
Fig. 2. Thermal analysis data for the mixture of lithium carbonate and aluminum hydroxide mechanically activated time in the APF activator during 5 min. Registration conditions: speed 10 °C/min, atmospheric air, weighed sample portion 20 mg.

pronounced endothermic effects at 80−180 and 220−280 °C. The first endothermic effect with a maximum at about 120 °C could be associated with removing the molecular water formed in the course of the mechanical activation of aluminium hydroxide. The mass loss at this stage is equal to about 10 %, which corresponds to the removal of approximately 1.3 H_2O molecules from the mixture with the composition of $2Al(OH)_3 + Li_2CO_3$. The second endothermic effect could be connected primarily with the dehydration hydroxo groups. The further mass loss at higher temperature values can be caused by the evolution of carbon dioxide due to the decomposition of lithium carbonate and lithium aluminate formation.

An effect of activation time on the phase composition of the products formed after the heat treatment of mechanically activated mixture aluminium hydroxide and lithium carbonate was investigated (Fig. 3). The heat treatment of an inactivated mixture during 4 h at 800 °C resulted in the formation of a product containing, a significant amount of α-modification of lithium monoaluminate alongside with the lithium γ-monoaluminate. The mechanical pre-treatment of the mixture during 3 min results in a significant decrease of the content of the α-modification. Finally, increasing the
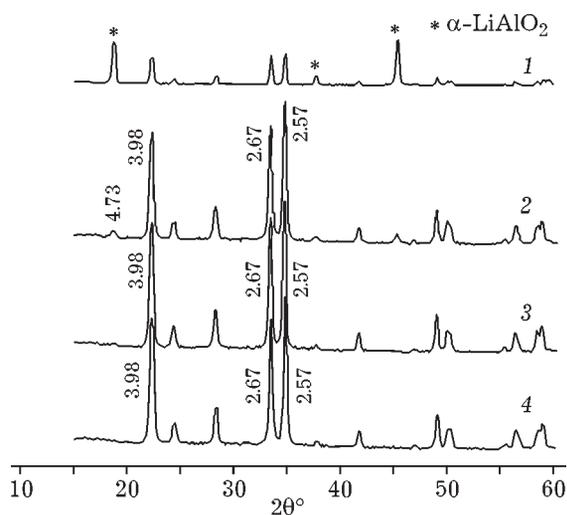
Fig. 4. XRD profiles for aluminum hydroxide and lithium carbonate mixture mechanically activated for 5 min: 1 − heated up to 850 °C, 2−4 heated and held at 850 °C during 1, 2 and 4 h, respectively.

activation time up to 5−10 min promotes the formation of nearly single-phase γ-$LiAlO_2$.

The investigation of influencing the heat treatment activation time upon the phase composition demonstrated that heating the mixture activated during 5 min up to 850 °C under the experimental conditions results in the formation of a product containing a small amount of α-modification (Fig. 4). In the case when the mixture being held at this temperature during 1 h one can observe an almost complete disappearance of reflexes inherent in γ-$LiAlO_2$. The further increase in the time of heat treatment exerts an insignificant effect on the character of the diffraction pattern.

The investigation of the influence of the process allowed us to determine the optimum conditions of heat treatment in the course of the synthesis of single-phase γ-$LiAlO_2$: the process temperature ranging within 825−850 °C, the duration being of 2−4 h.

In order to describe the morphological characteristics of the lithium gamma-monoaluminate synthesized we determined the size of CSR and microdeformation values for the samples synthesized under different conditions (Table 1). It can be seen that the CSR size increases, whereas the microdeformation values exhibit an increase with increasing the calcination time and the temperature of heat treatment. The results obtained indicate that there is the crystallization of the product occurring. Increasing the crystallite size results in a de-

Fig. 3. Effect of activation time on the phase composition of the products of calcining the aluminum hydroxide and lithium carbonate mixture. The duration of activation, min: 0 (1) 3 (2) 5 (3), 10 (4); reflexes not marked with symbol * belong to to γ-$LiAlO_2$; heat treatment conditions: temperature 800 °C during 4 h.

TABLE 1

Effect of heat treatment time and temperature on the size of coherent scattering region (CSR) and microdeformation level for the samples of lithium gamma-monoaluminate obtained under different conditions (activation time equal to 5 min)

Sample No.	T, °C	Time, h	CSR size, nm	Microstress level, %	Specific surface area of the sample, m^2/g (particle size, nm)
1	850	4	33	0.155	13 (180)
2	850	2	31	0.15	16 (150)
3	850	1	27	0.12	18 (130)
4	875	4	38	0.16	12 (195)
5	850	4	33	0.155	13 (180)
6	825	4	29	0.14	17 (140)

crease of the specific surface area of the solid phase. Table 1 demonstrates the particle size determined with the use of data concerning the specific surface area according to formula $D = 6/(\rho S)$, where ρ is the density of lithium gamma-monoaluminate equal to 2.56 g/cm^3; S is the specific surface area.

The comparative analysis of the results obtained demonstrated that the particle size D is approximately 5–5.5 times greater than the size of the CSR. Assuming that the aluminate particles are isometric, an average statistical particle with the size equal to D contains hundreds of crystallites. Data concerning the dispersity of γ-LiAlO$_2$ determined by laser light scattering demonstrate that the submicron particles form aggregates with a size ranging within 0.5–250 μm (Fig. 5).
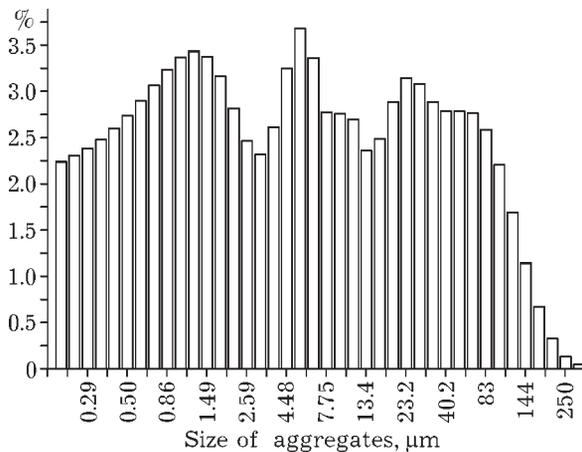
Fig. 5. Dispersity (particle size) distribution for γ-LiAlO$_2$ as determined by means of laser light scattering.

Studies on the possibility of using mechanochemically synthesized superfine lithium gamma-monoaluminate in electrochemical energy engineering

Testing the superfine lithium gamma-monoaluminate for obtaining a matrix electrolyte for fuel cells with molten carbonate electrolyte was performed at the laboratory of chemical current sources of the IHTE of the UrB RAS [12]. In the course of testing one perfected the conditions for obtaining a matrix electrolyte and the mode of technological launching the battery of cells as well as there was resource testing performed (300 h) for three three-cell batteries. All the current-voltage characteristics of the elements of batteries in the course of the testing procedure are linear, *i. e.*, no depletion of the electrode is observed to occur. One measured voltage changes across the cells depending on the time of operation. The cell voltage gradually decreases and reaches a plateau, whose level does not fall below 700–720 mV at the current density of 100 mA/cm^2, even after the operation time greater than 280 h. The data obtained indicate that the γ-LiAlO$_2$ synthesized with the use of mechanochemistry is suitable for producing a matrix electrolyte for carbonate fuel cells. The use of the material allows one to make batteries with a high power density.

The lithium gamma-monoaluminate synthesized was also tested at Uralelement JSC in the structure of a thermal battery separator. The separator was composed of a mixture of low melting point lithium halides (chloride, bromide and fluoride) and a thickener. As the thicken-

er, a powder of γ-LiAlO$_2$ was used. The cells were placed in a furnace and discharged at the temperature values ranging within $450-650$ °C during $22-23$ min. The strength of the discharge current was equal to 5 A, the discharge voltage was varied within the range from 0 to 2.5 V. The result of the test was considered positive in case that the operating time of the cell amounted to at least 13 min at a voltage of not less than 1.25 V. The data obtained indicate the possibility of using lithium gamma-monoaluminate as a separator for thermal batteries.

CONCLUSION

In the course of the study we determined the optimal conditions of the mechanochemical synthesis of superfine lithium gamma-monoaluminate with the use of a laboratory-scale planetary type activator APF. The specific surface area of the lithium gamma-monoaluminate obtained is higher than 10 m^2/g. It can be used in order to obtain a matrix electrolyte for carbonate fuel cells, as well as a separator material in thermal lithium batteries. The mechanochemical method of synthesizing γ-LiAlO$_2$

is advantageous due to a low cost of starting reagents used for the process, the process simplicity and environmental safety.

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