Mechanically Stimulated Thermal Synthesis of Highly Dispersed α-LiAlO$_2$ from Gibbsite and Lithium Carbonate

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Abstract

It was shown that mechanochemical activation of a mixture of gibbsite and lithium carbonate in a ball mill for 2–4 h, followed by heat treatment of activation products in air at 650 °C, allowed obtaining highly dispersed monophasic α-LiAlO$_2$ with a specific surface area more than 10 m^2/g.

Key words: mechanical activation, gibbsite, aluminium hydroxide, lithium carbonate, mechanochemical synthesis, alpha-lithium monoaluminate

INTRODUCTION

Highly dispersed nanostructured lithium monoaluminates (α, γ-LiAlO$_2$) are used in electrochemical power engineering as a component of matrix electrolyte in fuel elements (FE) based on carbonate melts [1]. At the early stages of the development of FE, the widest application was won by the high-temperature γ-form of lithium monoaluminate, which is used at present in electrochemical devices manufactured by Fuel Cell Energy company (USA) [2]. It was demonstrated during long-term (several thousand hours) tests that at the temperature of FE operation (650 °C) the phase transition of the high-temperature modification into its low-temperature form (α-LiAlO$_2$) occurs, and this has a negative effect on the operation of electrochemical devices. Because of this, publications dealing with FE with electrolytes composed of carbonate melt actively discuss the question concerning replacement of γ-LiAlO$_2$ in the matrix electrolyte with α-LiAlO$_2$ [3]. Along with traditional ceramic [4, 5] and sol-gel [6, 7]

methods of the synthesis of these compounds, possessing a number of substantial disadvantages, new approaches are developing. Among them, mechanochemical method attracts attention. For example, in [8] a mixture of gibbsite and lithium carbonate was ground in a ball mill in the aqueous medium for 3 h, and then dried at 110 °C for 1 day. Then the dried mixture was annealed in the air for 24 h at a temperature from 600 to 800 °C. The products formed at 600 and 700 °C contained monophase α-LiAlO$_2$ with specific surface area 9–11 m^2/g. A substantial disadvantage of the proposed synthesis method is the necessity of long-term drying of the pulp and thermal treatment of the products of drying. Another route of synthesis is connected with preliminary mechanical activation of a mixture of reagents followed by the thermal treatment of activation products in the air. Thus, it was demonstrated in [9] that mechanical activation of a mixture of gibbsite and lithium carbonate in a planetary activator AGO-2 with the centrifugal acceleration of 10g and subsequent thermal treatment of the

activation products within a temperature range from 650 to 700 °C allow obtaining monophase α-LiAlO$_2$ with specific surface area above 10 m^2/g. The low value of the centrifugal acceleration provides the possibility to use activators of other types to synthesize highly dispersed α-LiAlO$_2$. These activator types include ball mills which may be scaled up, unlike planetary activators.

The goal of the present work was to reveal the possibility and conditions for the synthesis of highly dispersed α-LiAlO$_2$ by means of mechanical activation of a mixture of gibbsite and lithium carbonate in a laboratory ball mill, followed by thermal treatment of the mechanically treated mixture in the air, and to study the processes at different stages of this synthesis.

EXPERIMENTAL

Crystal aluminium trihydroxide (gibbsite) of the analytical grade and lithium carbonate of the chemically pure grade were used in the experiment. Initial reagents were mixed at a molar ratio of 2 : 1, which is necessary to obtain α-LiAlO$_2$. Mechanical treatment of the mixture was carried out in a laboratory ball mill. Activation was carried out in porcelain cylinders with a volume of 1 L using porcelain balls 15 mm in diameter by means of the angular rotation of the cylinders at the frequency of 120 r.p.m. The mass of the ball load was 500 g, the mass of the mixture was 50 g. Activation time was varied from 1 to 8 h.

To synthesize lithium aluminate, mechanically activated mixture was heated under isothermal exposure in the air in a SNOL muffle furnace with the heating rate 10 °C/min to the necessary temperature, and then kept at this temperature for the required time.

The products formed after mechanical activation of the mixture of initial reagents and their thermal treatment were examined by means of X-ray phase analysis (XPA), *in situ* XPA, thermogravimetric (TG) analysis, mass spectrometry, and measurement of the specific surface area and size of particles.

Phase analysis of mechanically activated samples and the products formed after their thermal treatment was carried out with a D8 Advance diffractometer (Bruker, Germany, CuK_α-radiation). The degree of gibbsite amorphization A in the activated mixture was determined using the equation:

$$A = 100\ \% \times (I_0 - I_t)/I_0$$

where I_0 is the integral intensity of a selected reflection of gibbsite in the mixture before acti-

vation; I_t is the integral intensity of this reflection after activation of the mixture for time t (in min).

For high-temperature *in situ* investigations, a D8 Advance diffractometer was used. Sample heating was carried out in an HTK 1200N chamber (Anton Paar, Austria) in the air, stepwise, with the heating rate of 12 °C/min. Reaching 100, 200, 300, 400, 500, 600, 700, 800 °C, heating was stopped, and Z-ray diffraction patterns were recorded. To describe the changes of the phase composition of the initial and mechanically activated mixtures during heating, we measured the integral intensity of the reflections of gibbsite (112), lithium carbonate (110), and the products formed during the interaction: boehmite (020), α-LiAlO$_2$ (003) and γ-LiAlO$_2$ (101). The most intense reflections of γ-Al$_2$O$_3$ and χ-Al$_2$O$_3$, formed during the decomposition of gibbsite, overlap with the reflections of α-LiAlO$_2$ and lithium carbonate, so the measurements of their integral intensity were not carried out.

Thermogravimetric analysis was carried out using a modified derivatograph of the system of F. Paulic, I. Paulic and E. Erday in the air within the temperature range 10−800 °C using corundum crucibles, with the heating rate of 10 °C/min. The mass of each portion under investigation was 100 mg. In addition, gas evolution processes were analyzed with the instrument for synchronous thermal analysis STA 449 F1 Jupiter, associated with a quadrupole mass spectrometer QMS 403C Aeolos. The studies were carried out in argon flow (99.995 %) at a volume rate of 50 mL/min. Calorimetric measurements were carried out with a thermal flow calorimeter DSC 200 F3 Maia. A weighted portion of the sample 30−50 mg was placed in the cell, evacuated with a roughing-down pump to the pressure of 1 Pa, and then argon was passed. The heating rate was 10 °C/min.

The specific surface area of the activated samples and the products of thermal treatment was measured by means of argon desorption using a standard sample of specific surface area. Dispersion was measured with a laser meter of particle size Mikrosaizer-201A using ethanol as the dispersing medium.

RESULTS AND DISCUSSION

Mechanical activation of the mixture of gibbsite and lithium carbonate

Mechanical activation of the mixture leads to an increase in the specific surface area, which is practically linearly dependent on the time of me-
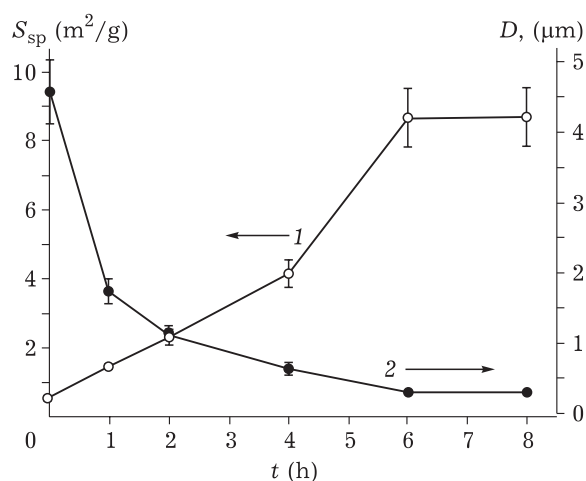
Fig. 1. Dependence of the specific surface area of the mixture of gibbsite and lithium carbonate (*1*) and average particle size (*2*) on the time of mechanical activation.

chanical activation reaching 9 m²/g after activation for 8 h (Fig. 1). The average size D of particles in the mixture, determined from the specific surface area using equation $D = 6/\rho S$, where ρ is the average density of the mixture (2.3 g/cm³), and S is the specific surface area of the mixture after activation, decreases from microns (4.5 μm) to the submicron size (0.3 μm). In the initial mixture of gibbsite and lithium carbonate, rather coarse particles with the size from 30 to 130 μm prevail; the maximum of their size distribution is about 70 μm, which relates both to gibbsite and to lithium carbonate (Fig. 2). Mechanical activation for 1 h causes a substantial decrease in the fraction of coarse particles and the rise of poly-

disperse distribution with the maxima at 5, 12, 22 and 40 μm. With an increase in the time of mechanical treatment to 4 h, a decrease in the fraction of particles with the size larger than 20 μm, and an increase in the fraction of particles with the size less than 10 μm. Finally, activation for 8 h is accompanied by the processes of aggregation of small particles. This is confirmed by an increase in the fraction of particles larger than 40 μm, and by the appearance of larger aggregates with the maximum around 100 μm. So, mechanical treatment involves not only dispersing of the initial reagents with the formation of submicron particles but also the formation of aggregates with a micron size and larger.

Mechanical activation leads not only to dispersing and aggregation of the components but also to an increase in the width of gibbsite and lithium carbonate reflections and a decrease in the integral intensity of these reflections (Fig. 3). Formation of new phases is not observed. Reflection broadening is the evidence of a decrease in crystallite size an increase in microdeformation in gibbsite and lithium carbonate. A decrease in the integral intensity of reflections may be connected with amorphization of gibbsite and lithium carbonate. The degree of gibbsite amorphization increases with an increase in activation time and may be described with a linear function of time with the correlation coefficient close to 0.96 (Fig. 4). Comparative analysis of the changes in specific surface area and amorphization degree shows that an increase in the specific surface area of the mixture by 1 m²/g is accompanied by an increase in
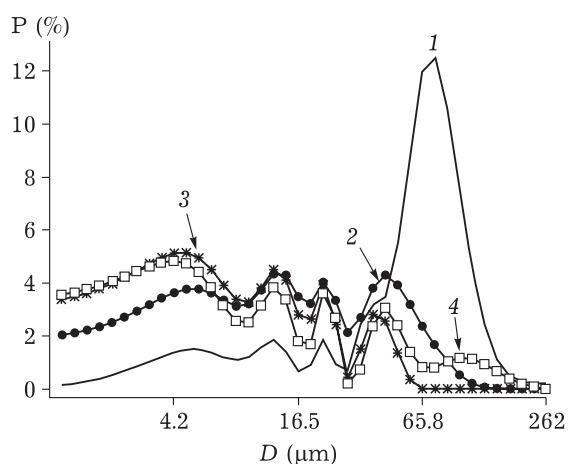

Fig. 2. Effect of the time of activation of the mixture of aluminium hydroxide and lithium carbonate in the ball mill on particle size distribution (P). Activation time (hours): 0 (*1*); 1 (*2*); 4 (*3*); 8 (*4*).
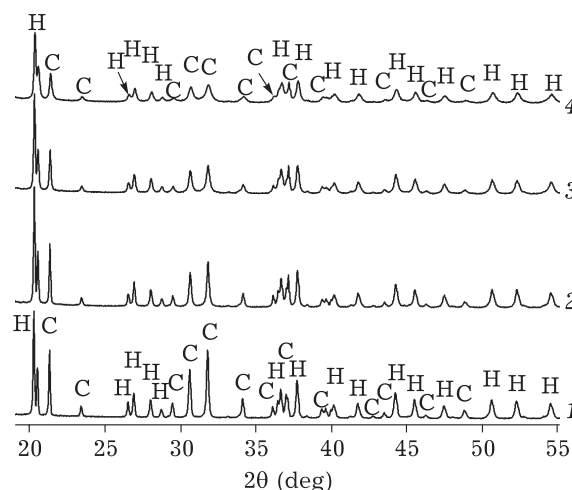

Fig. 3. X-ray diffraction patterns of initial mixture of aluminium hydroxide and lithium carbonate (*1*) and the products of its activation for different time, h: 1 (*2*); 4 (*3*); 8 (*4*). Reflections: H − Al(OH)₃, C − Li₂CO₃.
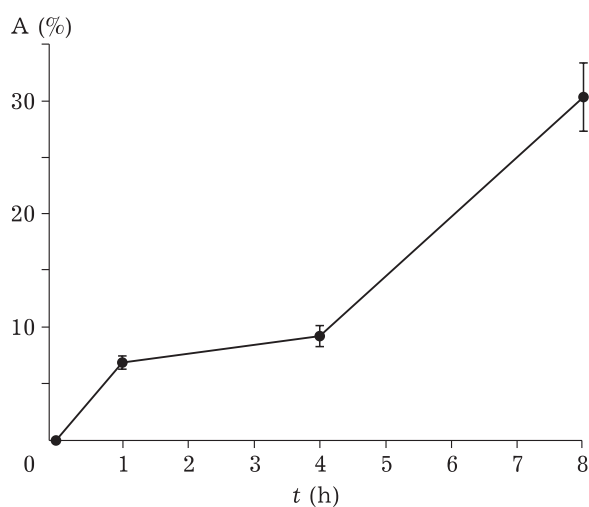
Fig. 4. Dependence of gibbsite amorphization degree on the time of the mechanical activation of the mixture.

gibbsite amorphization degree by about 3 %. So, mechanical activation in the ball mill under the experimental conditions causes both the changes of the nature of particle size distribution and amorphization.

Effect of mechanical activation on the interaction of gibbsite with lithium carbonate in the mixture under heating

Thermogravimetric analysis of the initial mixture showed that three temperature regions may be distinguished on the TG curve: 220−350, 350−550 and above 550 °C (Fig. 5). According to the data of mass spectrometry and XPA *in situ* for the first region (Fig. 6 and Fig. 7, *a*), gibbsite de-
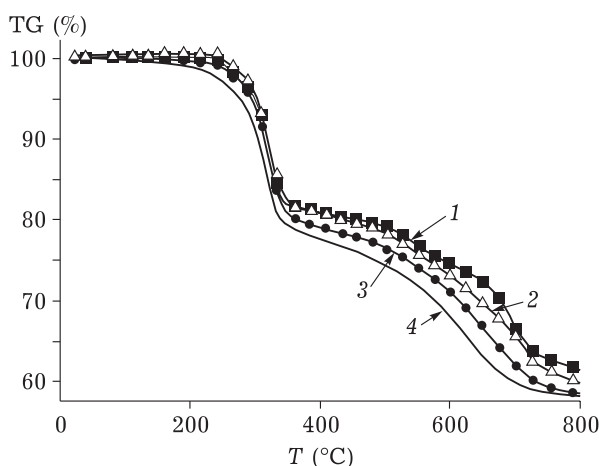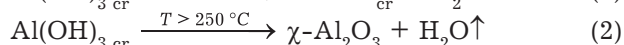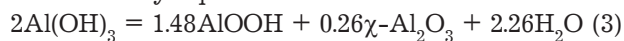
hydration and the formation of a mixture of boehmite and χ-Al_2O_3 proceed:

$$Al(OH)_{3\,cr} \xrightarrow{T > 220\,°C} AlOOH_{cr} + H_2O\uparrow \qquad (1)$$

$$Al(OH)_{3\,cr} \xrightarrow{T > 250\,°C} \chi\text{-}Al_2O_3 + H_2O\uparrow \qquad (2)$$

Relying on the data on mass loss, gibbsite decomposition as a result of heating to 350 °C may be described by equation:

$$2Al(OH)_3 = 1.48AlOOH + 0.26\chi\text{-}Al_2O_3 + 2.26H_2O \qquad (3)$$

Within the temperature range from 450 to 550 °C, boehmite decomposition and the formation of γ-Al_2O_3 proceed according to equation

$$1.48AlOOH_{cr} = 0.74\gamma\text{-}Al_2O_3 + 0.74H_2O\uparrow \qquad (4)$$
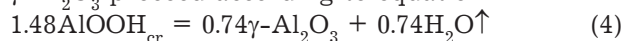
Finally, mass loss within the range 550−800 °C is connected with the interaction of γ-Al_2O_3 and χ-Al_2O_3 with lithium carbonate and the formation of α-$LiAlO_2$ according to equations:

$$\gamma\text{-}Al_2O_3 + Li_2CO_3 = 2LiAlO_2 + CO_2 \qquad (5)$$

$$\chi\text{-}Al_2O_3 + Li_2CO_3 = 2LiAlO_2 + CO_2 \qquad (6)$$

The sample mass loss as a result of heating to 800 °C is smaller than the mass loss corresponding to the formation of $LiAlO_2$ from gibbsite and lithium carbonate. Therefore, the interaction between the reagents under experimental conditions proceeds not completely.

Mechanical activation of the mixture for 1 h has a relatively weak effect on the profile of the TG curve, especially in the low-temperature region. An increase in activation time to 4 h leads to a decrease in the temperature of the start of gibbsite dehydration from 220 to 100 °C, and to a monotonous shift of TG curves within the whole temperature range, increasing with an increase in activation time to 8 h (see Fig. 5). A decrease in the temperature of the start of gibbsite dehydra-

Fig. 5. Thermograms of initial mixture of gibbsite and lithium carbonate (*1*) and products of its mechanical activation for different time, h: 1 (*2*); 4 (*3*); 8 (*4*).
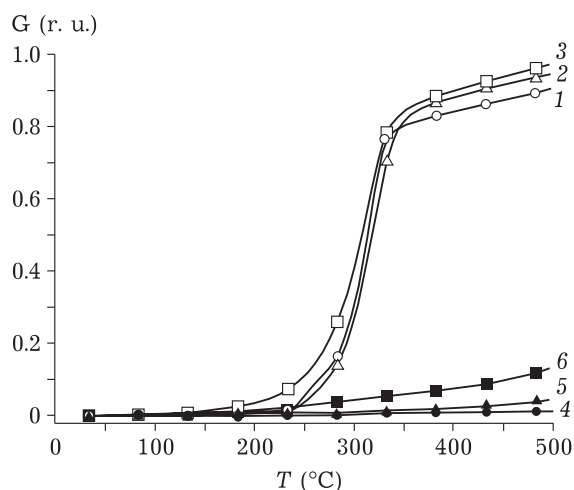

Fig. 6. Dependence of the degree of gas evolution G for water (*1*, *2*, *3*) and carbon dioxide (*4*, *5*, *6*) on the temperature of decomposition of the initial (*1*, *4*) and activated (*2*, *3*, *5*, *6*) mixture of lithium carbonate and gibbsite for 1 (*2*, *5*) and 8 (*3*, *6*) h.
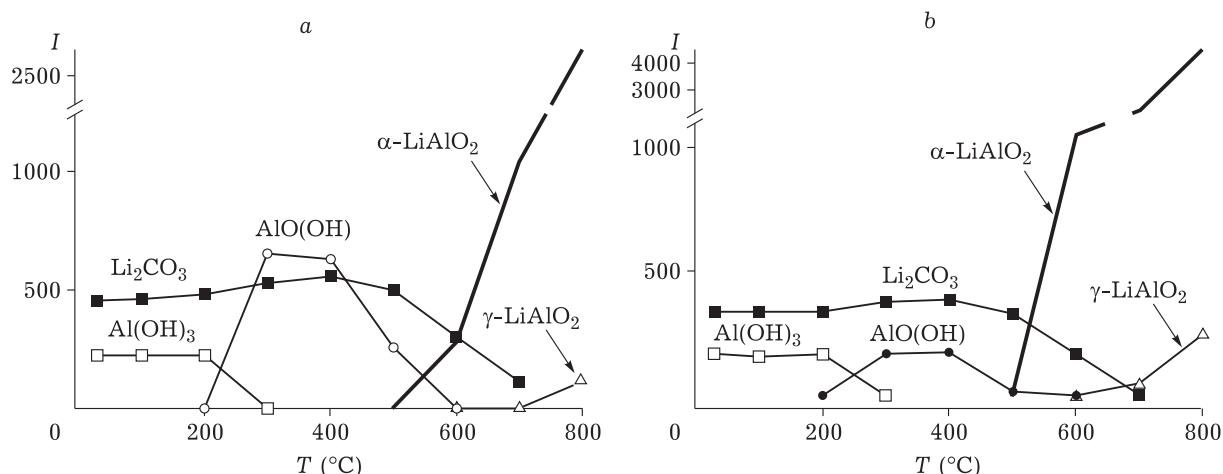
Fig. 7. Dependence of the integral intensity of the reflections of phases formed during the thermal treatment of a mixture of lithium carbonate and gibbsite (*a*), and a mixture of lithium carbonate with gibbsite activated for 8 h (*b*), on the temperature of thermal treatment.

tion may be due to an increase in its dispersion and imperfection, as well as its partial amorphization. In addition, as a result of mechanical activation, the concentration of boehmite formed by heating to 350 °C decreases (see Fig. 7, *a*, *b*), which points to a decrease in the contribution from reaction (1) into gibbsite decomposition. The degree of carbon dioxide evolution for mechanically activated samples during heating to 350 °C does not exceed 0.05. At higher temperature (350–550 °C), the mass change for activated samples is connected both with boehmite decomposition and with the evolution of gaseous carbon dioxide; the degree of gas evolution during heating to 500 °C reaches 0.12. At higher temperature (above 500–550 °C) the change of the sample mass is mainly due to the evolution of carbon dioxide as a result of the interaction of lithium carbonate with aluminium oxides and the formation of lithium aluminates. Mechanical activation of the mixture leads to an increase in the rate of this interaction. This is confirmed by the presence of a plateau on the TG curve even at 750 °C, corresponding to the completeness of the interaction between components for the mixture activated for 8 h.

On the basis of the data obtained in the experiments *in situ*, to study the effect of the conditions of mechanical activation and subsequent thermal treatment on the phase composition of lithium aluminates, we chose the temperature 600, 650 and 700 °C, and the duration of thermal treatment 4 h. The treatment at 600 °C, both for the initial mixture and for the mixture activated in the ball mill, leads to the formation of α-LiAlO₂

with an admixture of unreacted lithium carbonate (Fig. 8). An increase in synthesis temperature to 650 °C and the time of mechanical activation from 2 to 4 h allows obtaining monophase fine α-LiAlO₂ with specific surface area above 10 m²/g. The formed α-LiAlO₂ is composed of submicron particles with the average size from 0.15 to 0.18 μm, forming the aggregates of the micron size or larger (Fig. 9). Further increase in activation time to 6 h and more is accompanied by the appearance of an admixture of γ-LiAlO₂. After thermal treatment at 700 °C, the formation of monophase α-LiAlO₂ is observed for non-activated mixture, as well as for the mixture acti-
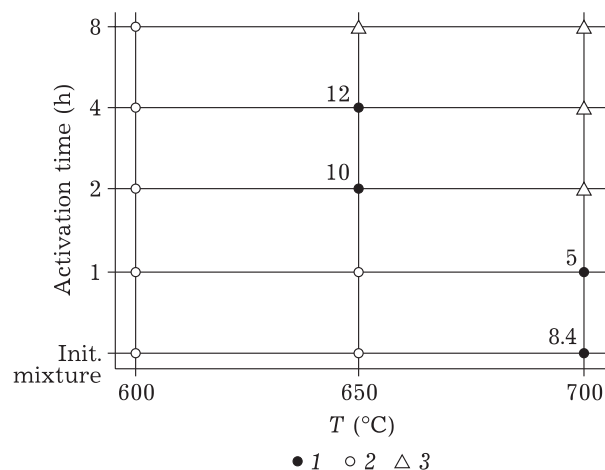

Fig. 8. Phase composition of α-LiAlO₂ formed after thermal treatment of the mechanically activated mixture of gibbsite and lithium carbonate in the air depending on activation time and annealing temperature (annealing time: 4 h). Phases: α-LiAlO₂ (*1*); α-LiAlO₂ > Li₂CO₃ (*2*); α-LiAlO₂ > γ-LiAlO₂(*3*); numbers indicate specific surface (in m²/g).
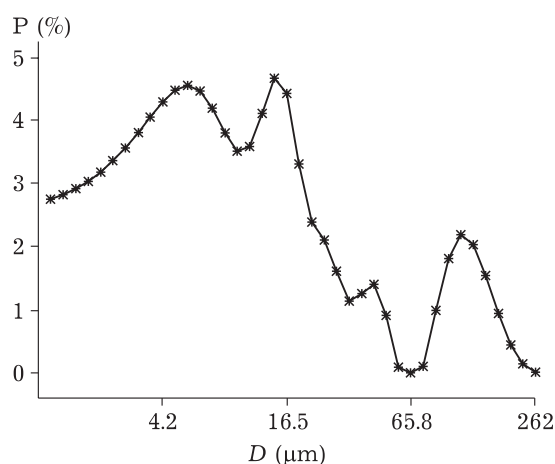
P (%)

Fig. 9. Particle size distribution for α-LiAlO₂ synthesized through thermal treatment (650 °C, 4 h) of mechanically activated mixture of gibbsite and lithium carbonate.

vated for one hour, but the specific surface area of these samples is less than 10 m^2/g. An increase in activation time to 4 h leads to the formation of the admixture of γ-LiAlO$_2$.

The data obtained in the present investigation allow us to propose the following scheme of the processes involved in the synthesis of α-LiAlO$_2$. Heating of the mixture of gibbsite and lithium carbonate to 550−600 °C involves the decomposition of gibbsite with the formation of a mixture of crystalline aluminium oxides (χ-Al$_2$O$_3$ and γ-Al$_2$O$_3$), which react with lithium carbonate at a temperature higher than 600 °C to form α-LiAlO$_2$. Aluminium oxides form a pseudomorph over rather large crystals of initial gibbsite, so the rate of the interaction of lithium carbonate and aluminium oxides is limited by the diffusion through a layer of lithium aluminate formed in the region of contact between lithium carbonate and aluminium oxide, that is, on the surface of aluminium oxide particles. Because of the substantial size of oxide particles and the diffusion nature of the reaction, long time (several ten hours) is necessary for the interaction to be completed. As a result, at low temperatures (600−650 °C) and acceptable time of thermal treatment (several hours) reaction products contain not only α-LiAlO$_2$ but also unreacted lithium carbonate and aluminium oxides. An increase in the process temperature to 700 °C and above accelerates the interaction between the reagents but also causes the phase transition of the alpha form into its high-temperature sort − gamma-form, which causes contamination of the target product − α-LiAlO$_2$.

Mechanical activation of a mixture of gibbsite and lithium carbonate in a ball mill leads at the initial stage to dispersing and mixing of the reagents, with the formation of aggregates composed of the micron-sized reagent particles. With a decrease in the size of gibbsite particles and, as a consequence, a decrease in the size of the formed aluminium oxide particles, the rate of the interaction of aluminium oxide with lithium carbonate at low (600−650 °C) process temperature increases. This provides the formation of α-LiAlO$_2$ with the low concentration of admixtures, that is, practically monophase product with the high specific surface area. More thorough grinding of the reagents with the formation of the submicron gibbsite particles is unreasonable because of the formation of X-ray amorphous aluminium hydroxide, which decomposes to form a product that reacts with lithium carbonate and gives γ-LiAlO$_2$ even in the region of α-LiAlO$_2$ stability [10, 11]. An increase in the temperature of thermal treatment of the mechanically activated mixture above 700 °C is not seasonable because of a decrease in the specific surface area of α-LiAlO$_2$, as well as the appearance of γ-LiAlO$_2$ admixture, may be due to the phase transition α-LiAlO$_2$ → γ-LiAlO$_2$ [12].

CONCLUSION

The performed investigation showed that the mechanical activation of a mixture of gibbsite and lithium carbonate in a ball mill followed by thermal treatment of the products of activation in the air leads to the formation of fine monophase α-LiAlO$_2$ with the characteristics allowing its use as the matrix electrolyte for FE with electrolytes composed of carbonate melts. For the formation of monophase α-LiAlO$_2$, it is necessary that the specific surface area of the mixture varies at the stage of mechanical activation within the range from 2 to 4 m^2/g, and thermal treatment should be carried out at a temperature of 650 °C. The data obtained in the investigation are of interest for the development of the mechanochemical technology of obtaining highly dispersed α-LiAlO$_2$.

Acknowledgements

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