

Low-Temperature Synthesis of Highly Disperse Lithium Gamma-Monoaluminate

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Abstract

A new method for the synthesis of highly disperse lithium gamma-monoaluminate is suggested. Binary lithium-aluminum hydroxide in carbonate form $[\text{LiAl}_2(\text{OH})_6]_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ is used for the precursor. Calcination of a mixture of this hydroxide with lithium carbonate above 800 °C forms $\gamma\text{-LiAlO}_2$. The sequence of chemical transformations leading to $\gamma\text{-LiAlO}_2$ has been studied. The first stage of the synthesis yields $\alpha\text{-LiAlO}_2$; when heated to a temperature above 800 °C, the latter is transformed into $\gamma\text{-LiAlO}_2$. The specific surface of the aluminate product is 3.5 m²/g. Test experiments showed that the product may be used as a holder for fuel elements with a melted carbonate electrolyte.

INTRODUCTION

Highly disperse lithium gamma-monoaluminate $\gamma\text{-LiAlO}_2$ has attracted attention as a promising material for use as a holder in fuel elements with a melted carbonate electrolyte. The particles of the holder keep the melted electrolyte within the matrix. This application requires that $\gamma\text{-LiAlO}_2$ should have dispersity of the order of 0.1 mm.

Two methods are conventionally used for the preparation of $\gamma\text{-LiAlO}_2$. The first is the ceramic technique based on caking a batch mixture of alumina and lithium carbonate [1]. High-temperature synthesis and long reaction times are major disadvantages of this process. Thus for synthesis of $\gamma\text{-LiAlO}_2$ from Al_2O_3 and Li_2CO_3 , reaction temperature is above 1000 °C and reaction time is up to 10 h; the product needs to be intermittently ground in the course of the reaction. The second is the gel-sol method by which gamma-aluminate is obtained from a gel containing aluminum and lithium cations

and inorganic anions [2–4]. The gel is formed by interaction of aluminum alkoxides with aqueous lithium chloride or nitrate. The gel synthesized in this way is filtered, dried, and calcinated. The reaction temperature is lowered to 700 °C, but the method employs rather expensive organoaluminum compounds and forms a lot of liquid organic waste. Therefore, developing new methods for the synthesis of highly disperse $\gamma\text{-LiAlO}_2$ devoid of the above-mentioned disadvantages has become a crucial problem.

The approach to the synthesis of $\gamma\text{-LiAlO}_2$ used in the present work is a continuation of our previous research [5, 6]; for precursors it employs binary aluminum and lithium hydroxides $[\text{LiAl}_2(\text{OH})_6]_n\text{X} \cdot m\text{H}_2\text{O}$. The structure of binary hydroxides consists of layers formed from hydroxide ions arranged as 2D close packing with aluminum and lithium cations in the octahedral voids and with anions and crystallization water in the interlayer space. The structure of $\gamma\text{-LiAlO}_2$ is an infinite 3D net formed

by distorted LiO_4 and AlO_4 tetrahedra. In the net, one can isolate chains of vertex-sharing AlO_4 tetrahedra [7]. Thus the structure of lithium-aluminum binary hydroxides, as well as that of $\gamma\text{-LiAlO}_2$, contains aluminum-oxygen chains with short distances between aluminum cations in the chain (Fig. 1). This facilitates structure formation of $\gamma\text{-LiAlO}_2$ from binary hydroxide. Moreover, the precursor already contains Al^{3+} and Li^+ cations "mixed" at the molecular level, which lowers the reaction temperature relative to the traditional ceramic procedure.

EXPERIMENTAL

For the precursor we employed the carbonate variety of binary hydroxide Al-Li $[\text{LiAl}_2(\text{OH})_6]_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ synthesized by the anion exchange method using the procedure of [8]. The precursor having an atomic ratio of lithium to aluminum of 0.5, for synthesizing $\gamma\text{-LiAlO}_2$ we added lithium in carbonate form

to the batch mixture. The batch mixture was thoroughly stirred, ground in an agate mortar, and heated in a SNOL muffle furnace in ambient conditions (heating rate $\sim 6^\circ\text{C}/\text{min}$). After the required temperature had been reached, the batch mixture was calcined for 2 h. An X-ray phase analysis (DRON-4 diffractometer, $\text{CuK}\alpha$ radiation, measurement rate $2^\circ\text{C}/\text{min}$) was undertaken to examine the composition of the reaction products. Furthermore, synthesis of the monoaluminate from a batch mixture of lithium carbonate and binary hydroxide was studied *in situ* on a Siemens D5000 diffractometer with a thermostatted accessory, and it was also investigated by thermal analysis. Thermogravimetric analysis was performed on a Perkin-Elmer instrument (ambient conditions, 15 mg samples, heating rate $6^\circ\text{C}/\text{min}$). The area of the specific surface of the synthesized powder was measured by the BET (Brunauer - Emmett - Teller) method using argon desorption. The morphology of the resulting particles of lithium monoaluminate was examined with a JSM-T20 scanning electron microscope.

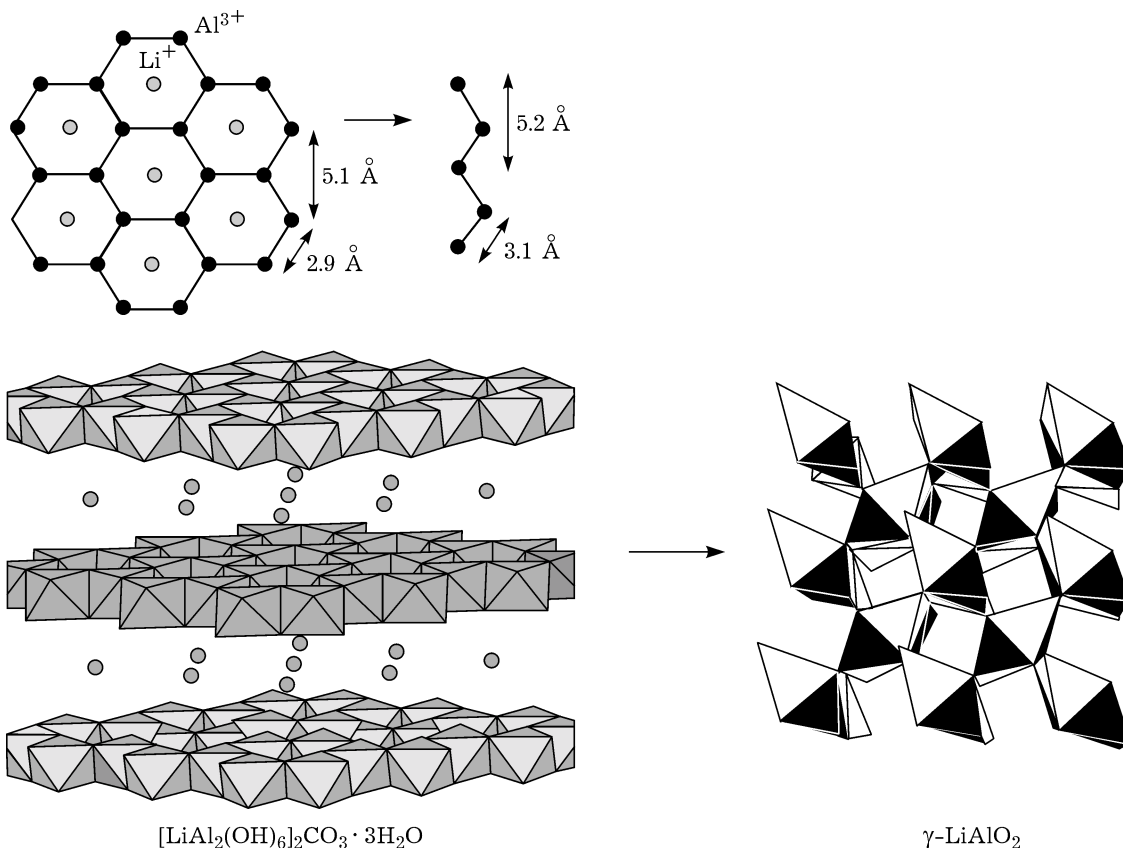


Fig. 1. Structural fragments of the $[\text{LiAl}_2(\text{OH})_6]_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ precursor and $\gamma\text{-LiAlO}_2$.

RESULTS AND DISCUSSION

Figure 2 presents the thermogram of a mixture of binary hydroxide and lithium carbonate $[\text{LiAl}_2(\text{OH})_6]_2\text{CO}_3 \cdot 3\text{H}_2\text{O} + \text{Li}_2\text{CO}_3$. As can be seen from the thermogram, the sample mass starts to change at 50–60 °C because of the loss of adsorbed and interlayer water. Mass loss corresponding to the first intense endothermic peak is ~20 %. As removal of three interlayer water molecules would lead to only 9–10 % mass loss, one can assume that the first peak is due not only to removal of interlayer water molecules, but also to decomposition of other structural fragments, namely, dehydration of metal hydroxide layers and decomposition of carbonate ions in $[\text{LiAl}_2(\text{OH})_6]_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$. The possibility for metal hydroxide layers to be destroyed simultaneously with carbonate ions during thermal decomposition of lithium-aluminum binary hydroxide in carbonate form was revealed in [6]. The second endothermic peak whose maximum lies at 230 °C may also be due to the concurrent removal of water and decomposition of the carbonate ions and metal hydroxide groups. Further heating leads to a plateau at 500 °C on the TG curve. At this point, mass loss is about 40 % and corresponds to an almost complete removal of water and carbonate ions from $[\text{LiAl}_2(\text{OH})_6]_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$. Further decrease in mass in the temperature range 500–800 °C may be caused by decomposition of the carbonate ion in lithium carbonate and formation of lithium monoaluminate.

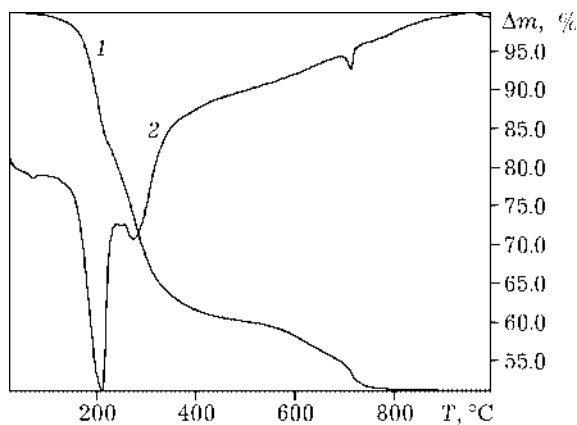


Fig. 2. Thermogram of the stoichiometric mixture of $[\text{LiAl}_2(\text{OH})_6]_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ and Li_2CO_3 . Heating in air, heating rate 6 °C/min: 1 – TG, 2 – DTA.

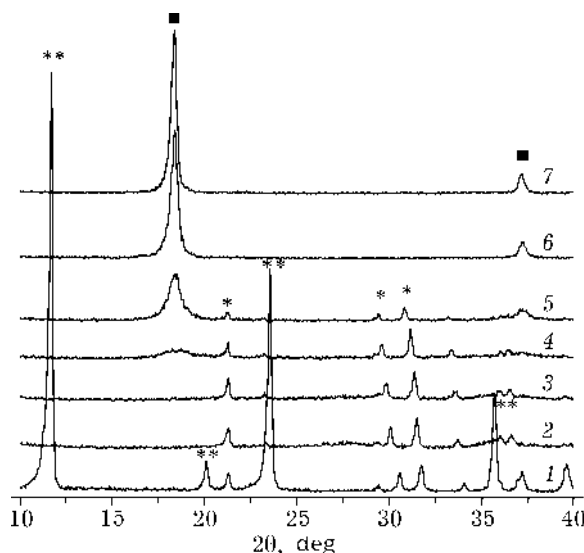


Fig. 3. X-Ray diffractograms of the products of thermal decomposition of a stoichiometric mixture of $[\text{LiAl}_2(\text{OH})_6]_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ and Li_2CO_3 obtained *in situ*: 1 – starting mixture; t , °C: 300 (2), 400 (3), 500 (4), 600 (5), 700 (6), 800 (7). Reflections: ** $[\text{LiAl}_2(\text{OH})_6]_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$; * Li_2CO_3 ; ■ $\alpha\text{-LiAlO}_2$.

The suggested scheme of structural transformations is confirmed by analysis of X-ray diffractograms obtained *in situ*.

When the mixture was heated to 300 °C (Fig. 3), the reflections of binary hydroxide $[\text{LiAl}_2(\text{OH})_6]_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ completely vanished. The reflections of lithium carbonate did not change in intensity at 300 and 400 °C, but slightly decreased at 500 °C; in the latter case, a weak broadened reflection of $\alpha\text{-LiAlO}_2$ appeared in the region $2\theta = 18\text{--}19^\circ$. When the temperature was elevated further, the intensity of the reflections of Li_2CO_3 decreased, while that of $\alpha\text{-LiAlO}_2$ increased. As can be seen from Fig. 3, $\gamma\text{-LiAlO}_2$ did not form below 800 °C because of the short calcination times of the batch mixture *in situ*. This compound formed when the calcination time was 2 h.

Calcination of the batch mixture at 400 °C led to destruction of the binary hydroxide and formation of a phase practically amorphous to X-ray diffraction (Fig. 4). When the temperature was raised to 700 °C, broadened reflections of $\alpha\text{-LiAlO}_2$ appeared. The reflections of Li_2CO_3 did not change in intensity. At 800 °C, the reflections of Li_2CO_3 vanished, and almost pure $\alpha\text{-LiAlO}_2$ formed. Further growth of temperature to 900 °C gave rise to weak reflections of $\gamma\text{-LiAlO}_2$.

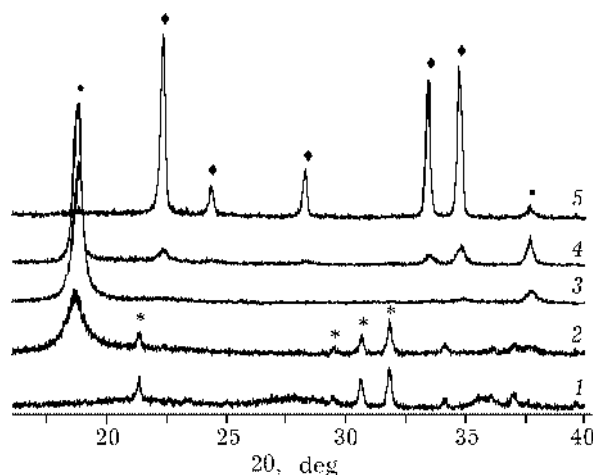
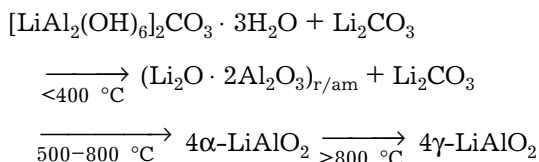


Fig. 4. X-Ray diffractograms of the products of thermal decomposition of a stoichiometric mixture of $[\text{LiAl}_2(\text{OH})_6]_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ and Li_2CO_3 at different temperatures, °C: 400 (1), 700 (2), 800 (3), 900 (4), 950 (5). Reflections: * Li_2CO_3 ; • $\alpha\text{-LiAlO}_2$; ♦ $\gamma\text{-LiAlO}_2$.

Finally, pure γ -monoaluminate (without an α -form impurity) formed at 950 °C (see Fig. 4). The reaction leading to $\gamma\text{-LiAlO}_2$ may be schematically represented as follows:



According to electron microscopy data, the particle size of the product was $\sim 0.2\text{--}0.3\text{ }\mu\text{m}$. The particles formed platelike aggregates sized $5\text{--}15\text{ }\mu\text{m}$, easily destroyed upon grinding to particles with dimensions of $2\text{--}3\text{ }\mu\text{m}$. The specific surface of this powder was $3.5\text{ m}^2/\text{g}$ (BET data).

The synthesized lithium aluminate was used to prepare matrix plates by rolling. For this, the aluminate powder was mixed with a solution of an organic binder (polyvinylbutyral) in ethanol with a plasticizer addition. The resulting mixture was rolled on roll mills. Electrolyte matrix plates were prepared directly in fuel elements after the binder had been burnt off in the course of element triggering.

The units of the fuel element were tested in two-element cells – batteries with parallel internal commutation of gases. Wetted hydrogen was used for the anode gas, and a mixture of oxygen and carbon dioxide ($0.5\text{O}_2 + \text{CO}_2$) was cathode gas. Porous electrode plates of nickel for anodes and of lithium-nickel oxide for cath-

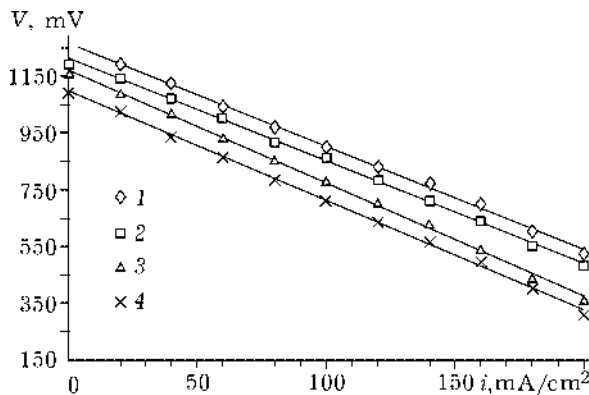


Fig. 5. Measurements of volt-ampere characteristics of the fuel element at different operating times, h: 0 (1), 33.5 (2), 55.3 (3), 86.9 (4).

odes were preliminarily annealed and prepared; then they were placed in metal separators – construction elements for dividing the gas flow. The matrix plate together with a plate of a lithium-potassium eutectic mixture served as a sealant between them. At an operating temperature (650 °C), the carbonate melted and impregnated the porous matrix plate. The resulting electrolyte-matrix plate was hermetically sealed and gas-proof.

Service trials of fuel elements based on the synthesized matrix material indicated that the latter may be used in electrolyte-matrix plates. Thus at a voltage of 0.7 V, current density was up to $150\text{ mA}/\text{cm}^2$, and the characteristics remained at the same level for 200 h (Fig. 5). When the load was off, the emf also remained constant throughout the whole period of trials.

CONCLUSION

Thus the given procedure is applicable to the synthesis of highly disperse lithium gamma-monoaluminate, which proved useful as a material for fuel elements. The temperature of thermal treatment of a batch mixture is lower and the specific surface of lithium aluminate is higher than the corresponding characteristics of the ceramic method. The procedure does not require expensive organoaluminum reagents, as was the case with the sol-gel method.

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