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The study of combustion synthesis of fine-particle γ-lithium aluminate

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Fine-particle γ-lithium aluminate has been prepared by the combustion of mixtures of the metal nitrates, $M(NO_3)_x$ ($M = Li, Al$) as oxidizers and urea and citric acid as fuels, at low temperature and short reaction time. The combustion products were identified from X-ray powder diffraction (XRD) patterns, scanning electron microscopy (SEM), and pore size distribution measurements. As the total composition of oxidizing and reducing elements of the reactants leave related to the thermochemistry of the system, a simple method of calculating the elemental stoichiometric coefficient was introduced. The physical significance of such a correlation based on thermochemical reasoning was investigated. It was found that a significant improvement was achieved in the reactant mixture with a molar ratio of urea:citric acid = 9:1. An improvement in the combustion synthesis of γ-lithium aluminate is due to the formation of an activated complex of the fuel with the corresponding oxidizer. © *2003 Kluwer Academic Publishers*

1. Introduction

Lithium aluminate is a potential candidate for the matrix of molten carbonate fuel cells (MCFC) and tritium breeding materials for fusion reactors, due to its thermophysical and mechanical stability at high temperature as well as favorable irradiation behavior [1, 2]. Lithium aluminate can be crystallized in three allotropic forms, α, β, γ, and they have hexagonal, monoclinic, and tetragonal crystal structures, respectively [1]. At an elevated temperature, the α- or β-$LiAlO_2$ could transform to γ-$LiAlO_2$. As a high-temperature form, γ-$LiAlO_2$ has been strongly considered as the most important form in those applications.

The morphology control of $LiAlO_2$ particles will affect the characteristics of the final product. Homogeneous fine crystalline powder is usually needed. In the interest of reinforcing the MCFC matrix [2] and controlling the rate of tritium release from the tritium-breeding blanket in fusion reactors [1], lithium aluminate powders have been synthesized from solid-state reaction, the reaction mixture of LiOH-γ-Al_2O_3-NaOH, or the sol-gel preparation method. However, the actual product of fine-particle γ-lithium aluminate is still limited by some questions, such as high cost of starting materials, complicated procedure and impure reaction product.

The emphasis in all these methods was in achieving the synthesis quickly at low temperatures so that the powders obtained from various reactant mixtures were in a finely divided state with large surface areas. Here, the combustion of corresponding metal nitrate-fuel mixtures at low temperature was employed to synthesize γ-$LiAlO_2$. The purpose of this work was to investigate the effect of starting materials and processing temperature on the crystallization and morphology of lithium aluminate, and the mechanism of combustion synthesis of γ-$LiAlO_2$.

2. Experimental procedure

2.1. Compound design and thermochemical calculations

Stoichiometric compositions of the metal nitrates (oxidizers), lithium nitrate, aluminum nitrate, and two different types of fuels, urea and citric acid, were used as the starting materials. According to propellant chemistry, the constitution of a combustible mixture is usually expressed in terms of parameters, such as equivalence ratio, mixture ratio, elemental stoichiometric coefficient, and so on. The equivalence ratio ϕ is defined as $\phi = \phi_s/\phi_m$, where ϕ_s is the stoichiometric ratio and ϕ_m is the mixture ratio (fuel/oxidizer) [3]. A value of $\phi > 1$ indicates that the mixture is fuel lean, whereas $\phi < 1$ shows it to be fuel rich. However, as ϕ does not take into account the intramolecular elements present in the oxidizer and in the fuel, two systems may give the same value of ϕ but may differ substantially with respect to oxygen balance. Jain *et al.* [4] reported an easier method of calculating the elemental stoichiometric

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coefficient, ϕ_e.

$$\phi_e = \frac{\sum \text{Coefficient of oxidizing elements in specific formula} \times \text{valency}}{(-1)\sum \text{Coefficient of reducing elements in specific formula} \times \text{valency}} = \frac{p}{r}$$

The elements Li, Al, C and H are considered as reducing elements with the corresponding valencies +1, +3, +4 and +1, respectively; oxygen is considered as oxidizing element with the valency −2, and nitrogen is taken as neutral. In order to release the maximum energy for the reaction, the stoichiometric composition of the redox mixture is calculated based on the principle that the total valencies in all reactants should add up to zero.

In this experiment, the total reducing valences of fuels (CH_4ON_2 and $C_6H_8O_7$) $= [1 \times 4 + 4 \times 1 + 1 \times (-2) + 0] + [6 \times 4 + 8 \times 1 + 7 \times (-2)] = 24$, and the total oxidizing valences of the oxidizer ($LiNO_3$ and $Al(NO_3)_3$) $= [1 \times 1 + 0 + 3 \times (-2)] + [1 \times 3 + 0 + 9 \times (-2)] = -20$. Assuming completely oxidized products, one can write the stoichiometrically balanced equation as:

$$\begin{aligned} &LiNO_3(aq) + Al(NO_3)_3{\cdot}9H_2O(aq) + \frac{5}{6}CH_4ON_2 \\ &\quad + \frac{5}{6}C_6H_8O_7{\cdot}H_2O \Rightarrow LiAlO_2(s) + \frac{35}{6}CO_2(g) \\ &\quad + \frac{17}{6}N_2(g) + \frac{89}{6}H_2O(g) \end{aligned} \tag{I}$$

The treatment could be extended to the general case, where the two fuels are taken in different molar proportions. In this work, when the fuels are taken in the ratio of 9:1, the system could be balanced as follows. The total reducing valences of fuels (9 CH_4ON_2 and 1 $C_6H_8O_7$) = 72, and the total oxidizing valences of the oxidizer ($LiNO_3$ and $Al(NO_3)_3$) = −20, so the balanced equation can be written as:

$$\begin{aligned} &LiNO_3(aq) + Al(NO_3)_3{\cdot}9H_2O(aq) + \frac{5}{2}CH_4ON_2 \\ &\quad + \frac{5}{18}C_6H_8O_7{\cdot}H_2O \Rightarrow LiAlO_2(s) + \frac{25}{6}CO_2(g) \\ &\quad + \frac{9}{2}N_2(g) + \frac{277}{18}H_2O(g) \end{aligned} \tag{II}$$

For those fuels, such as single urea or citric acid monohydrate, the corresponding equations could be deduced by analogy.

When the fuel is urea, the corresponding equation is listed as:

$$\begin{aligned} &LiNO_3(aq) + Al(NO_3)_3{\cdot}9H_2O(aq) + \frac{10}{3}CH_4ON_2 \\ &\quad \Rightarrow LiAlO_2(s) + \frac{10}{3}CO_2(g) + \frac{16}{3}N_2(g) + \frac{47}{3}H_2O(g) \end{aligned} \tag{III}$$

When the fuel is citric acid monohydrate, the corresponding equation is listed as:

$$\begin{aligned} &LiNO_3(aq) + Al(NO_3)_3{\cdot}9H_2O(aq) + \frac{10}{9}C_6H_8O_7{\cdot}H_2O \\ &\quad \Rightarrow LiAlO_2(s) + \frac{20}{3}CO_2(g) + 2N_2(g) + \frac{131}{9}H_2O(g) \end{aligned} \tag{IV}$$

2.2. Combustion synthesis of γ-lithium aluminate

The overall experimental flow chart for this work on synthesizing γ-$LiAlO_2$ particle is given in Fig. 1, and the details on experimental procedure for each step are described below. The equimolar mixture of the two metallic nitrates ($LiNO_3$ and $Al(NO_3)_3{\cdot}9H_2O$) and the calculated amounts of the fuels were dissolved in minimum quantity of distilled water, with batch I corresponding to equation (I), batch II corresponding to equation (II), and so on. The solution was allowed to evaporate and maintained at 100–300°C with continuous stirring. When the solution had nearly evaporated off completely, the stirring was stopped but the heating was continued. Immediately after gel formation, different batches burnt in different ways. Batch II underwent dehydration followed by decomposition with the evolution of large amounts of gases. The mixture then frothed and swelled forming a foam, which ruptured with a flame and glowed to incandescence. This autoignition was complete within a few seconds, and the flame temperature was over 1000°C, as measured by a thermo couple. In contrast, batch IV did not ignite at all,

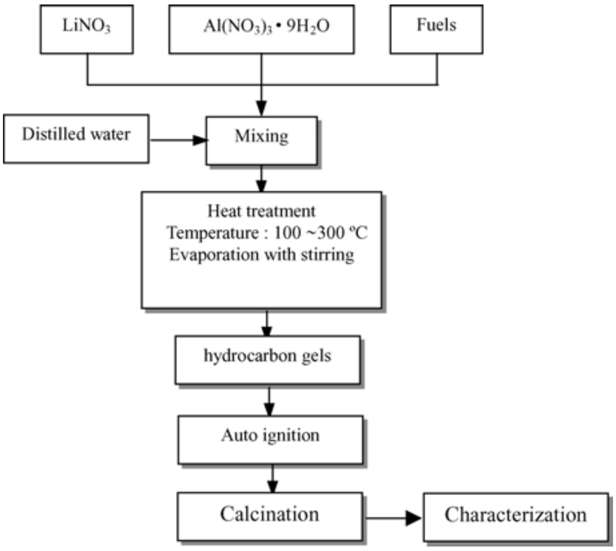

Figure 1 Flow chart for lithium aluminate preparation by combustion synthesis.

and batches I and III burnt quite slowly. The products from different batches were calcined at 600–800°C for formation of the desired oxide phase.

2.3. Characterization of the lithium aluminate

Crystalline phases of lithium and aluminum oxides obtained from different batches were identified by an X-ray powder diffractometer (Model D/max-RB, Japan) using Cu K_α radiation with 40 kV, 120 mA, at a scanning rate of 6 deg/min. The K_α wavelength was selected with a diffracted beam monochromator. The pore size distribution measurement was made by mercury porosimetry employing a micromeritics instrument (Autopore IV 9500, Micromeritics Instrument Corporation, USA).

The microstructure and morphology of lithium aluminate were studied by scanning electron microscopy (SEM) (Model 450, Tokyo, Japan).

3. Results and discussion

3.1. Crystallization behavior

Powder X-ray diffraction (XRD) patterns of the foams obtained from different batches show a dependence of their composition on the nature of decomposition of the gels and the exothermicity of the reaction. For the powders obtained from batch IV, initial crystallization into γ-$LiAlO_2$ structure had not taken place after heating at 110°C for 12 h, and it was found to be amorphous in nature, as shown in Fig. 2. Significant changes were observed from the patterns of the samples calcined at 600°C and 800°C. Some small peaks corresponding to the γ-$LiAlO_2$ were found at 600°C, but the crystallinity was still low. After heating at 800°C, the widths of the peaks became very narrow, indicating a rapid increase in the growth of the crystallite size. However, even though the gels were heated at 800°C, autoignition did not take place.

The XRD patterns obtained from the powders which came from batch I after heating sequentially at different temperatures are shown in Fig. 3. It was found that the reaction product consisted of γ-$LiAlO_2$ and lithium aluminum hydroxide hydrate ($LiAl_2(OH)_7{\cdot}xH_2O$) when the heating temperature was 300°C. On heating the gels sequentially to higher temperatures, the peaks of $LiAl_2(OH)_7{\cdot}xH_2O$ disappeared and the peaks of γ-$LiAlO_2$ became more and more intense. The process and product of batch III were almost the same as for batch I, with the only difference that the reaction for batch III was slower. Fig. 4 shows that the powders obtained from batch II consisted only of γ-$LiAlO_2$, due to its reaction temperature being the highest of the four batches.

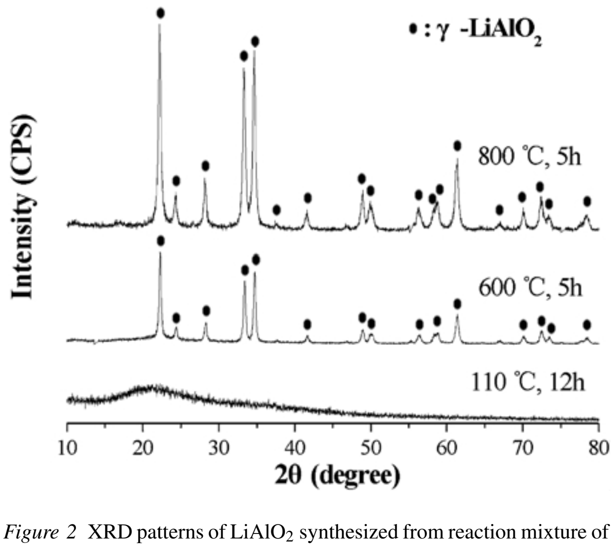

Figure 2 XRD patterns of $LiAlO_2$ synthesized from reaction mixture of 1 M $LiNO_3$, 1 M $Al(NO_3)_3{\cdot}9H_2O$ and 10/9 M citric acid, calcined at different temperatures for 5–12 h.

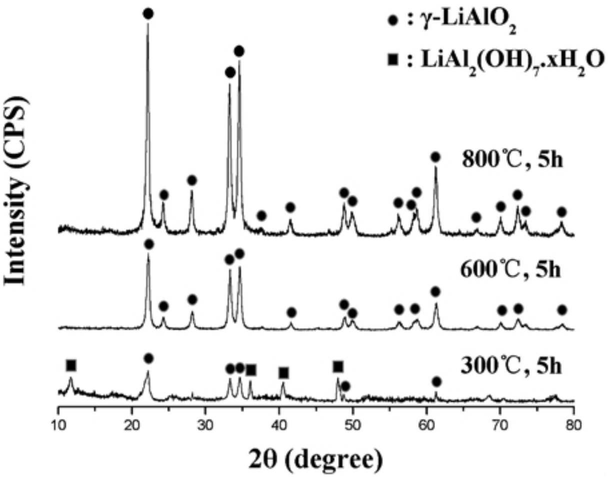

Figure 3 XRD patterns of $LiAlO_2$ synthesized from reaction mixture of 1 M $LiNO_3$, 1 M $Al(NO_3)_3{\cdot}9H_2O$, 5/6 M urea and 5/6 M citric acid, calcined at different temperatures for 5 h.

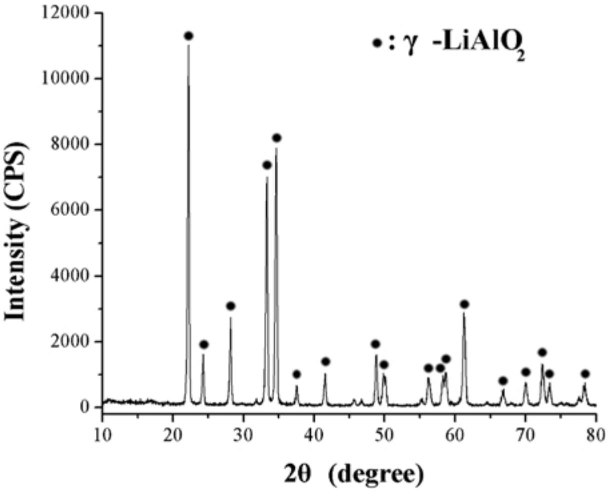

Figure 4 XRD patterns of $LiAlO_2$ synthesized from reaction mixture of 1 M $LiNO_3$, 1 M $Al(NO_3)_3{\cdot}9H_2O$, 5/2 M urea and 5/18 M citric acid.

3.2. Microstructure evolution and analysis

The SEM micrographs (see Fig. 5) show the microstructure and the surface of the $LiAlO_2$ particles. The foamy structure reflected the inherent nature of the reaction. The presence of solid phase could be seen in the cellular walls of the foam. The surface of the foam showed voids, cracks and pores formed by the escaping gases during the combustion reaction. As shown in Fig. 5, heating the gels sequentially to higher temperatures had

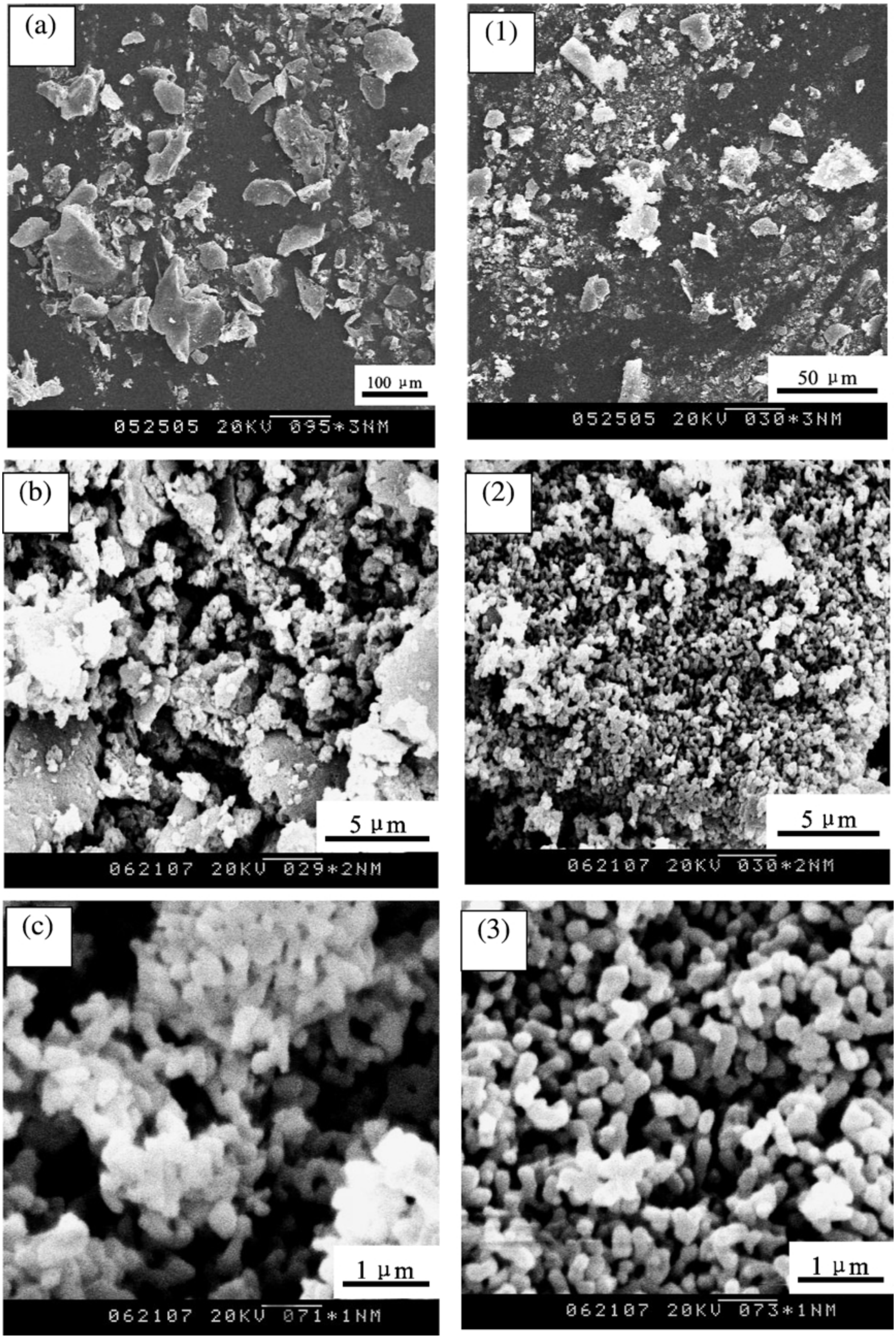

Figure 5 SEM micrographs of $LiAlO_2$ synthesized from reaction mixtures: Product from batch IV, calcined at different temperatures: (a) 300°C, (b) 600°C, (c) 800°C; Product from batch II, calcined at different temperatures: (1) 300°C, (2) 600°C, (3) 800°C.

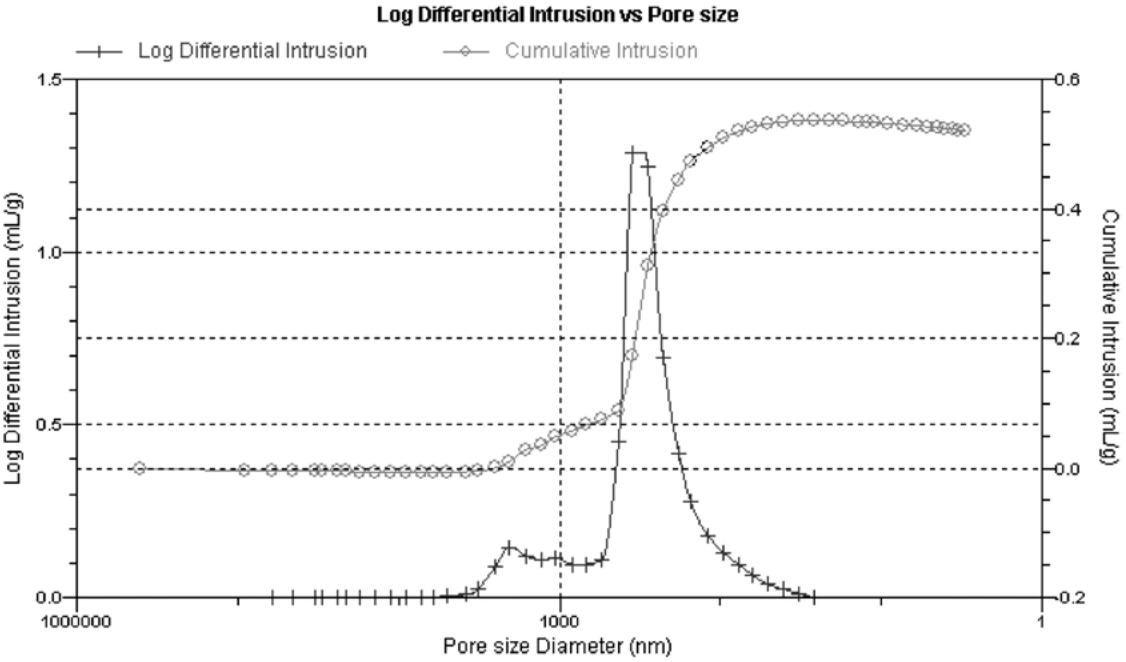

Figure 6 Results from the mercury porosimetry analysis.

a important effect on the morphology of $LiAlO_2$. This could result from the burnout of remnant hydrocarbon and the growth of the crystallites.

The component materials for the MCFC matrix or solid breeder materials need to operate at high temperature. For the porous lithium aluminate to have thermal shock resistance, the porosity and pore size distribution are very important for the final product [5, 6]. Using crystalline fine powders of γ-lithium aluminate, synthesized by employing combustion method, as the starting materials, porous thin-wall tubelike specimens were fabricated by uniaxial pressing. The pore size distribution measurement was carried out using mercury porosimetry. It was observed that the porous specimens had micropores with a narrow pore size distribution of 0.1–0.5 μm (see Fig. 6), and such values are very suitable for tritium breeding materials.

3.3. The mechanism of the synthesis of γ-$LiAlO_2$

As redox reactions are usually exothermic in nature, they often lead to explosions if not controlled. The combustion of aluminium nitrate-urea-citric acid mixtures appears to undergo a self-propagating and non-explosive exothermic reaction. With regard to the combustion process, there were two different descriptions. Kingsley *et al.* [7] suggest that aluminium

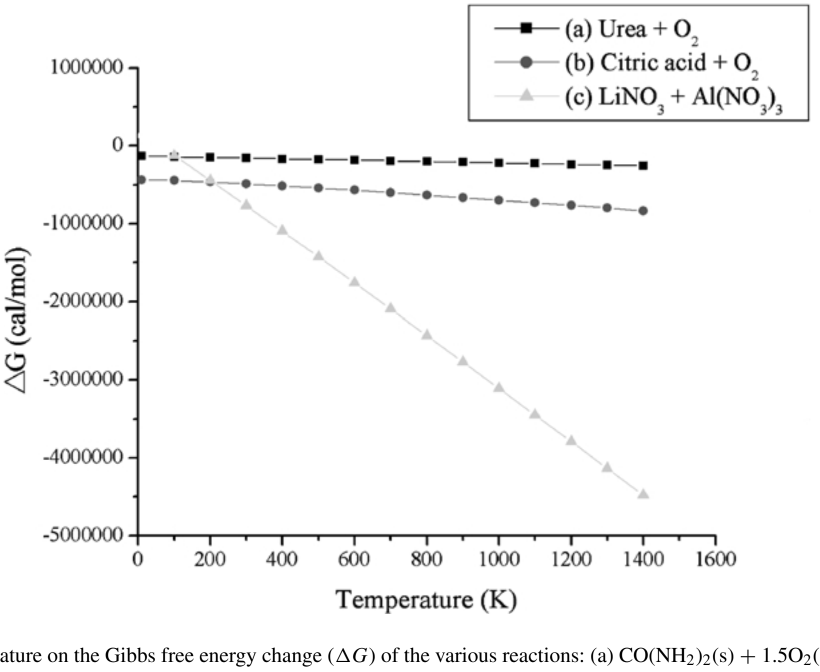

Figure 7 Effect of temperature on the Gibbs free energy change (ΔG) of the various reactions: (a) $CO(NH_2)_2(s) + 1.5O_2(g) \Rightarrow CO_2(g) + 2H_2O(g) + N_2(g)$; (b) $C_6H_8O_7{\cdot}H_2O(s) + 4.5O_2(g) \Rightarrow 6CO_2(g) + 5H_2O(g)$, and (c) $LiNO_3(s) + Al(NO_3)_3{\cdot}9H_2O(s) \Rightarrow LiAlO_2(s) + 2N_2(g) + 5O_2(g) + 9H_2O(g)$.

nitrate-urea mixtures first form $Al(OH)(NO_2)_2$ gel, and that the appearance of a flame may be attributed to the gas-phase reactions in the foam of combustible gases, such as those of ammonia and cyanic acid with oxides of nitrogen. However, Fumo *et al.* [8] disagree. In their opinion, reaction between metal nitrates, such as $Al(NO_3)_3 \cdot 9H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$, takes place first, and produces O_2. Then the active O atoms aid urea ignition, and the combustion process supplies enough heat to promote the synthesis of the aluminate.

In order to confirm the actual process of combustion reaction, thermodynamic data were used to calculate the Gibbs free energy changes ΔG involved in each reaction, as a function of temperature (see Fig. 7). This showed that the reaction between metal nitrates and citric acid should take place more readily than the reaction between metal nitrates and urea. This is contrary to the experiment result. Moreover, from the thermodynamics calculation, the decomposition of the mixed-metal nitrates and fuels was endothermic, and the heat needed for batch I was nearly equal to the heat needed for batch II, but only the gel prepared from batch II gave rise to a rapid and continuous exothermic decomposition. As the actual process of the reaction depended on the exact ratio of nitrate to fuel, it would appear that these combustion reactions were inexplicable by the mechanism of Fumo *et al.*

The reaction of batch II was instantaneous and continuous, while the reaction of batch I was quite slow. Although are four batches fit the mol stoichiometric balance of the mixed fuel to the corresponding oxidizer, the actual processes were different. So it can be concluded that in the initial stage of combustion synthesis, the reactant mixtures gradually formed a polymeric gel along with the vaporization of water, and this could reduce the triggering energy of combustion reaction [9], as lithium nitrate and citric acid, or aluminum nitrate and urea, form some activated complex. Once the mixture was ignited, a self-propagating fast chain reaction would take place readily and the highest temperature was achieved.

4. Conclusions

The effects of fuel types, processing temperature and the valency-based mole proportions of reactants on the combustion synthesis of γ-$LiAlO_2$ were studied. It was found that the reaction followed different mechanisms, depending on the fuel types and the ratio of oxidizer to fuel, and, therefore, the process of combustion and the obtained compounds varied. A significant improvement was achieved in the reactant mixture of molar ratio of urea:citric acid = 9:1, and γ-phase was directly developed without being preceded by α- or β-phase. It can be concluded that the combustion process has great potential in the preparation of phase pure γ-lithium aluminate powders of large quantity.

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