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Preparation of lithium aluminate via polymeric precursor routes

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Abstract

Gamma lithium aluminate is a potential candidate for tritium breeding material. Various preparation routes have been proposed including solid state reaction methods and wet chemical methods such as sol–gel process. But it is still needed to develop reliable and economic preparation methods that can be used for large production. In this paper, we examined three polymeric precursor methods – amorphous citrate process, Pechini process, and polyvinyl alcohol-assisted process – by studying thermal behavior of the precursor powders by X-ray diffractometry, differential thermal analysis, Infrared spectrometry, and BET surface area analysis. All these three processes produced phase pure gamma lithium aluminate powders at a relatively low temperature. The phase purity and processing temperature were comparable to the alkoxide derived sol–gel method and yet these polymeric precursor methods did not require high quality starting materials such as alkoxides.

1. Introduction

Lithium aluminate, $LiAlO_2$, is a potential candidate for the tritium breeder of a nuclear fusion reactor owing to its chemical and thermal stability as well as low radiation damage problem [1–5]. Among three allotropic forms of α-, β-, and γ-$LiAlO_2$, the γ-phase is most stable. The α- or β-$LiAlO_2$ transforms to the γ-$LiAlO_2$ at an elevated temperature.

Solid state reaction method and wet chemical method such as a sol–gel process are widely used to prepare multi-component oxide powders. The solid state reaction method is generally based on the mixing of fine powders. Wet chemical methods are known to be better than the solid state reaction methods in intimate mixing of reactants, high product purity, and low processing temperature [6,7].

Kwon and Park prepared phase pure gamma lithium aluminate at low temperature by sol–gel method [8]. In their work, the sol–gel method starting with long chain alkoxides such as lithium butoxide and aluminum butoxide was found to be excellent in terms of low processing temperature and phase purity. In spite of the advantages of the alkoxide derived sol–gel method, the method has some aspects to be improved: alkoxides are expensive and difficult to handle and store due to the high reactivity; the sol–gel preparation method has many steps to be precisely controlled [9]. Therefore, there are motivations to develop economic and simple processes to prepare high quality gamma lithium aluminate powders in large quantities. In this paper, we examine polymeric precursor methods as alternative routes for the gamma lithium aluminate powder.

The polymeric precursor method is known to be simple, cost effective and versatile low temperature route [10]. The general idea of the method is to distribute the cations atomistically throughout the polymer structure and to inhibit their segregation and precipitation from

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the solution [10,11]. Upon heating this organic material, multi-component oxides are obtained at a relatively low temperature. Typical polymeric precursor methods are amorphous citrate process and Pechini process [12–16]. The methods has been studied for the synthesis of $LiMn_2O_4$, $LiCoO_2$, $NdGaO_3$, Bi_2CaSr_2, $CuO_{8+\delta}$, and $(La_{1-x}Sr_x)MnO_3$ powders. Recently, PVA (polyvinyl alcohol)-assisted process was reported to be a versatile route for the preparation of mixed oxide systems at fairly low temperature [10,17].

In the amorphous citrate process, citric acid is generally used as a chelating agent of metal cations. Hydroxycarboxylic acid and hydroxyl alcohol are used together in the Pechini process. In the PVA-assisted process, PVA plays a role in the distribution of cations instead of hydroxycarboxylic acid.

In this study, the above three polymeric precursor methods were investigated to establish a more competent process than conventional wet chemical methods for the preparation of phase pure gamma lithium aluminate powders of large quantity.

2. Experimental

Table 1 is a list of reagents used in this experiment. Lithium and aluminum nitrates were used as starting cationic sources for each process. Citric acid was used as a hydrocarboxylic acid in the amorphous citrate process and the Pechini process. The degree of polymerization of polyvinyl alcohol (PVA) was 1500. All reagents were used without further purification.

In the amorphous citrate process as shown in Fig. 1, equimolar lithium and aluminum nitrates were dissolved in distilled water and this nitrate solution was mixed with aqueous citric acid solution. No precipitate was observed in the solution. Then, the mixed solution was evaporated on a hot plate at 80–90°C for 1–2 days under vacuum. NO_x gas was gradually evolved and the volume of the solution was slowly reduced. The color of the solution turned into yellow because of nitrate decomposition. After transparent yellowish gel was obtained, evaporation was continued in an electric oven at 105°C for 2–3 days. After 1–2 days, evolved gases caused the gel expanded more than five times of the original volume and a lump of bread-like material was formed. The bread-like material was ground and used for the further characterization. The prepared precursor powders were post-treated in an electric oven to form lithium aluminate. For the preparation of the gel precursor powders with a different citric acid/total metal ion mole ratio, the same procedure was repeated, with the mole ratio of citric acid to the total metal ions being varied as 0.5, 1.0, 1.5, and 2.0. When the mole ratio was 2.0, the swelling ratio of the gel was low and the prepared precursor was so sticky that it was not easily ground.

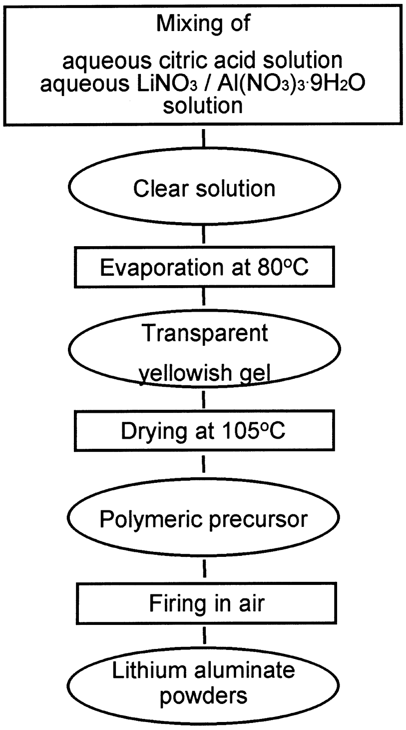

Fig. 1. Preparation procedure of gamma lithium aluminate by the amorphous citrate process.

The preparation procedure of the Pechini process was more complicated than the other two processes and was summarized in Fig. 2. The Pechini precursor powder was prepared with lithium and aluminum nitrates, citric acid, and ethylene glycol. Citric acid was dissolved

Table 1
Reagents used for the preparation of lithium aluminate

Reagents	Formula	Contents	Manufacturer
Lithium nitrate	$LiNO_3$	EP	Junsei
Aluminum nitrate	$Al(NO_3)_3 \cdot 9H_2O$	EP	Junsei
Citric acid	$HCOOCCH_2C(OH)(COOH)CH_2COOH \cdot H_2O$	GR	Junsei
Ethylene glycol	$C_2H_6O_2$	99%	Merck
Polyvinyl alcohol	$(-CH_2CHOH)_n = 1500$	CP	Yakuri

in ethylene glycol with a 1:6 mole ratio at 80–90°C. Equimolar lithium and aluminum nitrates were dissolved in the mixed solution of citric acid and ethylene glycol at the same temperature. The mole ratio of citric acid to total cations was 1.0. The mixed viscous solution was heated to give esterification between ethylene glycol and citric acid at 140°C. Then the resulting solution was heated at between 170°C and 190°C under reduced pressure to yield organic polymer. The temperature control was difficult because of exothermicity of this reaction. At this stage, ethylene glycol was removed and polyesterification occurred [14]. The prepared dark gray precursor was not easily disintegrated. The precursor was divided into small pieces and heated to form gamma lithium aluminate in an electric furnace.

Preparation procedure of the PVA-assisted process was similar to those of the citrate process and was shown in Fig. 3. A stoichiometric amount of lithium and aluminum nitrates (Li:Al = 1:1) was dissolved in water and the solution was mixed well with an aqueous polyvinyl alcohol solution. The mole ratio of PVA monomer unit to total cations was 1.0. No precipitate was observed in the solution. The resulting viscous mixture was heated under vacuum between 80°C and 90°C for 1–2 days. During the evaporation of water, the solution turned into yellowish transparent solution and NO_x gas was evolved from the solution. After a gel was obtained, dehydration was continued in an electric oven at 105°C. The gel swelled out to form a white bread-like material same as in the case of amorphous citrate process. This precursor powder was then ground and heated to study the thermal behavior.

Each precursor powder was heated to form gamma lithium aluminate in an electric furnace for 2 h at various temperatures. The heating behavior of each precursor powder was characterized with XRD (Rigaku, D/Max-RB), TG-DTA (TA Instrument, SDT2960), and IR (Perkin Elmer, 1725X). For the thermal analysis, 20–30 mg of the precursor powder was heated at a rate of 10°C/min in air flow of 100 ml/min. Carbon/Sulfur Analyzer (Leybohold, CSA302) and BET surface area analyzer (Quantachrome, Autosorb-6) were used to measure the carbon content and specific surface area of the prepared lithium aluminate powder.

3. Results and discussion

Phase purity of the product powders is an important criterion for the selection of gamma lithium aluminate

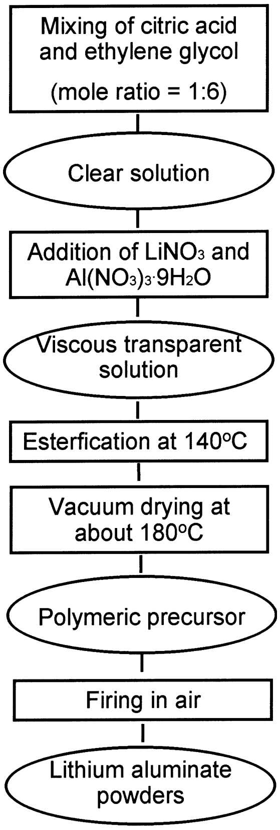

Fig. 2. Preparation procedure of gamma lithium aluminate by the Pechini process.

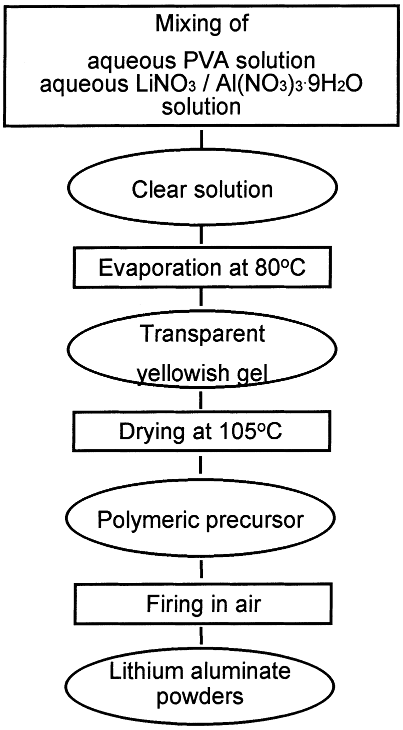

Fig. 3. Preparation procedure of gamma lithium aluminate by the PVA-assisted process.

production processes. Fig. 4 showed the changes in crystallinity as the precursor powders were heated at (a) 105°C, (b) 400°C, (c) 600°C, (d) 700°C, and (e) 800°C. The all precursor powders were staying amorphous up to 400°C. Some small peaks corresponding to the gamma lithium aluminate were begun to be developed about 600°C. Ash-like black powders were found at this temperature. But crystallinity was still very low up to 700°C. Phase pure gamma lithium aluminate was found at 800°C and white powders were obtained. It should be noted that no non-stoichiometric aluminate compounds were distinct at this temperature, which was an indication that no preferential evaporation of lithium was occurred. We concluded that all the three polymeric precursor processes produced gamma lithium aluminate powders around 800°C and the phase purities were about the same regardless of the preparation processes.

However, TG and DTA characteristics of precursor powders were observed to be different depending on the preparation processes. Figs. 5 and 6 showed the TG and DTA curves of the citrate precursor powder and citric acid, respectively. As shown in Fig. 5, there were several weight loss regions of 180–260°C, 260–500°C, and 560–620°C. The exothermic peak about 180°C appeared to be related with the nitrate decomposition. Baythoun and Sale reported that nitrate decomposition in citrate–nitrate gel took place about 200°C during the preparation of Mn_2O_3 [17]. The two peaks about 400°C corresponded to the decomposition of citric acid. At this stage, the precursor became black. About this temperature, similar peaks were found in the DTA curve of citric acid and the weight loss of the citric acid were finished about 440°C as indicated in Fig. 6. Saha et al. reported that the liberation of gases such as NO_2, CO, CO_2, and H_2O were helpful in disintegration of product and dissipation of the combustion heat which inhibited sintering of fine particles [10].

In this study, it was likely that the swelling during the precursor preparation along with the evolution of gases during heating the precursor improved the properties of

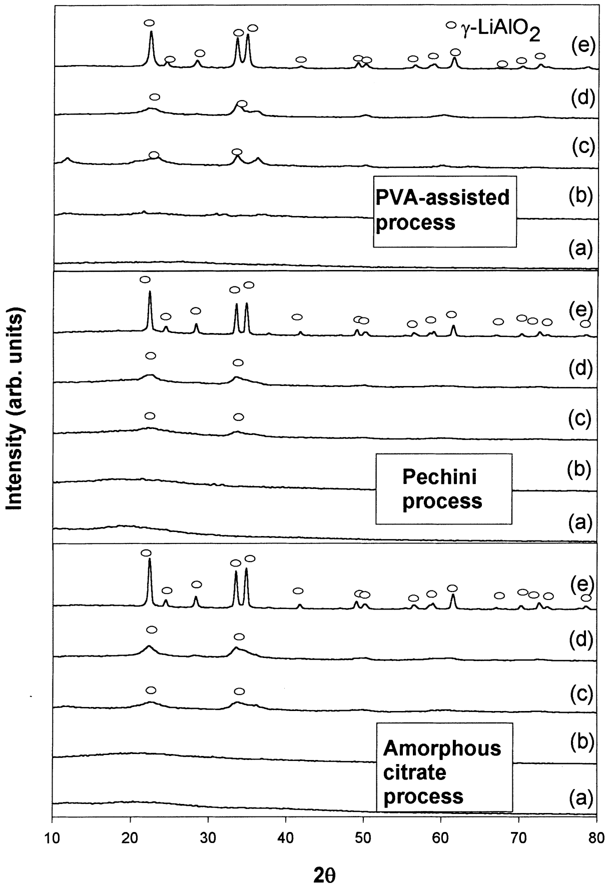

Fig. 4. Changes in XRD patterns of the citrate precursor, Pechini precursor, and PVA precursor powders upon heating at (a) 105°C, (b) 200°C, (c) 400°C, (d) 600°C, and (e) 800°C.

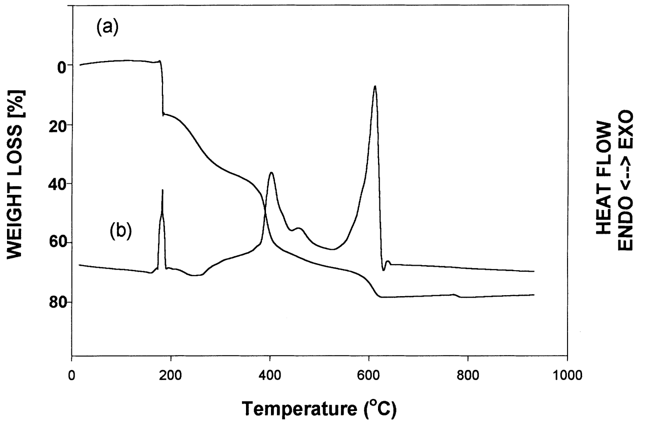

Fig. 5. (a) TG and (b) DTA curves of the citrate precursor powder in air flow of 100 ml/min.

the final product powders. The swelling of the gel at drying stage is not common and has not been reported elsewhere.

The last peak about 610°C in Fig. 5 was owing to the crystallization of lithium aluminate. This was confirmed by the fact that lithium aluminate phase began to appear in XRD patterns at 600°C. The thermogravimetric analysis showed that the major part of the weight loss associated with the decomposition and oxidation of the precursor was completed by 630°C. However, the color of precursor powder was still black because of residual carbon. The formation reaction of gamma lithium aluminate was continued up to the higher temperature. The sharpness of gamma lithium aluminate XRD peaks was increased with the temperature.

It can be assumed that the majority of NO_2 was evolved during the precursor powder preparation and thus hydrogen in a small portion of COOH groups of the precursor powder was replaced with NO_2. As shown in Fig. 5, the measured weight loss of the citrate precursor powder for the $LiAlO_2$ synthesis was 78%. The calculated weight loss was 84.1 wt% when we assumed that the precursor was composed of only citric acid and chelated cations and the ratio was one. The predicted value should not be higher than the measured value because the replaced NO_2 was not even taken into consideration. If some citric acid would be decomposed during the preparation of precursor powders and transformed to oligomeric or polymeric structure, the predicted value could be higher than the measured value. But it requires further investigation to prove this hypothesis.

Fig. 7 showed the TG and DTA curves of the Pechini precursor powder. Three exothermic peaks were found about 350°C, 430°C and 560°C, respectively. These temperatures were somewhat lower than those of citrate precursor powder. It was found that the precursor powders turned into black about 400°C. The two peaks

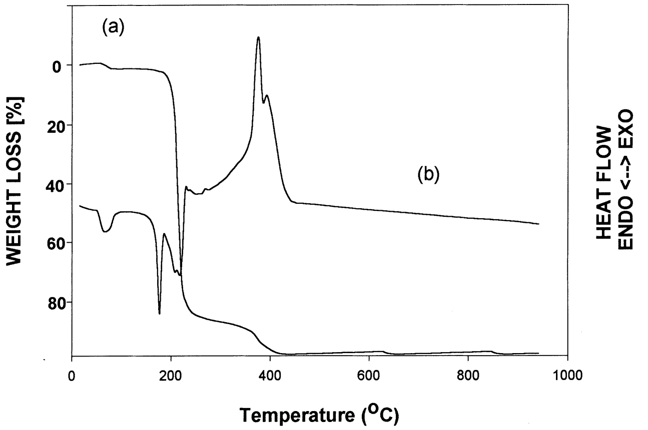

Fig. 6. (a) TG and (b) DTA curves of citric acid in air flow of 100 ml/min.

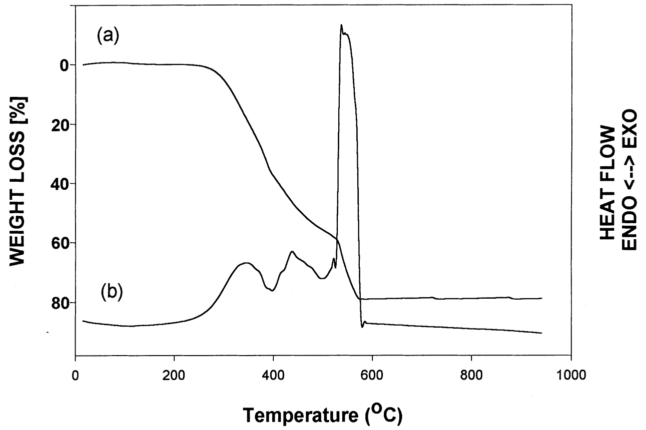

Fig. 7. (a) TG and (b) DTA curves of the Pechini precursor powder in air flow of 100 ml/min.

about 400°C appeared to be due to the decomposition of organic constituents. The peak about 560°C corresponded to the crystallization of lithium aluminate.

Figs. 8 and 9 showed the TG and DTA curves of the PVA precursor powder and PVA, respectively. The exothermic peak about 180°C, which was also observed in the citrate precursor powders, was attributed to the decomposition of nitrate. It was found that the precursor powders became black about 400°C. Two small peaks about 400°C appeared to be due to the decomposition of organic constituents as described in the citrate process. The peak about 610°C corresponded to the crystallization of gamma lithium aluminate, which was consistent with XRD results. There were some exothermic peaks in the region of 430–550°C in the DTA curve of PVA as shown in Fig. 9. These peaks were not observed in the PVA precursor.

The changes in functional group of the citrate precursor powder were examined by IR spectroscopy. Fig. 10 showed IR spectra of gel treated at various temperatures. At 105°C, carbonyl group (1730 cm^{-1}), carboxyl group (1638 cm^{-1}, 1232 cm^{-1}), and NO_3^- (1386 cm^{-1}) bands were observed [9,17]. Small band of CO_3^{2-} (875 cm^{-1}) was also observed. At 200°C, the bands of carbonyl group and NO_3^- disappeared. Carboxylate bands were still found at this temperature. At 600°C, the bands of gamma lithium aluminate and carboxylate (1382 cm^{-1}) were found. At 800°C, only the IR bands of gamma lithium aluminate were observed [18]. This result was consistent with the XRD result that phase of gamma lithium aluminate was very pure at this temperature.

The inherent disadvantage of the polymeric precursor method is the residual carbon present in the final product. Carbon content of lithium aluminate powders prepared by amorphous citrate process was examined. Table 2 showed the carbon content after firing of the citrate precursor powder in an air atmosphere at

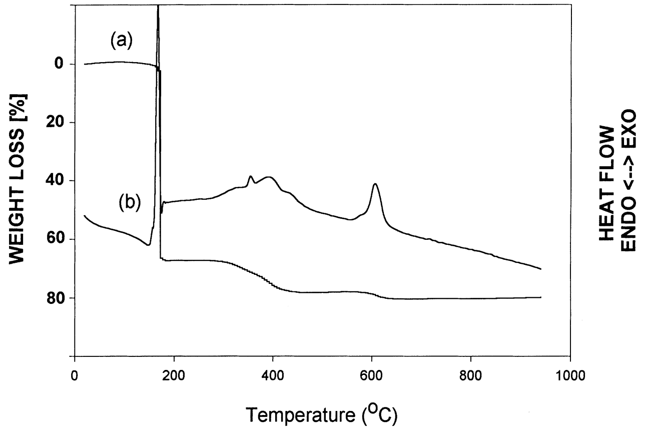

Fig. 8. (a) TG and (b) DTA curves of the PVA precursor powder in air flow of 100 ml/min.

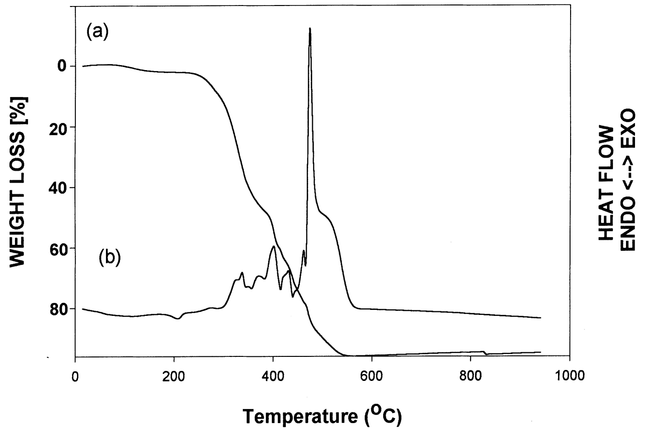

Fig. 9. (a) TG and (b) DTA curves of PVA in air flow of 100 ml/min.

temperatures of 950°C and 1100°C. The carbon content was lowered by extending the heating time and raising the temperature. This level of residual carbon in this study may give bad effect on the sinterability and other properties. There is a conflict in the experimental conditions required for high surface area and low carbon content [16]. Heating at high temperature can reduce the carbon content but it will lower surface area and give rise to particle growth. Baythoun and Sale proposed the firing of precursor powder in oxygen atmosphere to reduce the carbon content [17]. Further study should be conducted to reduce the residual carbon without firing at high temperature.

The effect of mole ratio of hydrocarboxylic acid to total cations was studied. The mole ratio of citric acid to total cations was varied as 0.5, 1.0, 1.5, and 2.0. The effect of the mole ratio on the content of residual carbon

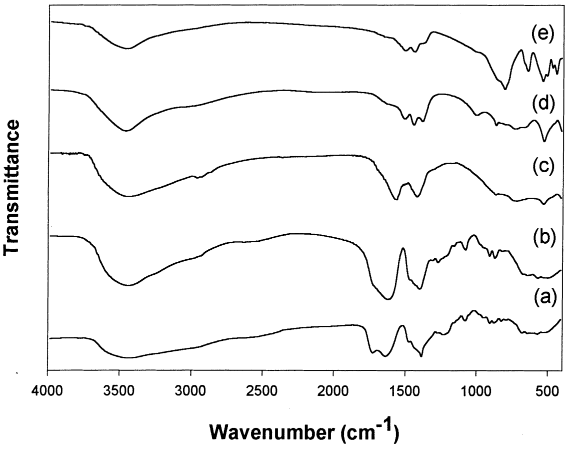

Fig. 10. IR spectra of the citrate precursor heated at (a) 105°C, (b) 200°C, (c) 400°C, (d) 600°C, and (e) 800°C.

was not significant as shown in Table 2. However, it was found that higher mole ratio gave low crystallinity in the XRD patterns of lithium aluminate powders prepared by heating of the precursors at 800°C. Considering that excess citric acid resulted in the sticky precursor, low swelling ratio, and low crystallinity, high mole ratio of citric acid to total cations were not favorable for the process.

The BET specific surface area of the lithium aluminate powders, prepared by heating of the precursors at 900°C for 2 h, was about 15 m^2/g. This value is slightly lower than the surface area of sol–gel derived lithium aluminate powders prepared by Kwon and Park [8], which was about 17.5 m^2/g at the same heating condition.

During the preparation of lithium aluminate powders, there was no critical parameter that should be controlled carefully at each step of the preparation procedure. γ-phase was directly developed from the three precursors without being preceded by α- or β-phase. This is helpful to get the phase purity of gamma lithium aluminate. Advantages of the Pechini process over other processes were not claimed in the present study because the Pechini process had more preparation steps.

Table 2
Residual carbon analysis in lithium aluminate powder prepared by the amorphous citrate process

Mole ratio (citric acid to total cations)	Heating temperature (°C)	Carbon content (wt%)	
		2 h	5 h
0.5	950	0.537	0.047
1.0	950	0.779	0.053
1.5	950	0.818	0.052
2.0	950	0.787	0.046
0.5	1100	0.020	0.014

The polymeric precursor routes adopted in this study are comparable to sol–gel process in the phase purity and specific surface area of gamma lithium aluminate and processing temperature, and yet the preparation procedures are simple and high quality starting materials such as alkoxides are not used.

4. Conclusions

Phase pure gamma lithium aluminate powders were prepared by three polymeric precursor methods – amorphous citrate process, Pechini process, and PVA-assisted process. XRD, TG-DTA, and IR studies showed that all the three precursor powders were begun to be gamma lithium aluminate at about 600°C. Phase pure crystalline lithium aluminate was formed about 800°C. There were no remarkable differences in terms of phase purity, processing temperature, and residual carbon. The amorphous citrate process and the PVA-assisted process were, however, more favorable than the Pechini process since the preparation procedures of the Pechini process were more complicated.

We conclude that the polymeric precursor routes adopted in this study are comparable to sol–gel process in the phase purity and processing temperature, and have more advantages over alkoxide derived sol–gel process in terms of the simplicity of the procedures and absence of handling of alkoxides.

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