

The transformation of LiAlO_2 crystal structure in molten Li/K carbonate

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Abstract

LiAlO_2 powder is used as a matrix material in the electrolyte substrate of molten carbonate fuel cells (MCFCs), and LiAlO_2 are known to undergo phase transformations between the α -phase and γ -phase in molten Li/K carbonate. In order to understand the phenomena involved in this phase transformation of LiAlO_2 , it is clear that it will be necessary to consider the fact that the solubility and mass transfer rate in molten Li/K carbonate differ between these two phases. Also, the solubility differs due to differences in the particle sizes of the LiAlO_2 powder, namely, the fine particles dissolve more easily than the large particles. The other factors conventionally considered are the partial pressure of CO_2 and the temperature of the surrounding gas. In the present paper, it has become possible that the seemingly complex phenomena of LiAlO_2 phase transformation within molten carbonate can be understood without any contradiction. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Molten carbonate fuel cells (MCFCs), are expected to potentially provide high-efficiency power generation, and their development is progressing to such an extent that some prototype demonstration power plant tests have been already experienced. Although the effort directed at their technical realization is substantial, optimized resolution in ensuring sufficient durability for such fuel cells still remains as a significant technical issue.

One of the important physical phenomenon affecting the cell durability is the thermodynamic stability of electrolyte substrate. The electrolyte substrate is a porous plate manufactured from LiAlO_2 powder, and is formed into a matrix which will be impregnated with molten carbonate of alkali metals. Since LiAlO_2 can take two crystal structures such as α - LiAlO_2 or γ - LiAlO_2 depending on thermodynamic states and chemical environmental conditions, phase transformation may occur during operation of the MCFCs. In particular, considering the fact that there is a substantial difference in the density between α - LiAlO_2 and γ - LiAlO_2 , this phase transformation may lead to cause a change in the pore size distribution of the matrix.

There have been many research studies on the phase transformation of LiAlO_2 for MCFC applications. An example of the available data concerning the thermodynamic phase diagram for LiAlO_2 crystal structures is the one proposed by Byker et al. [1], where the stable crystal structure under an air atmosphere condition were determined in terms of bulk pressure and temperature. According to this diagram, the stable crystal structure is well within a stable γ - LiAlO_2 domain for a condition with an atmospheric pressure and a temperature of 650 °C which is typical for the operating condition of MCFCs. Here, however, they did not take into account the effects of molten carbonate and gas phase carbon dioxide present in real fuel cell operating conditions.

Hato et al. [2] reported that all of the LiAlO_2 transformed into α - LiAlO_2 after 50 h when an electrolyte substrate was prepared using LiAlO_2 powder with an average particle size of 0.1 μm manufactured by Sumitomo Chemical Co. Ltd., which contained only minute amounts of α - LiAlO_2 . On the other hand, they also found that electrolyte substrates using γ - LiAlO_2 manufactured at Cyprus Foote Mineral Co. Ltd., remained stable even after 3000 h [2]. This suggests that the determination of crystal structure is affected by material physical properties and preparation procedures, and that it is essential to consider the rates of phase transformation to confirm that the thermodynamic equilibrium state is

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reached for an individual condition used in the reported experiments.

In the presence of molten carbonate, there are several works on the crystal structure. For example, Fairchild and Brown [3] have reported the irreversibility of transformation from α -LiAlO₂ to γ -LiAlO₂ in molten carbonate. Also, Tanimoto et al. [4] studied the effect of operating atmosphere on the rate and the final state of the transformation. In their experiment, where α -LiAlO₂ was heated in molten carbonate under conditions of a CO₂ atmosphere at 702 °C, α -LiAlO₂ remained intact after 442 h, but transformed into γ -LiAlO₂ after 1062 h. In addition, it has been reported that the α -LiAlO₂ content in the electrolyte tile matrices increases greatly after many hours of operation [4].

Furthermore, it has been reported that in an air gas flow, in which molten carbonate does not coexist, α -LiAlO₂ transformed into γ -LiAlO₂ after 40 h at 937 °C, but remained as α -LiAlO₂ after 64 h at 837 °C [5]. Furthermore, reports of heating mixed powders of α -LiAlO₂ and γ -LiAlO₂ in molten carbonates indicate that the proportion of α -LiAlO₂ tends to increase under conditions where the partial pressure of the CO₂ in the gas atmosphere is high and the temperature of the molten carbonate is low, but that the proportion of γ -LiAlO₂ is likely to increase under conditions where the CO₂ partial pressure in the atmosphere gas is low and the molten carbonate temperature is high [6].

As outlined earlier, there have already been many reports concerning the transformations between α -LiAlO₂ and γ -LiAlO₂, but the findings of these reports are often conflicting.

We supposed that phase transformation based on dissolution–deposition mechanism of LiAlO₂ in molten carbonate. That is, the final crystal structure is decided by the interaction between a crystal structure that is easy to melt and a crystal structure that becomes crystal nucleus where deposition takes place.

In the dissolution–deposition mechanism of LiAlO₂, growth of particles progresses by the process that small-size particles dissolve in molten carbonate and deposit on the surfaces of large-size particles [7]. In a system where solid phase is dispersed in liquid phase, the solubility in liquid phase is in inverse proportion to the particle size, and small-size particles have larger solubility than large-size particles. Due to the difference of the solubility, there arises concentration gradient in liquid phase. Dissolved substance is transported from small-size particles to large-size particles by diffusion and the growth of particles will progress. This phenomenon is called Ostwald ripening [8]. It is expected that the growth of particles will be affected by filling state of particles [7].

We turned our attention to the solubility of crystal structure and the particle size which were factors in dissolution–deposition mechanism. We report on a study to investigate in detail the phase transformation phenomena between the α -LiAlO₂ and γ -LiAlO₂ in molten Li/K carbonate.

2. Experimental

2.1. Materials and reagents

Four different types of LiAlO₂ powder were prepared for the present experiment. They are (1) α -LiAlO₂ powder(A): α -phase with fine particle size, (2) α -LiAlO₂ powder(B): α -phase with coarse particle size, (3) γ -LiAlO₂ powder(a): γ -phase with fine particle size and (4) γ -LiAlO₂ powder(b): γ -phase with coarse particle size. The particle size for fine powder ranges between 0.1 and 4 μ m with a median particle size of approximately 0.5 μ m, whilst for coarse particles it ranges between 1 and 20 μ m with a median particle size of 5 μ m. In the following sections, preparation procedure for each powder category is described.

2.1.1. α -LiAlO₂ powder(A)

α -LiAlO₂ powder with fine particle size was prepared following the process shown in Fig. 1. LiAlO₂ powder (HSA-19, Cyprus Foote Mineral Co. Ltd.) was mixed with Li/K eutectic carbonates in a weight proportion of 1:1. The mixture was blended in a ball mill in ethanol and heat treated for 100 h at 650 °C in an air atmosphere after drying at 80 °C to remove the ethanol. The eutectic carbonates were then dissolved in a mixture solution of acetic acid and acetic anhydride. After filtration, they were agitated for 18 h in a

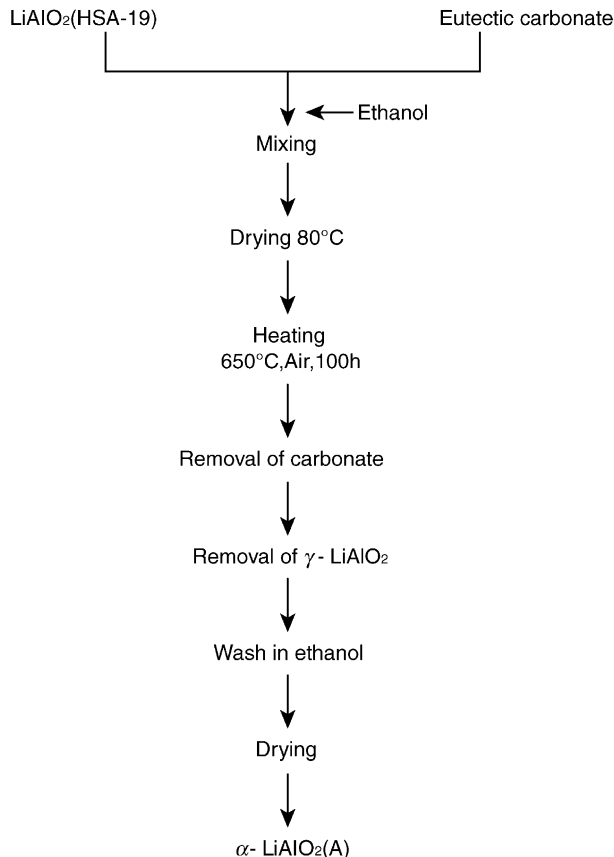


Fig. 1. Method of preparing α -LiAlO₂ powder(A).

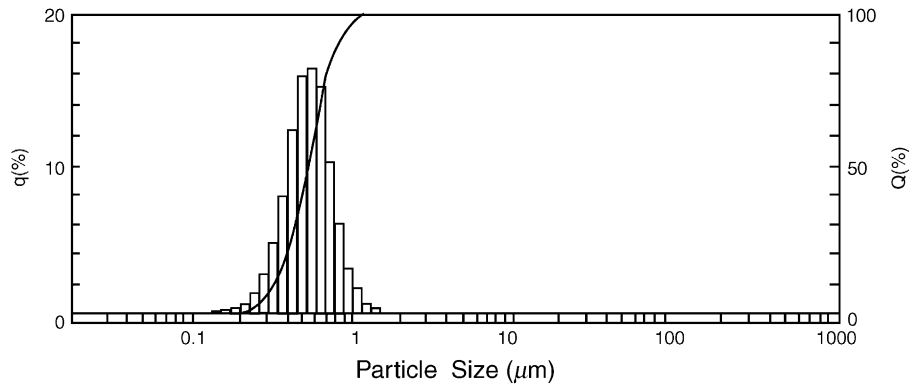


Fig. 2. Particle size distribution of α -LiAlO₂ powder(A). Median size = 0.457 μ m.

12% aqueous hydrochloric acid solution, and the γ -LiAlO₂ was dissolved. After the undissolved powder was collected, it was washed and dried.

Analysis of the resulting powder by X-ray diffraction verified that it was α -LiAlO₂. The results of particle size distribution measurement, performed according to a method described later, are shown in Fig. 2.

2.1.2. α -LiAlO₂ powder(B)

Fig. 3 shows the method for preparing α -LiAlO₂ with coarse particle sizes. Equal moles of γ -Al₂O₃ powder (with a specific surface area of 10 m²/g) and lithium carbonate were mixed, and the mixture was heated in an electric furnace with a carbon dioxide gas flow at 900 °C for 24 h. The resulting powder was verified as α -LiAlO₂ by X-ray diffraction analysis. It was then mixed with γ -Al₂O₃, lithium carbonate, and Li/K carbonates in a weight ratio of 1:2.4:1.6:15 and heat treated for 100 h at 650 °C in an air atmosphere. After the non-reacted eutectic carbonates were then dissolved in a mixture of acetic acid and acetic anhydride, further the γ -LiAlO₂ powders were dissolved in a 12% aqueous hydrochloric acid solution. This procedure was repeated to gradually increase the size of the α -LiAlO₂ particles until an α -LiAlO₂ powder with large particle sizes was obtained. The results of measuring the particle size distribution are shown in Fig. 4.

2.1.3. γ -LiAlO₂ powder(a)

As shown in Fig. 5a, equal moles of aluminum triisopropoxide and lithium hydroxide monohydrate were first heated at 70 °C in isopropyl alcohol. After removing the isopropyl alcohol, the mixture was heated for 1 h at 1000 °C in an air atmosphere in an electric furnace. The resulting powder was finely pulverized in a ball mill to obtain a powder. The powder was verified to be γ -LiAlO₂ by X-ray diffraction analysis. Fig. 6a shows the results of particle size distribution measurements.

2.1.4. γ -LiAlO₂ powder(b)

As shown as Fig. 5b, γ -LiAlO₂ powder(a) was blended with Li/K carbonates in a ball mill in ethanol. After removing

the ethanol, the mixture was heat treated in an electric furnace for 100 h at 700 °C in an air atmosphere. The eutectic carbonates were then dissolved in a mixture of acetic acid and acetic anhydride. The powder was then immediately washed in ethanol and dried. The results of X-ray diffraction analysis verified that the resulting powder

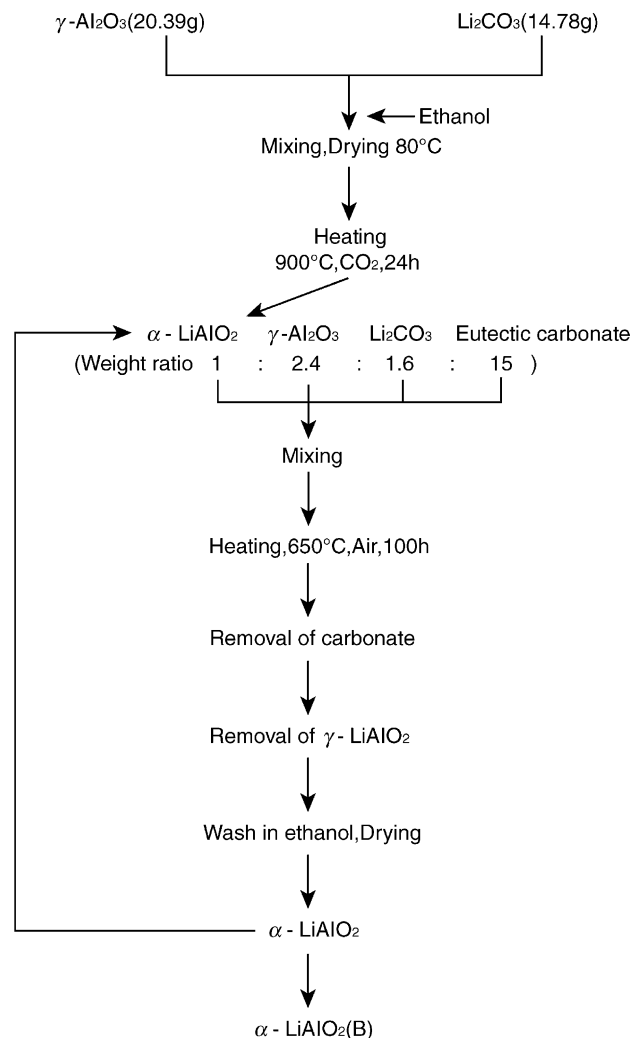


Fig. 3. Method of preparing α -LiAlO₂ powder(B).

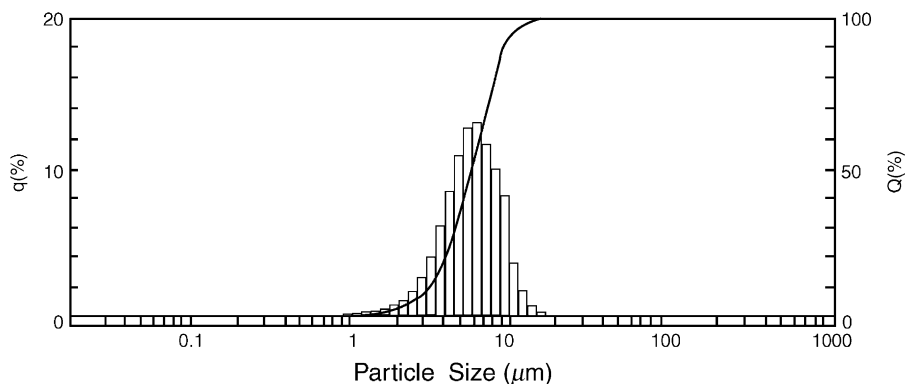


Fig. 4. Particle size distribution of α -LiAlO₂ powder(B). Median size = 6.017 μ m.

was γ -LiAlO₂. Fig. 6b shows the particle size distribution measurements of the powder.

2.2. Method for immersion into molten carbonate

A sketch of the experimental apparatus used is shown in Fig. 7. It has been reported that the sintering pellet of LiAlO₂ is used as immersion test sample [6]. However, we have reported that the growth of LiAlO₂ particles in molten carbonate tends to start in areas having a high degree of particle filling and the state of coagulation has a great influence on the growth of particles [7]. So, we used the LiAlO₂ powder to eliminate the effect of the coagulation. LiAlO₂ powder and Li/K carbonates were mixed and placed in a gold Tanmann tube. The tube was maintained for a

specified time at a specified temperature while a specified atmospheric gas flowed in at a rate of 20 ml/min.

After heat treatment in the molten carbonate was completed, the tube was cooled and the mixture of the sample and eutectic carbonates was removed and pulverized in a mortar. Following pulverization, it was mixed into a 1:1 mixture of acetic acid and acetic anhydride, and the eutectic carbonates were dissolved. The LiAlO₂ sample was filtered out, washed with ethanol, and dried.

2.3. Method of separating α -LiAlO₂ and γ -LiAlO₂ powders

Mixed α -LiAlO₂ and γ -LiAlO₂ powders were placed in a 12% aqueous hydrochloric acid solution. After agitation for

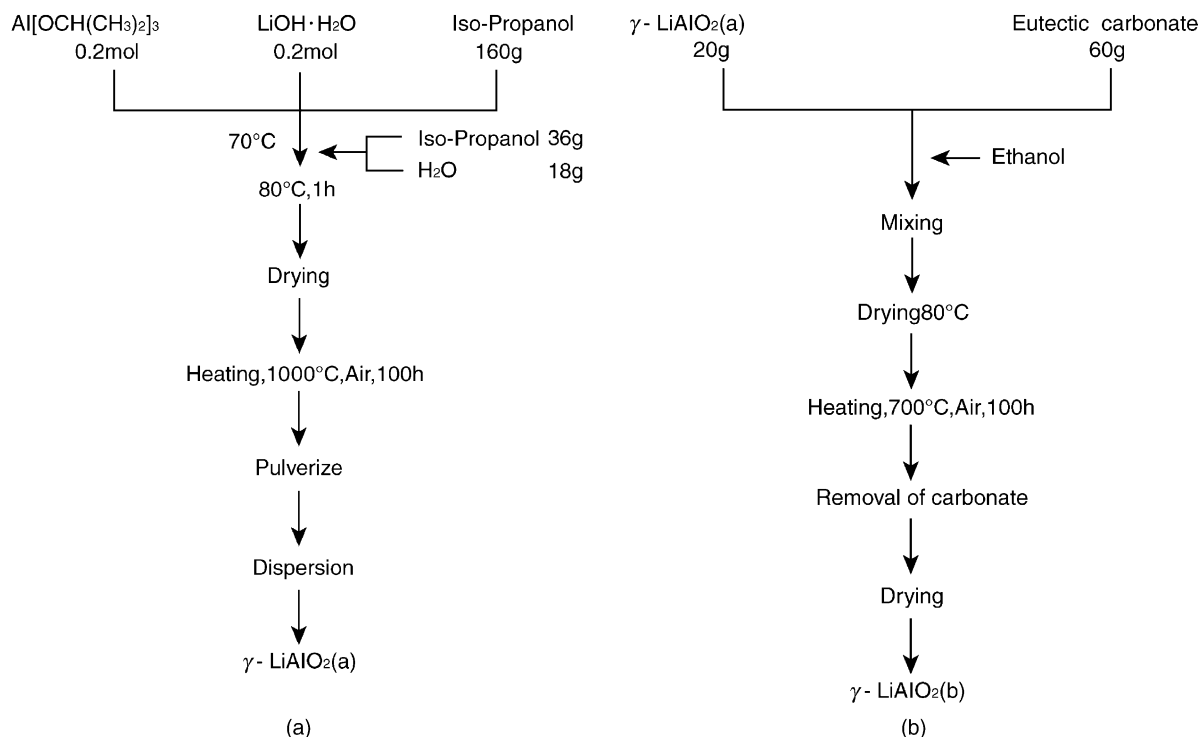


Fig. 5. Method of preparing γ -LiAlO₂: (a) γ -LiAlO₂ powder(a); (b) γ -LiAlO₂ powder(b).

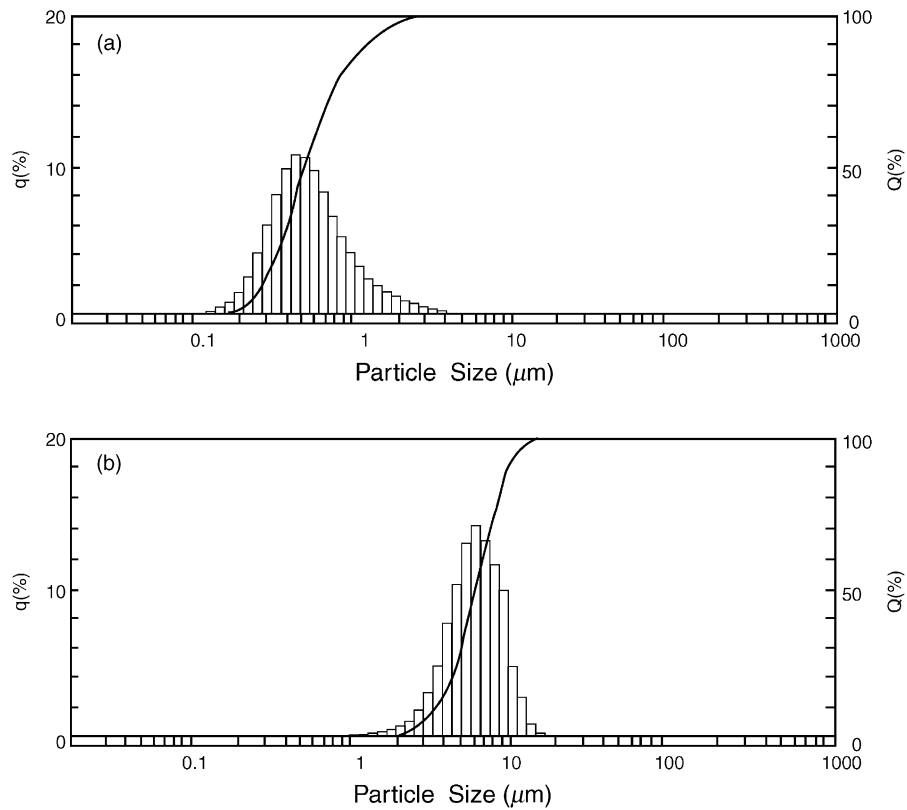


Fig. 6. Particle size distribution of γ -LiAlO₂ powders: (a) γ -LiAlO₂(a), median size = 0.481 μm ; (b) γ -LiAlO₂(b), median size = 6.240 μm .

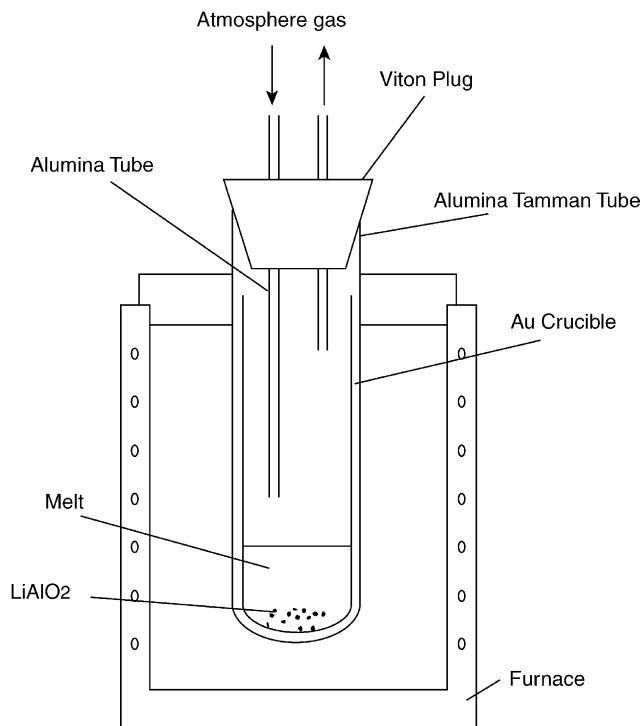


Fig. 7. Diagram of experimental apparatus for immersing LiAlO₂ in molten carbonate.

18 h, the undissolved α -LiAlO₂ powder was collected by filtration, washed in ethanol, and dried.

2.4. Method of measuring particle size distribution

A laser diffraction/scattering particle size distribution measuring apparatus made by Horiba Manufacturing Co. Ltd. (LA-910) was used to measure the particle size distribution of the LiAlO₂ powder.

3. Results

3.1. Experiment 1

α -LiAlO₂(A) and γ -LiAlO₂(a) powders with roughly the same particle sizes were mixed and immersion-treated in molten carbonate with a gas atmosphere having a CO₂ partial pressure of 0.3 atm at 650 °C for 25 h. This immersion treatment condition was within the range of crystal phase stability for α -LiAlO₂ according to Tomimatsu et al. [6]. The resulting powder was examined to determine a particle size distribution and it was found that the distribution had two peaks as shown in Fig. 8a.

Since, γ -LiAlO₂ dissolves easily in a 12% aqueous hydrochloric acid solution unlike α -LiAlO₂, the separation of α -LiAlO₂ from the resulting powder could be possible by applying such solution. Actually, the collected powder was

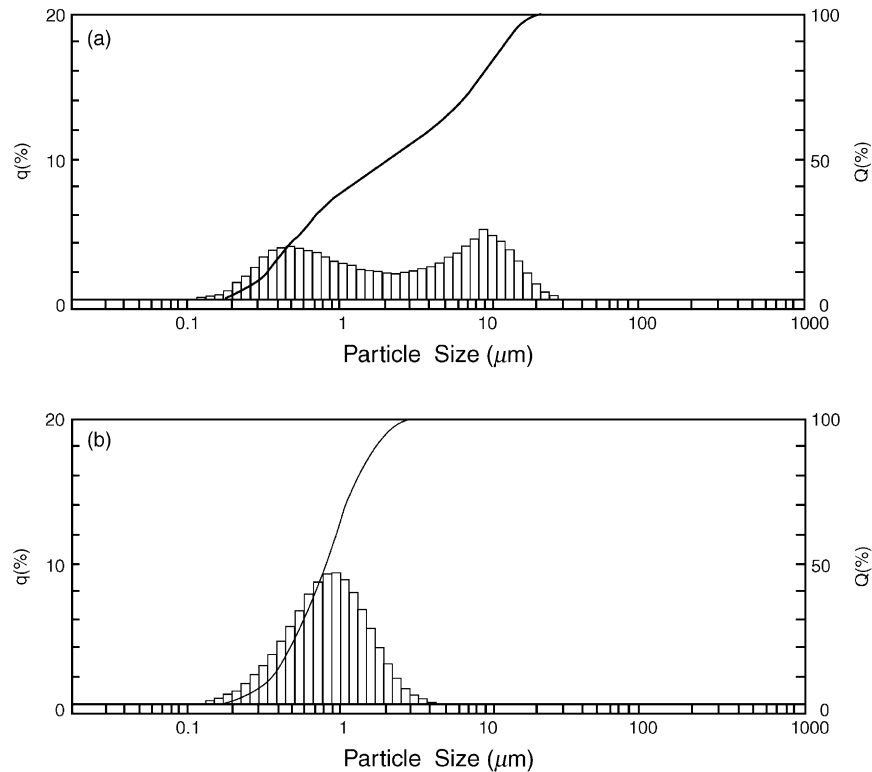


Fig. 8. Changes in particle size distribution following heat treatment of mixture of α -LiAlO₂(A) and γ -LiAlO₂(a) powders. $T = 650\text{ }^{\circ}\text{C}$, time = 25 h, $P_{\text{CO}_2} = 0.3\text{ atm}$. (a) Before HCl cleaning, (b) after HCl cleaning.

analyzed to determine particle size distribution, and the results is shown in Fig. 8b. From the results of the particle size distribution measurements shown in the two figures it can be seen that the peak for the larger particle size shown in Fig. 8a is γ -LiAlO₂, and the peak for the smaller particle size is α -LiAlO₂.

However, the average particle size of the γ -LiAlO₂ became larger than that of the α -LiAlO₂. Thus, the mass transfer rate between particles of γ -LiAlO₂ in molten carbonate can be considered to be faster than that of α -LiAlO₂, with the growth rate of the γ -LiAlO₂ particles being extremely rapid.

3.2. Experiment 2

γ -LiAlO₂ powder(a) was heated in molten carbonate in a gold Tanmann tube for 50 h under conditions of $650\text{ }^{\circ}\text{C}$ and a CO₂ partial pressure of 0.3 atm in the atmosphere gas. The

results of X-ray diffraction analysis of the powder following this treatment are shown in Fig. 9.

Although the conditions were those reported to be in the “range of α -LiAlO₂ stability” according to Tomimatsu et al. [6], no transformation from γ -LiAlO₂ to α -LiAlO₂ was observed here.

3.3. Experiment 3

α -LiAlO₂ powder(A) only was inserted into an alumina crucible and heat treated at varying temperatures and heating times in an electric furnace with an air atmosphere. The results of the α -LiAlO₂/ γ -LiAlO₂ ratio of the LiAlO₂ powder obtained by X-ray diffraction following treatment are shown in Table 1. The transformation from α -LiAlO₂ to γ -LiAlO₂ progressed much more rapidly as the heat treatment temperature rose and the heating time increased.

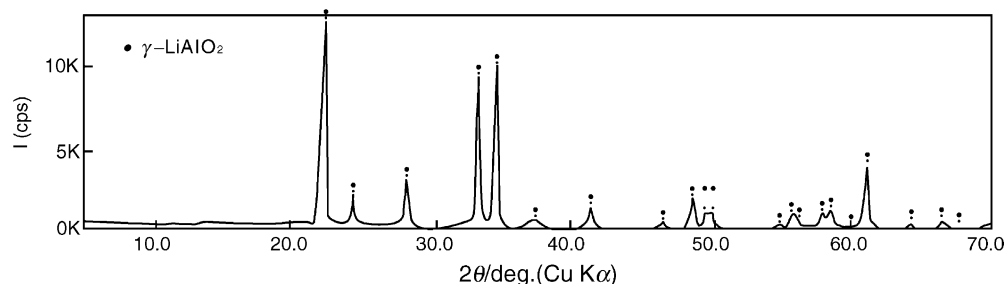


Fig. 9. X-ray diffraction analysis results following immersion experiments on γ -LiAlO₂ powder(a). $T = 650\text{ }^{\circ}\text{C}$, time = 50 h, $P_{\text{CO}_2} = 0.3\text{ atm}$.

Table 1
Ratio (α/γ) following heat treatment of α -LiAlO₂ powder(A) only^a

Temperature (°C)	Time (h)	Product (α/γ weight ratio)
600	100	100/0
650	100	100/0
700	200	100/0
725	100	100/0
725	200	99/1
750	50	100/0
750	55	0/100
775	25	99/1
775	50	92/8
800	10	94/6
800	25	0/100

^a Ambient air atmosphere.

3.4. Experiment 4

α -LiAlO₂(B) powder and γ -LiAlO₂(b) powder were mixed in a weight ratio of 62:38, and the powder was mixed with Li/K eutectic carbonates. The mixture was heat treated for 200 h in a gold Tanmann tube at 650 °C under a gas atmosphere with a CO₂ partial pressure of 0.3 atm. The results of measurement of the LiAlO₂ that was collected after the heat treatment by X-ray diffraction showed that the α -LiAlO₂/ γ -LiAlO₂ ratio had become 64:36. With large LiAlO₂ particle sizes, it is less likely that differences in solubility in molten carbonate will emerge due to particle size differences. Considering this, it may be surmised that the solubility of α -LiAlO₂ will be less than that of γ -LiAlO₂

under conditions where solubility in molten carbonate is unlikely to be influenced by the particle sizes.

4. Discussion

The present study aimed at obtaining a comprehensive explanation of the crystal structure transformation for LiAlO₂, that has remained in some confusion when previous literatures on this subject are reviewed. As can be seen in Fig. 10, the major task here is to evaluate the importance of individual passages for the changes of crystal structure and particle size; they are the passages (a) to (h). Also, a summary of the following discussion is given in Table 2 where the modes of crystal phase transformation and particle size growth are indicated according to the process conditions that LiAlO₂ particle may undergo in various experimental works.

4.1. Single phase powder as starting material in an air atmosphere

Considered here are powders with either α -phase or γ -phase as starting material. The transformation of crystal phase was examined under the conditions with a temperature of around 650 °C in the previous literature. For example, the phase diagram given by Byker et al. [1] shows that, in an air atmosphere, γ -LiAlO₂ should be more stable than α -LiAlO₂ under the operating temperature conditions for MCFCs. Therefore, passages (a) and (b) in Fig. 10 are conspicuous.

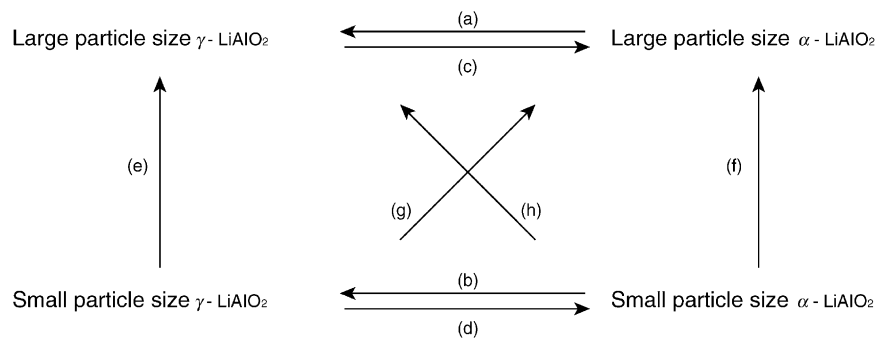


Fig. 10. Relation between allotropic form and particle size.

Table 2
Summary of the conditions for phase transformation

Conditions			α -LiAlO ₂		γ -LiAlO ₂		Passages in Fig. 10
Atmosphere	Phase	Particle size	$\alpha \rightarrow \alpha$	$\alpha \rightarrow \gamma$	$\gamma \rightarrow \gamma$	$\gamma \rightarrow \alpha$	
Air	Single	–	× ^a	○ ^b	○	×	(a), (b)
CO ₂	Single	–	○	×	○	×	(e), (f)
	Mixed	Small ($\alpha = \gamma$)	○	×	○	×	(e), (f)
	Mixed	Large ($\alpha = \gamma$)	×	×	×	○	(c)
	Mixed	$\alpha > \gamma$	×	×	×	○	(g)
	Mixed	$\alpha < \gamma$	×	○	×	×	(h)

^a X: Phase-transformation and/or particle-growth does not occur.

^b O: Phase-transformation and/or particle-growth occur.

4.2. Single phase powder as starting material in a CO₂ atmosphere

Even when used a single phase powder as starting material, however, α -LiAlO₂ becomes stable under conditions where the temperature of the molten carbonate is around 650 °C and the CO₂ partial pressure in the atmosphere gas is high, as has been reported by Tomimatsu et al. [6]. This indicates that it is possible that the existence of molten carbonate exerts the effect of stabilizing the α -LiAlO₂ powder.

On the other hand, there observed no transformation from γ -LiAlO₂ to α -LiAlO₂ in experiment 2 where the powder was treated under the condition of 650 °C with a CO₂ partial pressure of 0.3 atm. It indicates that passages (c) and (d) in Fig. 10 do not occur in this condition. This is in accordance with the result of Fairchild and Brown [3] where the irreversibility of transformation between α -phase and γ -phase was discussed.

Perhaps, most interesting result here is that the no phase transformation occurs when a single phase LiAlO₂ powder is treated under a condition with a temperature of 650 °C and a sufficient amount of CO₂ to be present. Therefore, the transformation passages relevant to this condition may be passages (e) and (f) that express the growth of particle size only.

4.3. Mixed powder condition with small particle size under a CO₂ atmosphere

Considered here is the case where α -LiAlO₂ and γ -LiAlO₂ particles are both present and there is little difference in particle size between them initially. As for the crystal growth rates of particles in molten carbonate, passage (e) is much faster than passage (f), as can be seen from the result of experiment 1. That is, γ -LiAlO₂ powder with small particle sizes changes into γ -LiAlO₂ with large particle sizes in a shorter period of time than that for α -LiAlO₂, and thus, the difference in particle size between γ -LiAlO₂ and α -LiAlO₂ should rapidly increase. This difference is especially pronounced when the temperature is high or the CO₂ partial pressure in the atmosphere gas is low [9]. Therefore, under this condition, no phase transformation can be observed until the particle size growth is reached to that extent where there is significant difference in particle sizes for the two phases, as discussed later.

4.4. Mixed powder condition with large particle size under a CO₂ atmosphere

The result of experiment 4 shows that when the particle sizes of the α -LiAlO₂ and γ -LiAlO₂ powders are both large (in other words, under conditions where the particle size itself will have little influence on solubility of LiAlO₂ in the molten carbonate), γ -LiAlO₂ powder will dissolve into molten carbonate and deposit on α -LiAlO₂ particles. This tendency exhibits that the solubility of γ -LiAlO₂ particles in molten carbonate is greater than that of α -LiAlO₂. For this

condition, the transformation goes from γ -phase to α -phase via passage (c) in Fig. 10.

4.5. Mixed powder condition with different particle size (α -LiAlO₂ > γ -LiAlO₂)

If the difference in particle size becomes large enough, a difference in the solubility of the LiAlO₂ particles in the molten carbonate will also arise. When there is a substantial difference in initial particle sizes for α -LiAlO₂ and γ -LiAlO₂ particles, passages either (g) or (h) progresses. For example, when the initial particle size is greater for α -LiAlO₂, since powder with small particle size is more soluble in molten carbonate than powder with large particle size, α -LiAlO₂ becomes less soluble in molten carbonate. As a result, the γ -LiAlO₂ will dissolve and deposit onto the surface of the α -LiAlO₂ particles, so that the particle size will tend to increase. In this case, passage (g) is relevant.

4.6. Mixed phase powder with different particle size (α -LiAlO₂ < γ -LiAlO₂)

On the contrary to the previous case in 4.5, when the initial particle size for γ -LiAlO₂ is greater, the solubility of the γ -LiAlO₂ powder will decrease. As a result, the α -LiAlO₂ powder will dissolve and re-deposit on the surface of the γ -LiAlO₂ powder. The γ/α ratio in the LiAlO₂ sample will tend to increase. Relevant passage for the phase transformation is passage (h) in this case.

5. Conclusions

When the crystal phase transformation of LiAlO₂ is discussed, it is important to take into consideration the initial particle size and the condition of process atmosphere such as temperature and presence of carbon dioxide. The elements of overall phenomena can be listed in the following: (i) small-size particles dissolve in molten carbonate and deposit onto the surfaces of large-size particles; (ii) as can also be seen from the phase diagrams, γ -LiAlO₂ is more stable than α -LiAlO₂ under the temperatures and pressures of MCFC operating conditions; (iii) where there is little effect of particle size on solubility, it is harder for α -LiAlO₂ to dissolve in molten carbonate than γ -LiAlO₂; (iv) the growth rate of γ -LiAlO₂ particles in molten carbonate is extremely large in comparison to that of α -LiAlO₂. The difference in growth rates between the two phases becomes especially pronounced at high temperature and low CO₂ partial pressure within the atmosphere gas, the conditions that tend to accelerate the growth of LiAlO₂ particles.

When these points are considered, the seemingly complex phenomena of LiAlO₂ phase transformations within molten carbonate can be understood without any contradiction, though still is required more quantitative approach such as evaluating the rates of transformation in relation to

particle size and atmosphere. Also, there may be other aspects to take into consideration. For example, because alumina fiber is usually used as a support material in the electrolyte tiles of the MFCs, there is a possibility that particles of α -LiAlO₂, a reaction product of alumina and molten carbonate, may function as nuclei for the growth of α -LiAlO₂. The influence of this on phase transformations over time in the proportions of LiAlO₂ crystal structures in molten carbonate must be considered.

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