

## Influence of stabilizer ( $\text{Li}_2\text{O}$ ) on the sintering density and ionic conductivity of K- $\beta/\beta''$ -aluminas

Woo-Sung Kim, Jae-Ho Shin, Seok-Jun Kim, Hee-Min Kim and Sung-Ki Lim\*

Department of Materials Chemistry and Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Korea

Sintering of K- $\beta$ -aluminas in the system  $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{Li}_2\text{O}$  was carried out at atmospheric pressure. The influence of  $\text{Li}_2\text{O}$  as a stabilizer on densification and ionic conductivity, depending on its content, has been investigated. In order to lower the sintering temperature, the calcined powders were ultra-fine milled by an attrition mill. Relations between sintering density, microstructure and ionic conductivity were studied. The samples were prepared in the molar ratio range  $[\text{K}_2\text{O}]:[\text{Al}_2\text{O}_3]=1:5-1:11$ , and the  $\text{Li}_2\text{O}$  content was varied from 0 to 1.6 wt%. The maximum ionic conductivity has been observed with the sample having a molar ratio of  $[\text{K}_2\text{O}]:[\text{Al}_2\text{O}_3]=1:5$  and containing 0.8 wt% of stabilizer. This sample showed 97% density and its ionic conductivity was measured to be  $1.1 \times 10^{-1}$  and  $5 \times 10^{-3}$  S/cm at 800 °C and 300 °C, respectively.

**Key words:** K-beta-aluminas, Sintering, Ionic conductivity, Stabilizer ( $\text{Li}_2\text{O}$ ).

### Introduction

Ceramic electrolytes possessing a high ionic conductivity have been focused at solid oxide fuel cells (SOFC) and much effort has been made to reduce the operation temperature. There are many candidates operating between 300 and 700 °C such as cationic-doped ceria, e.g. gadolinium-doped ceria (GDC), yttrium-doped ceria (YDC) and lanthanum gallate (LSGM)-based electrolytes, that are currently being investigated [1, 2]. From this point-of-view, proton- $\beta/\beta''$ -aluminas may be a promising competitor to these materials.

Proton- $\beta/\beta''$ -aluminas exhibit a conductivity value of  $5 \times 10^{-3}$  S/cm at 300 °C [3]. Nicholson et al. [3] demonstrated the use of proton- $\beta''$ -alumina in a water electrolysis cell that operated between 100 and 300 °C. In the structure of  $\beta/\beta''$ -aluminas, the aluminum and oxygen ions form spinel blocks. The mobile ions (monovalent or multivalent ions) are located in layers between them. The spinel blocks are connected to each other by oxygen ion bridges within the conducting layer. The ionic conductivity for various mobile ions in the  $\beta/\beta''$ -aluminas structure along the conduction planes, shows a maximum for an optimum size of the ions [4, 5]. The working temperature of the fuel cells, based on this solid electrolyte material, is lower than that of the other materials mentioned before. The preparation of proton- $\beta/\beta''$ -aluminas, however, has limitations similar to other materials. For the use of proton- $\beta/\beta''$ -aluminas as a

solid electrolyte, they have to be sintered to make dense materials. However, the  $\text{H}_3\text{O}^+$  ions in proton- $\beta/\beta''$ -aluminas evaporate during the sintering process and this causes the destruction of the  $\beta/\beta''$ -aluminas structure. For the preparation of proton- $\beta/\beta''$ -aluminas, conventional ion-exchange using M- $\beta/\beta''$ -aluminas (M: alkali metals) as a precursor is the most available technology. Specifically, K- $\beta/\beta''$ -aluminas are the ideal precursor on account of the similarity in ionic radius between  $\text{H}_3\text{O}^+$  ( $r=0.138$  nm) and  $\text{K}^+$  ( $r=0.133$  nm). This similarity in size between these two ions constrains any mechanical stress built up during ion exchange [6-9]. However, K- $\beta/\beta''$ -alumina materials are difficult to densify due to the anisotropic and exaggerated grain growth and high vapor pressure of the alkali oxides, which causes porosity and even a phase transition to an undesired phase. Technical attempts have been reported to overcome these problems. These include post-sinter annealing [10-12], a two-peak firing schedule [13], zone sintering with rapid heating rates [14-17], and using hot pressing (HP) or hot isostatic pressing (HIP) [18, 19]. Even though these various methods have been applied to prepare dense  $\beta/\beta''$ -aluminas, few reports concerning sintering of K- $\beta/\beta''$ -aluminas at atmospheric pressure and the influence of the stabilizer on its densification were made in the last decade.

In this study, a dense K- $\beta/\beta''$ -alumina is prepared at atmospheric pressure, and its ionic conductivity is determined. The major efforts for this investigation are focused on lowering the sintering temperature using ultra-fine particles and determining the effects of the stabilizer content on its sintering density and ionic conductivity.

\*Corresponding author:  
Tel : +82-2-450-3500  
Fax: +82-2-444-3490  
E-mail: sklim@konkuk.ac.kr

## Experimental

### Preparation and characterization of samples

K- $\beta/\beta''$ -aluminas were prepared with various potassium contents and stabilizer ( $\text{Li}_2\text{O}$ ) additions. The potassium content was varied in the molar range  $\text{K}_2\text{O}:\text{5Al}_2\text{O}_3$  to  $\text{K}_2\text{O}:\text{11Al}_2\text{O}_3$  and the amount of  $\text{Li}_2\text{O}$  was varied from 0 to 1.6 wt%. The samples were prepared with combinations of  $\text{K}_2\text{O}$  and  $\text{Li}_2\text{O}$  contents, and they are summarized in Table 1.

Fine  $\alpha\text{-Al}_2\text{O}_3$  (ALO14PB, High Purity Chemicals, Japan) powder was mixed with  $\text{K}_2\text{CO}_3$  (Junsei Chemicals, Japan) and  $\text{Li}_2\text{CO}_3$  (99+%, Sigma-Aldrich, USA). The mixed materials were ball-milled for 5 h using alumina balls ( $\Phi=10$  and 5 mm) and acetone as the liquid medium. After drying, the compounds were packed in  $\text{MgO}$  crucibles and calcined at  $1200^\circ\text{C}$  for 2 h. The heating rate in calcinations was  $5\text{ Kmin}^{-1}$  and heat treatment carried out at  $800^\circ\text{C}$  for 1 h to release the carbon dioxide from  $\text{K}_2\text{CO}_3$  and  $\text{Li}_2\text{CO}_3$ . The calcined powders were milled to prepare the ultra-fine particles by an attrition mill using zirconia balls ( $\Phi=1$  mm) with methanol as the medium. Each sample listed in Table 1 was prepared into tablets by uniaxial pressing at 20 MPa. The tablets were inserted into an alumina crucible filled with the same K- $\beta/\beta''$ -aluminas powder (an atmosphere powder) to minimize the alkali loss and sintered at  $1600^\circ\text{C}$  for 1 h using a tube furnace (Lenton LTF 18, UK). After sintering, samples were characterized by density measurements using the Archimedes' method (ASTM C 373-88), qualitative and quantitative X-ray diffraction analysis (Rigaku Rint 2000, Japan), scanning electron microscopy (JEOL JSM-6308, Japan) and impedance spectroscopy (Solartron 1260 and 1287, UK). The size of particles and slurry were also analyzed by photon correlation spectroscopy (Brookhaven, 90 puls, USA).

### Measurement of AC impedance

For the measurement of ionic conductivity of K- $\beta/\beta''$ -aluminas, impedance measurements were performed at temperatures from 300 to  $800^\circ\text{C}$ . The tablets 2.3-3.0 mm in diameter, with a thickness of 1.5 mm, were coated with Pt-paste (Herauss CL11-5100, Germany) as electrodes, and heat-treated at  $900^\circ\text{C}$  for 1 h. The samples were placed on a typical cell measurement device as

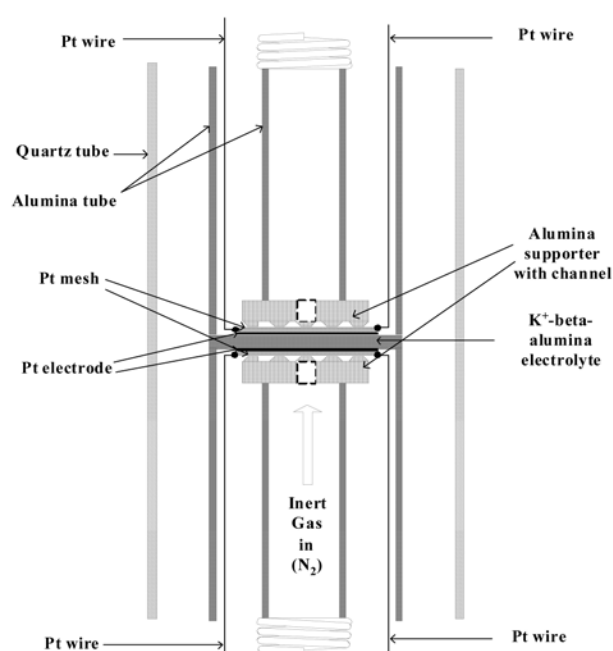


Fig. 1. Apparatus for ionic conductivity measurements.

shown in Fig. 1. Pt gauze supplied by Alfa (52 mesh, 0.1 mm wire) was used to increase the contact points on the electrodes. The inside of the quartz tube was purged with  $\text{N}_2$ -gas and a thermocouple was placed near the sample to measure the sample temperature. The AC impedance spectra in the frequency range of  $0.01\text{ Hz}-10^3\text{ kHz}$ , with an excitation voltage of 10 mV, were taken to ensure a linear response. All measurements have been carried out at both high and low temperatures. Data analysis was used to identify the sample's ohmic resistance in the Nyquist and admittance representation of the impedance spectra.

## Results and Discussion

Figure 2 shows the XRD patterns of A3 and E1 samples representing all the samples calcined at  $1200^\circ\text{C}$  for 2 h. Most of the calcined samples consisted of polycrystalline K- $\beta/\beta''$ -aluminas, except D1-D3 and E1-E3 samples, which show the characteristic reflections of the  $\alpha$ -alumina phase at crystal planes (104) and (113). Since D and E samples have alkali-poor compositions compared to the others, the  $\alpha$ -alumina phase remained in these compositions. As the  $\text{Li}_2\text{O}$  content increased, however, the  $\alpha$ -alumina phase reacted to form K- $\beta/\beta''$ -aluminas phases and gradually disappeared. This is confirmed with the D4, D5 and E4, E5 samples. Overall the phase formation of calcined and sintered samples is listed in Table 2.

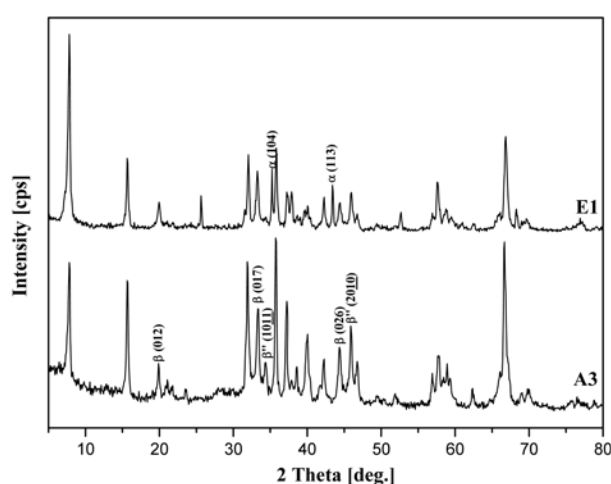
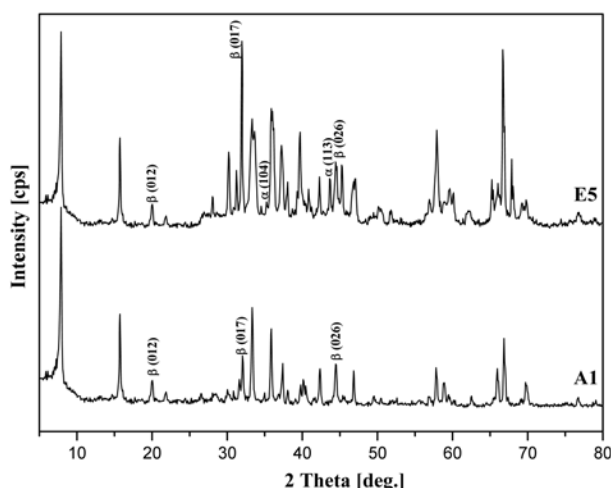
Figure 3 shows the XRD patterns of A1 and E5 samples representing all samples sintered at  $1600^\circ\text{C}$  for 1 h. Most of sintered samples show reflections of the K- $\beta$ -alumina phase as seen in Fig. 3(A1). However, E4 and E5 samples show the  $\alpha$ -alumina phase. This

Table 1. Sample designations corresponding to their compositions

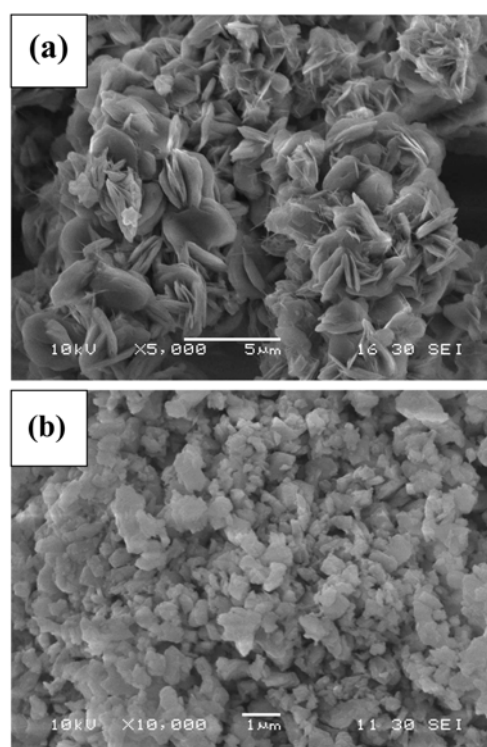
| $\text{Li}_2\text{O}$<br>(wt %) | [ $\text{K}_2\text{O}$ ]:[ $\text{Al}_2\text{O}_3$ ] (mol) |       |     |       |      |
|---------------------------------|------------------------------------------------------------|-------|-----|-------|------|
|                                 | 1:5                                                        | 1:6.5 | 1:8 | 1:9.5 | 1:11 |
| 0                               | A1                                                         | B1    | C1  | D1    | E1   |
| 0.4                             | A2                                                         | B2    | C2  | D2    | E2   |
| 0.8                             | A3                                                         | B3    | C3  | D3    | E3   |
| 1.2                             | A4                                                         | B4    | C4  | D4    | E4   |
| 1.6                             | A5                                                         | B5    | C5  | D5    | E5   |

**Table 2.** Phase formation in powders calcined at 1200 °C for 2h and samples sintered at 1600 °C for 1 h

| Sample | Composition                                      |                             | Phase<br>calcined at 1200 °C for 2 h                                                                                                                                    | Phase<br>sintered at 1600 °C for 1 h                                                                               |
|--------|--------------------------------------------------|-----------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|
|        | $\text{K}_2\text{O}:\text{Al}_2\text{O}_3$ (mol) | $\text{Li}_2\text{O}$ (wt%) |                                                                                                                                                                         |                                                                                                                    |
| A      | 1:5                                              | 0-1.6                       | K- $\beta/\beta''$ - $\text{Al}_2\text{O}_3$                                                                                                                            | K- $\beta$ - $\text{Al}_2\text{O}_3$                                                                               |
| B      | 1:6.5                                            | 0-1.6                       | K- $\beta/\beta''$ - $\text{Al}_2\text{O}_3$                                                                                                                            | K- $\beta$ - $\text{Al}_2\text{O}_3$                                                                               |
| C      | 1:8                                              | 0-1.6                       | K- $\beta/\beta''$ - $\text{Al}_2\text{O}_3$                                                                                                                            | K- $\beta$ - $\text{Al}_2\text{O}_3$                                                                               |
| D      | 1:9.5                                            | 0, 0.4, 0.8<br>1.2, 1.6     | $\alpha$ - $\text{Al}_2\text{O}_3$ , K- $\beta/\beta''$ - $\text{Al}_2\text{O}_3$<br>K- $\beta/\beta''$ - $\text{Al}_2\text{O}_3$<br>(with trace of lithium aluminates) | K- $\beta$ - $\text{Al}_2\text{O}_3$<br>K- $\beta$ - $\text{Al}_2\text{O}_3$<br>(with trace of lithium aluminates) |
| E      | 1:11                                             | 0                           | $\alpha$ - $\text{Al}_2\text{O}_3$ , K- $\beta/\beta''$ - $\text{Al}_2\text{O}_3$                                                                                       | K- $\beta$ - $\text{Al}_2\text{O}_3$                                                                               |
|        |                                                  | 0.4, 0.8                    | $\alpha$ - $\text{Al}_2\text{O}_3$ , K- $\beta/\beta''$ - $\text{Al}_2\text{O}_3$                                                                                       | K- $\beta$ - $\text{Al}_2\text{O}_3$                                                                               |
|        |                                                  | 1.2, 1.6                    | K- $\beta/\beta''$ - $\text{Al}_2\text{O}_3$<br>(with trace of lithium aluminates)                                                                                      | (with trace of lithium aluminates)<br>K- $\beta$ - $\text{Al}_2\text{O}_3$ , $\alpha$ - $\text{Al}_2\text{O}_3$    |

**Fig. 2.** XRD patterns of powders of A3 and E1 calcined at 1200 °C for 2 h.**Fig. 3.** XRD patterns of samples of A1 and E5 sintered at 1600 °C for 1 h.

can be explained by the high vapor pressure of potassium at the higher temperature, which causes the phase transition K- $\beta/\beta''$ -aluminas  $\alpha$ -alumina. The atmosphere powder was not enough to prevent the alkali loss in the case of the composition E, which has an alkali-poor content.

**Fig. 4.** SEM images of K- $\beta/\beta''$ -aluminas powder (a) before attrition milling and (b) after attrition milling.

Other samples did not show  $\alpha$ -alumina phase reflections.

For the higher densification of samples, the calcined powders were attrition-milled to reduce their particle size. Previous reports have shown that the densification of K- $\beta$ -aluminas at atmospheric pressure is only possible above 1780 °C with the addition of dopants [19, 20]. In our experiments, however, sufficient sintering densification could be attained at lower temperatures using ultra-fine particles and adding  $\text{Li}_2\text{O}$ .

Figure 4 shows the SEM results from particles before and after attrition milling. Before the powder was milled by an attritor, the particles show a plate-like shape, as shown in Fig. 4(a). This is a typical shape of polycrystalline  $\beta/\beta''$ -aluminas and these plate-like particles

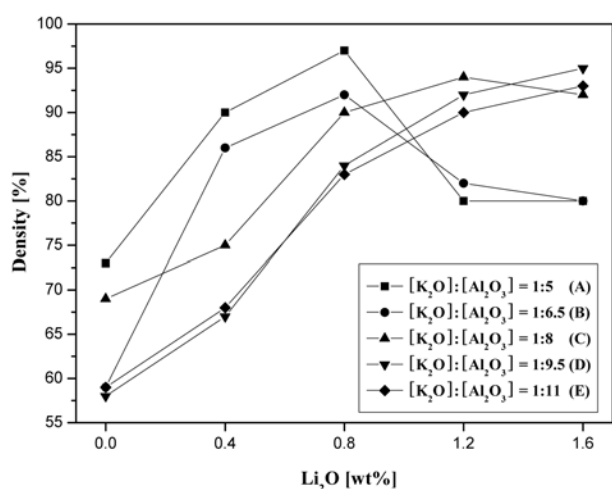


Fig. 5. Sintered density of samples as a function of stabilizer content.

cause a lower efficiency of the initial powder packing by limiting the number of contact points which are directly related to densification [19]. The contact points between particles play an important role in the initial stage of densification. Increasing the contact points can reduce the rearrangement time of particles and accelerate the formation of necks. After the powder was attrition-milled, the plate-like particles, having a mean particle size of 1.5–3  $\mu\text{m}$ , were reduced to a mean size of 20 nm in the slurry state. After drying, the particles were softly agglomerated and showed a particle size distribution in the range of 180–220 nm. This is revealed by particle size analysis (PSA) and SEM imaging in Fig. 4(b). The soft agglomerates can increase the initial packing and green density of the sample, and lower the densification temperature by increasing the contact points between the particles.

Figure 5 shows the densities of samples sintered at 1600 °C for 1 h and Fig. 6 shows the microstructures of A and D samples. As shown in Fig. 5, the densities of samples increase as the  $\text{Li}_2\text{O}$  content increases, except for the A and B series. A and B show the highest density at a  $\text{Li}_2\text{O}$  content of 0.8 wt% (Fig. 6(c)), but a further addition of  $\text{Li}_2\text{O}$  shows a decreased density. This is strongly related to its microstructure. As seen in Fig. 6(e), the excess addition (above 1.2 wt%) of  $\text{Li}_2\text{O}$  causes exaggerated grain growth to above 5  $\mu\text{m}$  in grain size and decreases the density with increasing pores between the grains. For the compositions of C, D, and E, however, the density is increased continuously with a  $\text{Li}_2\text{O}$  increase. These samples showed similar microstructures as seen in Fig. 6(f)–(j). Figure 6(f) shows the microstructure of the D1 sample which contains no stabilizer, and its grains have a mean size of 0.5–1  $\mu\text{m}$  and densification was occurred the least. With 0.8 wt% of  $\text{Li}_2\text{O}$  addition (Fig. 6(h)), however, densification proceeds and further addition of  $\text{Li}_2\text{O}$  promotes the densification between grains (Fig. 6(j)). Li ions in the stabilizer

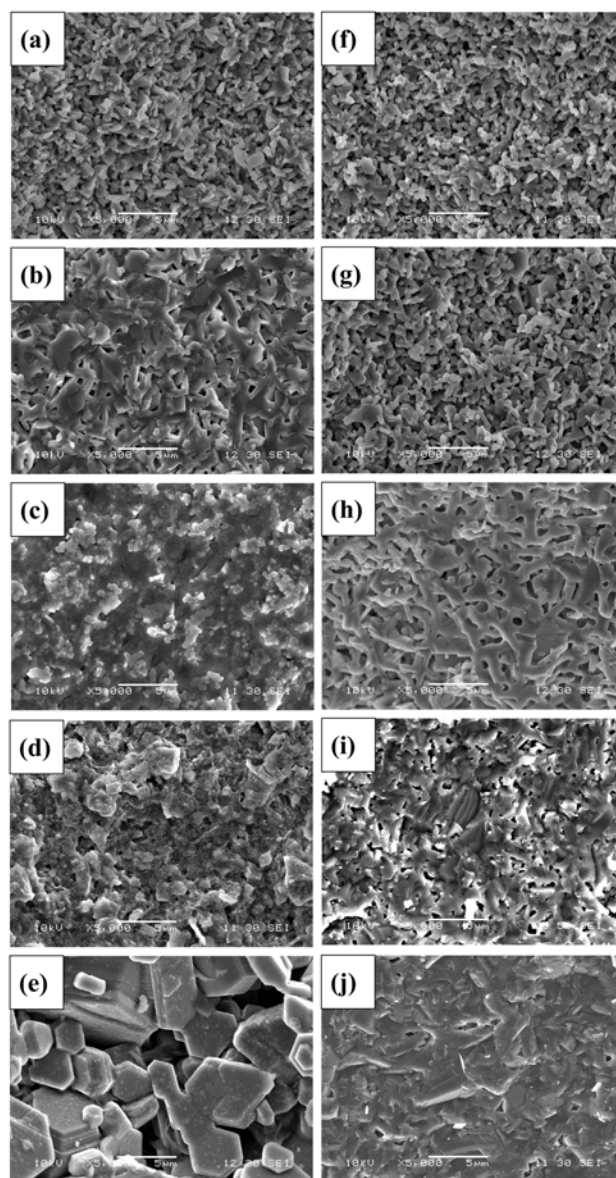


Fig. 6. SEM images of samples sintered at 1600 °C for 1 h; (a) A1 (73% of density), (b) A2 (90%), (c) A3 (97%), (d) A4 (80%), (e) A5 (80%), (f) D1 (58%), (g) D2 (68%), (h) D3 (83%), (i) D4 (92%), and (j) D5 (95%).

cause the formation of transient eutectic liquids which play a part in fast diffusion path between grains. The higher Li content leads to more formation of eutectic liquids and it increases the density of the K- $\beta$ -alumina [21].

The Arrhenius plots for the ionic conductivity of the composition A series are shown in Fig. 7 and the relationship between ionic conductivity and  $\text{Li}_2\text{O}$  contents at 300 °C and 800 °C are shown in Fig. 8. Ionic conductivities of samples are strongly related to their densities, microstructures and phases. As shown in Fig. 7 and 8, the A3 sample which contained 0.8 wt%  $\text{Li}_2\text{O}$  shows the highest ionic conductivity and it gives the highest density of 97%. A4 and A5 samples have almost the same densities. A5, however, shows a higher ionic

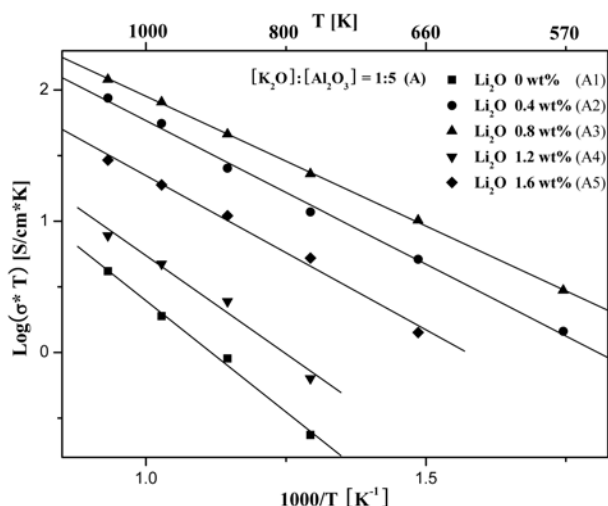


Fig. 7. Arrhenius plots for sintered samples of the composition A series ( $[\text{K}_2\text{O}]:[\text{Al}_2\text{O}_3]=1:5$ ) with different stabilizer content.

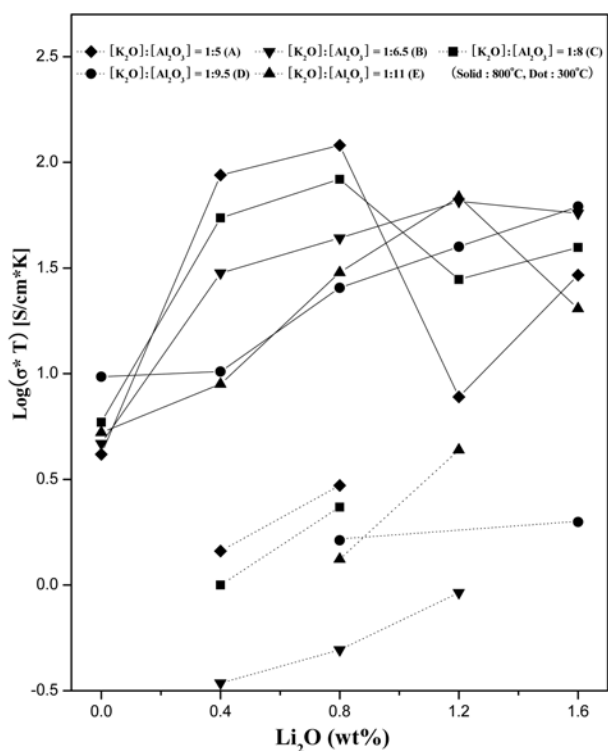


Fig. 8. Ionic conductivity of samples with different  $\text{K}_2\text{O}$  contents as a function of stabilizer content at 300 °C and 800 °C.

conductivity compared with A4. This can be explained by their microstructures. The structures consisting of a larger grain size have an increased conductivity since the quantity of grain boundaries, acting as a resistance path, decrease. As shown in Fig. 6(e), the A5 sample shows larger grains. As shown in Fig. 8, the ionic conductivity proportionally increases as the  $\text{Li}_2\text{O}$  content increase. In the case of the E series, a higher ionic conductivity was measured for E4, which has a lower density compared with E5. It can be reasoned that an undesired  $\alpha$ -alumina phase fraction in E5 was observed

at about 15 at%, which is higher than that of E4 (2-3 at%). The existence of  $\alpha$ -alumina as a secondary phase interrupts the ion conduction, which causes a lowering of the ionic conductivity. Any ionic conductivity, for samples having a density below 80%, is hardly measured in the lower temperature range (300-400 °C). The maximum ionic conductivity among the samples is achieved with sample A3 (density 97%) having value of  $1.1 \times 10^{-1}$  and  $5 \times 10^{-3}$  S/cm at 800 °C and 300 °C, respectively.

## Conclusions

Dense K- $\beta$ '-aluminas in the system  $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{Li}_2\text{O}$  were prepared at atmospheric pressure with ultra-fine powder and the addition of the stabilizer,  $\text{Li}_2\text{O}$ . The sintering temperature was lowered to 1600 °C and the maximum density achieved was 97%. The size and shape of particles and  $\text{Li}_2\text{O}$  content were strongly related to the densification of K- $\beta$ '-aluminas. Soft agglomerates of fine particles favored the initial packing of particles and Li ions in the stabilizer formed transient eutectic liquids during the sintering process. These factors play an important role in lowering the densification temperature. Ionic conductivity was strongly related to the density, and the maximum ionic conductivity was measured as  $1.1 \times 10^{-1}$  S/cm at 800 °C.

## Acknowledgments

This work was supported by grant No. (R01-2006-000-10332-0) from the Basic Research Program of the Korea Science & Engineering Foundation.

## References

1. B. Zhu, X.T. Yang, J. Xu, Z.G. Zhu, S.J. Ji, M.T. Sun, and J.C. Sun, *J. Power Sources* 118 (2003) 47-53.
2. A. Weber and E. Iners-Tiffée, *J. Power Sources* 127 (2004) 273-283.
3. P.S. Nicholson, M. Nagai, K. Yamashita, M. Sayer, and M. F. Bell, *Solid State Ionics* 15[4] (1985) 317-326.
4. J.O. Besenhard, in "Handbook of battery materials" (Wiley-VCH, 1999).
5. L.W. Strock, *Z. Phys. Chem.* B25 (1934) 441.
6. M. Nagai and P.S. Nicholson, *Mat. Res. Bull.* 17 (1982) 1131-1139.
7. J.T. Kummer, *Prog. Solid State Chem.* 7 (1972) 141-175.
8. A.P. de Kroon, G.W. Schäfer, and F. Aldinger, *Chem. Mater.* 7 (1995) 878-887.
9. T.R.N. Kutty, V. Jayaraman, and G. Periaswami, *Solid State Ionics* 128 (2000) 161-175.
10. S.N. Heavens, *J. Mat. Sci.* 19 (1984) 2223-2232.
11. E. Youngblood, G.R. Miller, and R.S. Gordon, *J. Am. Ceram. Soc.* 61 (1978) 86-87.
12. D. Jatkar, I.B. Culter, and R.S. Gordon, *Ceram. Microstructure* 76 (1977) 414-422.
13. H. Duncan, P. Barrow, and P.V. Brown, *Advanced ceramics in chemical process engineering, Electroceramics* (1988) 231.

14. J. McEntire, M.L. Miller, and R.S. Gordon, *Ceram. Bull.* 63 (1984) 792-802.
15. R. Tan and G.J. May, *Sci. Ceram.* 9 (1977) 103.
16. W. Jones and L.T. Miles, *Proc. Brit. Ceram. Soc.* 99 (1971) 161-178.
17. E. Youngblood, A.V. Virkar, W.R. Cannon, and R.S. Gordon, *Am. Ceram. Soc. Bull.* 56 (1977) 206-210.
18. W. Schäfer, H.J. Kim, and F. Aldinger, *Solid State Ionics* 77 (1995) 234-239.
19. P. de Kroon, F. Gstrein, G.W. Schäfer, and F. Aldinger, *Solid State Ionics* 133 (2000) 107-120.
20. P. de Kroon, Dr. rer. Nat. Thesis, Max-Planck-Institut für Metallforschung, Bericht nr. 34, Stuttgart, Germany, 1996.
21. H. Park, K.H. Kim, and S.K. Lim, *J. Mater. Sci.* 33 (1998) 5671-5675.