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Analysis of the rate of ion exchange of K^+ to H_3O^+ during the preparation of H_3O^+ - β "-aluminas by a hydrothermal process

Seok-Jun Kim, Hee-Min Kim, Woo-Sung Kim and Sung-Ki Lim*

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

 H_3O^+ - β "-aluminas were synthesized by a hydrothermal process in an autoclave, using K⁺- β "-aluminas and acetic acid (10 wt. %) as a precursor and an ion exchange medium, respectively. The potassium concentration of the precursor was varied within the molar ratio range, $[K_2O]$: $[Al_2O_3] = 1 : 4 \sim 1 : 8$, and the acetic acid contents were chosen at the ratios of $[K_2O]$: $[CH_3COOH] = 1 : 10, 1 : 50, and 1 : 100$. The exchange reaction was carried out at 150, 170, and 200 for 2, 4, 6, 8, and 24 h. By repeating a 2 hour reaction twice, the first reaction followed by washing, the highest rate was able to be observed at above 90%. The phase stability and transformation was confirmed by XRD and an IR spectrum, and the ion exchange (rate) was analyzed by ICP and TGA.

Key words: proton-\beta"-aluminas, low temperature SOFC, ion exchange reaction.

Introduction

Fuel cell technology has been developed for many decades. Specifically, solid oxide fuel cells (SOFCs) have high energy density and capacity, and are expected to be the next generation fuel cells. Currently, the calciaor yittria-doped zirconias are usually used as a solid electrolyte for SOFCs. However, they are operated normally between 700 °C and 1000 °C, which results in a low energy efficiency and requires complex installations [1]. Therefore, Electrolytes for low temperature SOFCs which can operate below 500 °C are being actively studied. Among them, $NH_4^+/H_3O^+-\beta$ "-aluminas and $H_3O^+-\beta$ "-aluminas which are protonic conductors with ionic conductivities in the range of 10^{-2} to 10^{-4} S/cm at 300 °C emerge as candidates [2]. The preparation of these protonic ion conductors is performed by ion exchange from the Mbeta-aluminas (M: alkali metals). In the case of Na⁺- β "aluminas which are widely used for the precursor, mechanical stress is built up during ion exchange which can disturb the crystalline structure since the ionic radii of Na⁺ and H₃O⁺ (Na⁺ = 0.095 nm, H₃O⁺ = 0.138 nm) are quite different. Also owing to the slow speed spread of H_3O^+ during the ion exchange reaction, proton- β "-aluminas are able to be fully prepared only as powder only [3]. In order to solve these problems, Research for K^+ - β^- aluminas where the ionic radius is similar ($K^+ = 0.133$) nm) and ion conductivity is excellent began [4]. This assures that the K^+ - β "-aluminas are an ideal precursor for the preparation of the proton- β "-aluminas. The crystalline structure of β "-aluminas is a rhombohedral

structure with a R3m space group and the lattice constants are 'a' = 5.614 and 'c' = 33.85Å. Generally, its 'a' axis is similar compared with the β -alumina's structure, but the length in the 'c' axis is 1.5 times longer and the concentration of alkaline ions on the conduction plane is higher. Therefore, the β "-aluminas show much higher ionic conductivity, relatively [5, 14].

Farrington and Briant [8] performed an ion exchange of Na⁺- and K⁺- β -aluminas to the proton- β/β "-aluminas in sulfuric acid at a high temperature over several days. However, the treatment by strong sulfuric acid was troublesome and the ion exchange time was also too long. Scheafer et al.[6, 9] prepared proton- β "-aluminas via an ion exchange reaction using K^+ - β "-alumina powder as a precursor which had a mean particle size of about 20 µm. In their study, the ion exchange to proton-\beta"-aluminas was carried out in sulfuric acid for an exceedingly long time, which caused an instability of phase and a waste of time. In the case of acetic acid as a reaction medium, the Al^{3+} in K^+ - β "-aluminas reacts with CH₃COO⁻ as a secondary reaction, resulting in $Al(CH_3COO)_2OH$ which is an undesired phase, as the reaction proceeds over 4 weeks under atmospheric pressure. Kutty et al. [7] prepared the proton- β -aluminas by an ion exchange reaction via a hydrothermal process at high temperature and pressure. They prepared K^+ - β aluminas by a gel-to-crystallite conversion method and carried out the ion exchange reaction with a precursor composed of a low potassium content (K_2O : $Al_2O_3 = 1 : 17$). In their study, however, no quantitative analysis of the ion exchange rate was made. Recently, the ion exchange of K⁺- β/β "-aluminas to proton- β/β "-aluminas was carried out in acetic acid by Kim et al. [10]. However, the ion exchange rate was poor and an instability of the phase occurred.

^{*}Corresponding author:

Tel : 82-2-450-3500

Fax: 82-2-444-3490

E-mail: sklim@konkuk.ac.kr

In this study, H_3O^+ - β "-aluminas were synthesized by a hydrothermal process in an autoclave, using ultra-fine K^+ - β "-alumina powder and acetic acid (10 wt.%) as a precursor and an ion exchange medium, respectively. Also the effects of the potassium concentration of the precursor, ion exchange time, temperature, and concentration of acetic acid on the ion exchange rate of K^+ to H_3O^+ were quantitatively analyzed. Additionally, the thermal stability of the H_3O^+ - β "-aluminas was studied in relation to K^+ - β "-aluminas. Moreover, the possibility and the conditions to achieve a higher exchange rate are discussed.

Experimental

Composition and raw material

Pure K^+ - $\beta^{"}$ -alumina precursor was synthesized in the ternary system K₂O-Li₂O-Al₂O₃. γ -alumina (99.9%, Kojundo Chemical Lab Co., Ltd., Japan) was used as a starting material for the alumina source, and a solid state reaction was carried out. The calcination was performed at 1200 °C [11, 12]. To determine the ion exchange rate dependence of the potassium content of the precursor, K⁺- β "-aluminas were synthesized with molar ratios of [K₂O] : [Al₂O₃] from 1 : 4 to 1 : 8 by adding 0.2 wt.% Li₂O as a stabilizer. As raw materials, K₂CO₃ (99.5%, Junsei Chemical Co., Ltd., Japan) for K₂O, and Li₂OO were used. Dilute acetic acid of 10 wt.% (CH₃COOH, 99%, Duksan pure chemical Co., Ltd., Korea) was used as an ion exchange medium.

Synthesis and milling

To attain a homogenous mixture, these raw materials were ball-milled for 5 h in methanol. The mixture was dried at 100 for 24 h and the powders were calcined at 800 °C and 1200 °C for 2 h. [12] To prepare the ultra fine sized particles, these powders were attrition-milled



Fig. 1. SEM images of (a) ball-milled powder and (b) attrition-milled powders.

for 2 h again and dried at 100 °C for 24 h. Figs. 1 and 2 show the morphology and the particle size distribution of the precursors. The average diameters of particles of ball-milled and attrition-milled powders were measured to be about 1.0-2.0 and 0.3-0.5 μ m, respectively. The microstructure and the particle size distribution were determined by a scanning electron microscope; SEM (JEOL



Fig. 2. The size distribution of (a) ball-milled powder and (b) attrition-milled powders.

JSM-6308, Japan) and particle size analyzer (Brookhaven instruments Co.), respectively.

The ion exchange and analysis

Figure 3 shows the procedure of the ion exchange experiment using acetic acid as a medium. The reaction temperature, the reaction time, the molar ratio of the media, and the agitation speed have been considered as the prominent parameters for ion exchange conditions. Ion exchange was accomplished under a hydrothermal reaction in a Teflon-lined autoclave (Eco solution Co., Ltd., Korea). The reaction was performed at temperatures between 150 °C and 200 °C for 2 h, 4 h, 6 h, 8 h, and 24 h. The molar ratio of potassium contents in the K⁺- β "-aluminas to acetic acid was varied at 1 : 10, 1 : 50, and 1 : 100. The agitation speed in the autoclave was chosen as 200, 500, and 800 rpm.

The phase analysis was performed by an X-ray diffractmeter; XRD (Rigaku Rint 2000, Cu Ka 10°/min) and Fourier transform infrared spectrometer; FT-IR

Fig. 3. Schematic diagram of the ion exchange experiment.

(Mattson, Genesis II, USA). The ion exchange rate and the weight change were analyzed by inductively coupled plasma atomic emission spectrometers; ICP-AES (spectro, Modular EOP), and thermo gravimetric analysis; TGA (TA Instruments 2050), respectively.

The samples for ICP-AES measurement were prepared by mixing 0.1 g of exchanged proton- β "-alumina powder with 10 ml of dilute sulfuric acid solution (H₂SO₄ : H₂O = 1 : 2 in moles) and heating at 180 for 18 h in autoclave. After heating, the remaining solid particles were dissolved using concentrated sulfuric acid. The samples were then diluted using de-ionized water [10].

Results and discussion

The effect of precursor composition

Figure. 4 shows the XRD pattern of the K⁺- β "-alumina precursor which has the composition of [K₂O] : [Al₂O₃] = 1 : 6 and was calcined at 1200 °C. The pattern exactly corresponds to the pure K⁺- β "-alumina phase. Since the oxygen layers of γ -alumina forms a cubic close-packed structure and is similar to the rhombohedral structure of the layers forming spinel blocks of the β "-aluminas, γ -alumina is structurally favorable to the formation of β "-aluminas [13, 14, 15]. As shown in Fig. 4, the peaks of γ -alumina (2 0 10, 2 2 0) were directly transferred to characteristic peaks of K⁺- β "-alumina. The other compositions of 1 : 4 and 1 : 8 showed similar results.

In Fig. 5, the results of ion exchange according to the potassium contents in K^+ - $\beta^{"}$ -aluminas and reaction time are shown with the XRD patterns. The reaction was performed by stirring at a speed of 200 rpm at 150 °C for 2 h and 8 h. In the case of the composition of $[K_2O] : [Al_2O_3] = 1 : 8$, the structure of $\beta^{"}$ -aluminas was maintained during the reaction of 8 h. On the other hand, the composition of $[K_2O] : [Al_2O_3] = 1 : 6$ formed $\beta^{"}$ -aluminas completely until 2 h, but a small amount of AlOOH (boehmite) appeared after 8 h. The phase

Fig. 4. XRD pattern of the K^+ - β "-alumina precursor.

Fig. 5. XRD patterns after ion exchange reaction for the molar ratio of $[K_2O]$: $[Al_2O_3]$ and ion exchange time (a) 1 : 4 for 2 h, (b) 1:4 for 8 h(c) 1:6 for 2 h, (d) 1:6 for 8 h, (e) 1:8 for 2 h, and (f)1 : 8 for 8 h, $([K_2O] : [CH_3COOH = 1 : 50)$.

change of $[K_2O]$: $[Al_2O_3] = 1 : 6$ in relation to reaction time is shown in detail in Fig. 6. For the composition of $[K_2O]$: $[Al_2O_3] = 1 : 4$, AlOOH appeared after only 2 h. The peaks of AlOOH are identified at reflection planes (0 2 0), (1 2 0), (0 3 1), and (0 5 1). In this case, the reaction proceeds quite rapidly, owing to the higher partial pressure of potassium, which could cause partially collapsed β "-aluminas. This structurally loose β "-aluminas react with the OH⁻ group in acetic acid and forms AlOOH [7]. In Fig. 7 and Table 1, the amount of the remaining potassium ions from the ICP measurements and the calculated ion exchange rate are shown in relation to the composition and reaction time. Within the composition range of $[K_2O]$: $[Al_2O_3]$ from 1 : 4 to 1:8, the ion exchange rate increased with increased amounts of potassium, accompanied by a higher partial pressure of potassium in the K^+ - β "-alumina precursor. Also the ion exchange reaction proceeded rapidly at an early stage and was almost completed within 2 h.

The effect of ion exchange time

To determine the phase change according to the reaction time, the K⁺- β "-alumina precursor with a composition of $[K_2O]$: $[Al_2O_3] = 1 : \overline{6}$ was chosen and the

Fig. 6. XRD patterns of the composition with the molar ratio of $[K_2O]$: $[Al_2O_3] = 1:6$ according to ion exchange time (a) precursor, (b) 2 h, (c) 4 h, (d) 6 h, (e) 8 h, and (f) 24 h.

Fig. 7. Amounts of remaining potassium ion and ion exchange rate according to the reaction time, herein the molar ratio of $[K_2O]$: $[Al_2O_3]$ (a) 1 : 4, (b) 1 : 6, (c) 1 : 8, (d) 1 : 8, (e) 1 : 6, and (f) 1 : 4.

reaction time was varied from 2 h to 24 h at 150 (Fig. 6). During the ion exchange reaction, K⁺ is substituted with H_3O^+ at a high temperature and pressure according to the following reactions.

Table 1. Concentration of remaining potassium ions from the ICP measurements and ion exchange rates according to the $[K_2O]$: $[Al_2O_3]$ molar ratio

	Amount of remaining K ⁺ (ppm) / Ion exchange rate (%)			
Molar ratio Time (h)	1:4	1:6	1:8	
0 (precursor)	22.8500 / 0	17.0260 / 0	18.2500 / 0	
2	2.6760 / 88.3	3.0980 / 81.8	6.1100 / 66.5	
4	2.1940 / 90.4	2.5750 / 84.9	5.2700 / 71.1	
6	1.9760 / 91.4	2.4940 / 85.4	5.2000 / 71.5	
8	1.5080 / 93.4	2.3750 / 86.1	5.0900 / 72.1	

(2)

alumina + $C_2H_3KO_2$

In a short period, the OH⁻ group in the acetic acid did not react with alumina owing to insufficient reaction time. As seen in Fig. 6(b), pure H_3O^+ - β "-aluminas have been formed by a fast ion exchange reaction until 2 h and the by-product $C_2H_3KO_2$ was dissolved in a solution state. As the reaction time increased continuously, however, the OH⁻ group reacted gradually with alumina, resulting in the formation of AlOOH (Fig. 6 (c)-(f)) [10]. The AlOOH peaks are obviously identified at the reflection planes (0 2 0), (1 2 0), (0 3 1), and (0 5 1) with the sample after 24 h, as shown in Fig. 6(f).

The formation of AlOOH with the passage of the reaction time was confirmed by FT-IR analysis. A combination of hydroxyl group appears in the absorption spectral range at near 1100 cm^{-1} and $3000-3500 \text{ cm}^{-1}$ [10, 16]. After 8 h, as can be seen in Fig. 8, AlOOH was obviously observed in the corresponding spectral range.

The ion exchange rate, according to the reaction time, was analyzed quantitatively by ICP measurements. As can be seen in Fig. 9, most of the ion exchange has been completed at 2 h (81.8%) at 150 °C and after 4 h (84.9%) little change has been observed. To improve the ion exchange rate, the 2 hour reaction was repeated twice by filtering and washing after the first reaction. As a result, the ion exchange rate increased from 81.8% to 88.1% without a change of phase and crystal structure.

The effect of ion exchange temperature

The phase stability and the ion exchange rate according to the reaction temperature were investigated at 150 °C, 170 and 200 with the precursor having the molar ratio of $[K_2O]$: $[Al_2O_3] = 1 : 6$. The reaction proceeded for 2 h. The result of the phase analysis at each temperature is shown by XRD patterns in Fig. 10. With increased pressure in the autoclave, AlOOH appeared above 170 °C. A higher pressure in the autoclave resulted in a

Fig. 8. Infrared spectra of the composition with the molar ratio of $[K_2O]$: $[Al_2O_3] = 1 : 6$ according to ion exchange time.

fast ion exchange reaction, which caused partially collapsed β "-aluminas. These structurally loose β "-aluminas react with the OH⁻ group in acetic acid and are transformed to AlOOH. In spite of the phase instability, however, the ion exchange rate was improved from 81.8% at 150 °C to 92.4% at 200 °C. (Table 2)

The effect of the molar ratio of acetic acid

To determine the effect of the molar ratio of acetic acid on the ion exchange rate, acetic acid concentrations are varied with a ratio of $[K_2O]$: $[CH_3COOH] = 1 : 10$, 1 : 50, and 1 : 100 in moles. As described in the previous experiments, the precursor having the composition of $[K_2O]$: $[Al_2O_3] = 1 : 6$ was used and reacted at 150 °C, and the ion exchange rate and the phase stability were analyzed after 2 h, 4 h, 6 h, and 8 h. The molar ratio of acetic acid did not influence the phase change and the result appeared same as shown in Fig. 6. At the molar ratio of acetic acid at $[K_2O] : [CH_3COOH] = 1 : 10$, the content of acetic acid was not sufficient and a low ion exchange rate was measured for the whole reaction

Fig. 9. Ion exchange rate of the composition with the molar ratio of $[K_2O]$: $[Al_2O_3] = 1 : 6$ according to ion exchange time.

Fig. 10. XRD patterns of the composition with the molar ratio of $[K_2O]$: $[Al_2O_3] = 1 : 6$ as a function of reaction temperature (a) 150 °C, (b) 170 °C, and (c) 200 °C.

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	Temperature (°C)	Amount of remaining K^+ (ppm)	Ion exchange Rate (%)	Phases	
	150	3.0980	81.8	$K^+/H_3O^+-\beta$ "-aluminas	
	170	2.8260	83.4	K ⁺ /H ₃ O ⁺ -β"-aluminas AlOOH	
	200	1.2900	92.4	$K^+/H_3O^+-\beta''$ -aluminas AlOOH	

Table 2. Phase Stability and Ion Exchange Rate according to the Reaction Temperature. The precursor has the molar ratio of $[K_2O]$: $[Al_2O_3] = 1:6$ and was reacted for 2 h

period as shown in Fig. 11 and Table 3. The highest exchange rate was observed at $[K_2O] : [CH_3COOH] = 1 : 100$ after 8 h. In this excess acetic acid content, however, the powder has been gradually changed to a gel with longer reaction times. Moreover, AlOOH as an undesired phase appeared after 8 h. On the other hand, the highest exchange rate after 2 h was observed at $[K_2O] : [CH_3COOH] = 1 : 50$ without the formation of AlOOH.

Thermal stability

The thermal stabilities of the K^+ - β "-alumina precursor with the composition of $[K_2O] : [Al_2O_3] = 1 : 6$ and the H_3O^+ - β "-aluminas ion-exchanged at 150 °C for 2 h with the acetic acid mole ratio of 1 : 50 were analyzed in the range from room temperature to 1000 °C by TGA and the results are shown in Fig. 12. In the case of the precursor, the absorbed surface water was removed with a weight loss of about 1% up to 150 °C. Also up to 350 °C, a continual loss of about 2% more occurred, which results from the removal of the water that is composed of OH formed during the ion exchange or exists on the conduction plane from air. Above 400 °C, no more weight loss appeared. On the other hand, the H_3O^+ - $\beta^{"}$ aluminas indicated a 1.2% loss up to 150 °C by the absorbed surface water and up to 400 6% more by the water composed of OH or on the conduction plane. With an increase in temperatures up to 800 °C, the H_3O^+ ion was also dissociated from the conduction plane and removed as water accompanied with a weight loss of about 2.5% and the $\beta^{"}$ -aluminas structure was no longer sustained. Above 800 °C, there was no additional weight change.

Conclusions

Our paper shows the preparation of proton- β "-aluminas by a hydrothermal process in an autoclave and the results of ion exchange rate of K⁺ to H₃O⁺ quantitively, for which K⁺- β "-aluminas and acetic acid were used as a precursor and an ion exchange medium, respectively. In the range of the molar ratios of [K₂O] : [Al₂O₃] from 1 : 4 to 1 : 8, pure K⁺- β "-aluminas were synthesized and the ion exchange rate increased with an increase of potassium content. Most reactions have been completed

Fig. 11. Ion exchange rate according to the molar ratio of $[K_2O]$: [CH₃COOH] for the composition of $[K_2O]$: $[Al_2O_3] = 1:6$ at 150 °C.

Fig. 12. Result of TGA for the (a) $K^+\text{-}\beta^{\prime\prime}\text{-alumina}$ precursor and (b) H_3O^+ $\beta^{\prime\prime}\text{-aluminas}.$

Table 3. Ion exchange rate according to the mole ratio of $[K_2O]$: $[CH_3COOH]$ for the composition of $[K_2O]$: $[Al_2O_3] = 1:6$ at 150 °C.

	Amount of	Amount of remaining K^+ (ppm) / Ion exchange rate (%)			
Time (h)	1:10	1 : 50	1 : 100		
2	4.7880/71.9	3.0980/81.8	3.8460/77.4		
4	4.2280/75.2	2.5750/84.9	3.2520/80.9		
6	3.5900/78.9	2.4940/85.4	2.6710/84.3		
8	3.2210/81.1	2.3750/86.1	1.9610 88.5		

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within 2 h in its early stage, indicating a rate of about 80%, and after 8 h little change has been observed. AlOOH (boehmite) as an undesired secondary phase appeared as the potassium content, the reaction time, and the reaction temperature were increased. However, Al(CH₃ COO)₂OH was not detected during the whole reactions. The acetic acid concentration has not influenced the ion exchange rate, but as the acetic acid concentration and reaction time increased, the precursor powder was changed to a gel. A high agitation speed also slightly improved the ion exchange rate. In our experiments, the highest ion exchange rate that has been achieved is about 90% by repeating a 2 hour reaction twice with the precursor having the molar ratios of $[K_2O]$: $[Al_2O_3] = 1:6$ and $[K_2O] : [CH_3COOH] = 1 : 50$ at 150 °C, at which pure b"-aluminas were formed only. In the result for the thermal stability of the prepared proton- β "-aluminas, H₃O⁺ was dissociated from the conduction plane and formed water near 400 °C and was removed completely up to 800 °C, which caused the collapse of β "-alumina structure.

Finally, H_3O^+ - β "-aluminas must be prepared at higher temperatures accompanied with a higher pressure so that the ion exchange reaction may be completed as fast as possible without the formation of secondary phases. Additionally, nano-sized precursor powder is expected to effectively improve the ion exchange rate.

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