The preparation of H_3O^+/NH_4^+ -β"-alumina by ion-exchange reactions from K^+-β"-alumina in aqueous solutions and molten salts

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H_3O^+/NH_4^+ -β"-alumina was synthesized using K^+-β"-alumina and two types of ion-exchange mediums, NH_4NO_3 aqueous solutions and molten NH_4NO_3 salts, by an ion-exchange reaction in an autoclave and a heating mantle, respectively. In the autoclave reaction, the potassium concentration of the K^+-β"-alumina was varied among the $[K_2O]$: $[Al_2O_3]$ composition ratios of 1 : 4-1 : 8, and the concentrations of the NH_4NO_3 solution was chosen to be either 1 M and 2 M, depending on the experiment. Each ion-exchange reaction was carried out at 130, 150 or 180 °C for 2, 4, 6, 8 or 24 h under high pressure. In the heating mantle reaction, the ion-exchange reaction was performed at 180 °C or 200 °C for 2-48 h in molten NH_4NO_3 salts under atmospheric pressure. After repeating the preceding reaction 5 times with 5 hour re-reactions followed by washing, the highest ion-exchange rate achieved was 90% in the autoclave, and 98% in the heating mantle. The phase stability and phase transformation were analyzed by X-ray diffraction(XRD) and the ion-exchange rate was measured using an inductively coupled plasma(ICP).

Key word: K^+- β"-alumina, ion-exchange reaction, H_3O^+/NH_4^+ -β"-alumina.

Introduction

Fuel cell technology has been developed especially in proton exchange membrane fuel cell(PEMFC), which use a Nafion polymer electrolyte. However, the working temperature of commercial PEMFCs is limited to ~80 °C because of the properties of the polymer electrolyte at high temperatures, such as a low thermal resistance. In the PEMFC system, some problems arise due to the low working temperature. First, electrolytes can be destroyed because of swelling or shrinkage which is caused by water in the liquid and gas states below 100 °C. It is also very difficult to control the input temperature of the fuel gas supplied. Second, the Pt catalyst in the anode can be poisoned by a very small amount of CO easily at low working temperatures. In general, the available level of CO is 20 ppm at 80 °C, but the amount of CO needed to poison the catalyst can be improved by increasing the working temperature above 100 °C.(1000 ppm at 130 °C and 30,000 ppm at 200 °C) [1].

It is known that H_3O^+/NH_4^+ -β"-alumina, which is a proton conductive ceramic, has high hygroscopicity and ionic conductivities between 10^{-4}-10^{-2} S/cm at 300 °C [2]. Also, this material is expected to be used as a new medium temperature fuel cell electrolyte because of the specific properties of ceramic materials, such as high thermal resistance, strength and good chemical stability. In general, β"-alumina, a modification of Al_2O_3, is synthesized by

heating at ~1200 °C, but the loss of H_3O^+/NH_4^+ ions occurs above 300~400 °C. To prevent this loss, H_3O^+/NH_4^+-β"-alumina is only prepared by substitution between M-β"-alumina (M : alkali metals) as a precursor and an ion-exchange medium through an ion-exchange reaction after synthesis of the β"-alumina. Considerable efforts have been invested in trying to prepare H_3O^+/NH_4^+-β"-alumina by an ion-exchange reaction from Na^+-β"-alumina single crystals, but ion-exchange experimental conditions are favorable for powders rather than single crystals with respect to time and efficiency, due to the low diffusion rate of NH_4^+, H_3O^+ [3, 4].

As will be shown later, the alkali ion in β"-alumina can be replaced by many different ions through an ion-exchange reaction from molten salts or from aqueous solutions. The most severe problem during ion-exchange reactions is the change of the lattice constant of β"-alumina. In the case of using Na^+-β"-alumina as a precursor for the ion exchange, the crystal structure of β"-alumina can break because the different ionic radius cause an internal stress during the substitutions between Na^+, NH_4^+ and H_3O^+ (NH_4^+ : 0.150 nm, H_3O^+ : 0.138 nm, Na^+ : 0.095 nm) [5]. To solve this problem, therefore, K^+-β"-alumina which has a similar ionic radius (K^+ : 0.133 nm) to those of NH_4^+ and H_3O^+ is preferred for the starting material compared to Na-β"-alumina. The crystal structure of β"-alumina is classified as R3m and the lattice constant is rhombohedral with an 'a'-axis = 5.614 Å and 'c'-axis = 33.85 Å. A unit cell of β"-alumina consists of a three-fold screw axis using three spinel blocks and each spinel block is separated by the conduction plane which is linked up with the alkali ion layer and Al-O-Al combination layer. Generally, the

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'a'-axis of the β and β''-alumina are similar, whereas the 'c'-axis of β''-alumina is 1.5 times longer than that of the β-alumina (Fig. 1). Hence, β''-alumina has a relatively higher ionic conductivity due to the higher concentration of its alkali ion in the conduction plane [6, 7, 8].

It was found by Kummer and his research staff [9] that ion-exchange reactions in molten salts can be readily accomplished more easily than those in aqueous solutions in the case of using Na^+-β''-alumina for a precursor. This is because ion exchange between β''-alumina and alkali ions in an aqueous solution is inhibited by the reaction of water with the edges of the β''-alumina crystals. The inhibition of ion exchange is stronger in acid solutions than in basic solutions. It is not known if this inhibition is due to the replacement of Na^+ by a relatively immobile H_3O^+, if it is due to neutral water molecules entering the lattice, or if is due to some chemical degradation of the edges of the crystals.

Farrington and Briant [2, 10] reported that H_3O^+/NH_4^+-β''-alumina crystals were prepared easily using Na^+-β''-alumina single crystals and molten NH_4NO_3 as a precursor and ion-exchange medium, respectively, by the immersion method. However, the method is unfavorable because it takes several days at high temperatures. In addition, in the case of using β''-alumina, NH_4^+ and H_3O^+ were both detected after the ion exchange, but in the case of using β-alumina, only the NH_4^+ ion was detected. It is known that this results from a gap of the thermodynamic equilibrium and a relative diffusion rate difference for the NH_4^+ and H_3O^+ ions. In the thermal analysis investigation, the NH_4^+ ion loss began at 300 °C and then, after 400 °C, the H_3O^+ ion loss was confirmed [11].

Schaefer *et. al.* [7] also reported that H_3O^+/NH_4^+-exchanged β''-alumina polycrystals cannot be made directly from a K-β''-alumina precursor material due to the strong mechanical tensions occurring during the exchange process. However, they determined the lattice constants of the

K-β''-alumina materials at a certain stoichiometric compositional field that allowed the preparation of polycrystals without cracking.

In this paper, H_3O^+/NH_4^+-β''-alumina is prepared from a K^+-β''-alumina powder by an ion-exchange reaction in an NH_4NO_3 aqueous solution and in molten NH_4NO_3 salts; the optimal conditions for this preparation, such as suitable reaction time, temperature and precursor material composition, were determined.

Experimental

K^+-β''-alumina was synthesized by a solid state reaction using γ-Al_2O_3 (99.9%, Kojundo chemical Lab Co., Ltd., Japan), K_2CO_3 (99.5%, Junsei Chmical Co., Ltd., Japan), and Li_2CO_3 (99%, Aldlich Chemical Company, Inc., USA) as starting materials. K_2CO_3 and Li_2CO_3 were used as sources of K_2O and Li_2O, respectively, for completing the $K_2O \cdot Li_2O \cdot Al_2O_3$ ternary system. The above starting materials were mixed and crushed by ball-milling in methanol for 5 h and then dried at 90 °C for 24 h. The compositions of the K^+-β''-alumina were chosen differently according to the ion-exchange method. First, in an autoclave, to investigate the ion-exchange rate according to the potassium concentration change of the K^+-β''-alumina precursor, the molar ratio of $[K_2O] : [Al_2O_3]$ was varied among the ratios of 1 : 4, 1 : 6, 1 : 8. And second, in a heating mantle, the molar ratio of $[K_2O] : [Al_2O_3]$ was fixed at 1 : 5, based on the previous experimental results in the autoclave. After mixing, the K^+-β''-alumina was prepared by the following steps. The mixture was put into a MgO crucible and calcined at 1200 °C in an electric furnace (Lenton, UAF 18/5 super furnace, UK). After elimination of CO_2 through pre-calcination at 800 °C, the 0.2 wt% Li_2O works as a stabilizer during the synthesis of the K^+-β''-alumina [10, 12, 13]. When γ-Al_2O_3 transforms to β''-Al_2O_3, the partial pressure change of the K_2O caused by K^+ evaporation induces the decomposition to α-A_2O_3. To prevent loss of K^+, the MgO crucible was covered with a MgO plate. After calcination, the mixture was milled again to obtain nano-sized particles by attrition-milling for 2 h in methanol. The particle size distribution of the ball-milled mixture was 1.0-2.0 μm and the attrition-milled mean particle size was 0.3-0.5 μm. The above results were determined by scanning electron microscopy (SEM, JEOL JSM-6308, Japan) and particle size analysis (PSA, Brookhaven Instruments Co.). The ion-exchange procedure was divided into an autoclave reaction that maintained a high temperature and high pressure, and a heating mantle reaction that only maintained a high temperature. In the case of the autoclave reaction, the ion-exchange reaction was carried out using 1 M and 2 M NH_4NO_3 aqueous solutions at 130, 150 or 180 °C for 2, 4, 6, 8 or 24 h. The composition of the K^+-β''-alumina precursor was varied among $[K_2O] : [Al_2O_3]$ ratios of 1 : 4, 1 : 6 and 1 : 8. In the case of the heating mantle reaction, the ion-exchange reaction was performed using molten NH_4NO_3
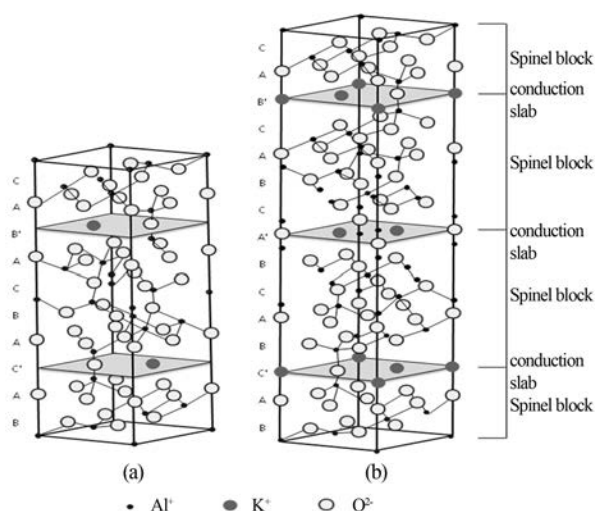
Fig. 1. Perspective drawings of the idealized structures of (a) β-alumina (b) β''-alumina.

salts at 180 and 200 °C for 2-48 h, and a 5 hour reaction was repeated up to 5 times at 180 °C. After the ion-exchange reaction, the powders were filtered twice with de-ionized water in an aspirator and then, finally dried at 90° for 24 h. The phase analysis and ion-exchange rate of each specimen was measured with an X-ray diffractometer (Rigaku Rint 2000, Cu Kα-radiation scanning range 5 to 70 °C 2θ, step width 0.08°, scanning speed 10°/minute) and ICP (spectro, Modular EOP), respectively. The ion-exchange rate, that is the amount of exchanged H_3O^+/NH_4^+ ion, was calculated by subtracting the remaining potassium after the ion exchange and the initial starting composition.

Results and Discussion

The synthesis of K^+-β''-alumina

The XRD phase analysis of the K^+-β''-alumina prepared following the above-mentioned procedure is shown in Fig. 2(b). The same XRD pattern was obtained in all compositions. As a result, it was identified that all specimens were transformed from γ-Al_2O_3 to β''-Al_2O_3. Notably, the (20$\underline{10}$, 220) plane corresponding to β''-Al_2O_3 was directly formed at about 45° and 67°. The 2θ values and the intensities of all peaks were in agreement with those of the reference samples (JCPDS card No. 31-960 (β-alumina), 21-618 (β''-alumina)). β''-alumina is the only phase that remains stable, while the amount of β-alumina is negligible, probably due to a devitrification phenomenon during synthesis of the K^+-β''-alumina[14].

The ion-exchange reaction in the autoclave

The ion-exchange reaction in the autoclave was performed at a high temperature and high pressure [15]. For the reaction, the composition of the K^+-β''-alumina precursor, reaction time, temperature and the concentration of the ion-exchange medium were varied. First, Fig. 3 shows the phase analysis of the ion-exchanged H_3O^+/NH_4^+-β''-alumina at 150 °C for 2 h and 8 h according to the composition of the K^+-β''-alumina precursor. In the $K_2O\cdot4Al_2O_3$ and $K_2O\cdot6Al_2O_3$ systems, AlOOH(boehmite)

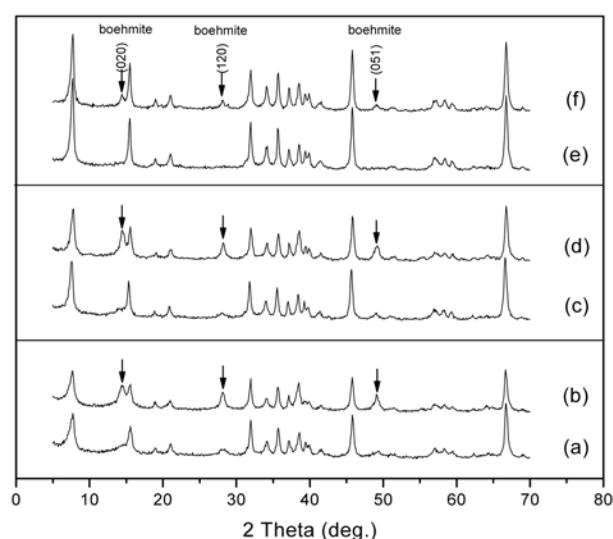**Fig. 3.** XRD patterns after the ion-exchange reaction of various $K_2O\cdot Al_2O_3$ compositions and ion-exchange times (a) 1 : 4 for 2 h, (b) 1 : 4 for 8 h (c) 1 : 6 for 2 h, (d)1 : 6 for 8 h, (e) 1 : 8 for 2 h, and (f) 1 : 8 for 8 h.
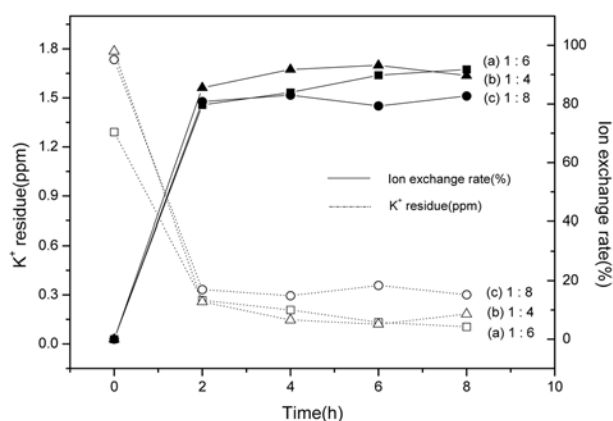

Fig. 4. The remaining K^+ and ion-exchange rate according to the reaction time and the composition of $K_2O\cdot Al_2O_3$ (a) 1 : 6, (b) 1 : 4, (c) 1 : 8.

was formed after 2 h and 4 h, respectively. In the $K_2O\cdot8Al_2O_3$ composition, which has the lowest K^+ content, AlOOH appeared after 6 h. Consequently, in the 1 : 4 composition with the highest K^+ content, the β''-alumina structure was collapsed in a short period of time and AlOOH was formed. Specific conditions, such as internal stress and an appreciable equilibrium vapor pressure of K^+ and H_3O^+/NH_4^+ during the ion-exchange reaction, lead to the alumina's decomposition to AlOOH. Fig. 4 and Table 1 indicate the ion-exchange rates and the remaining K^+ as functions of the composition of the precursor and the reaction time. For all compositions, the ion-exchange reaction was almost completed within 2 h.
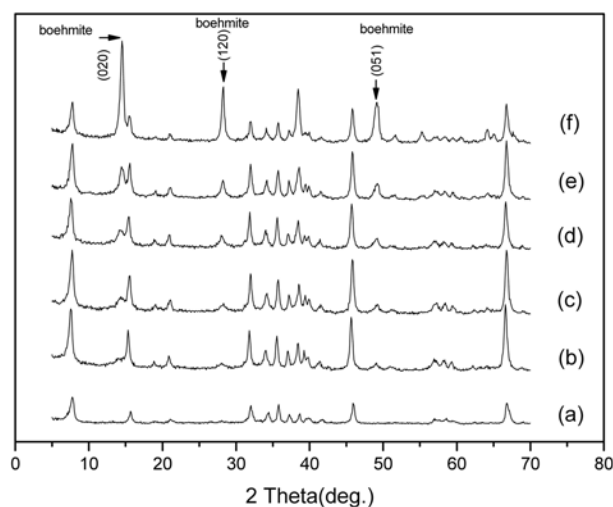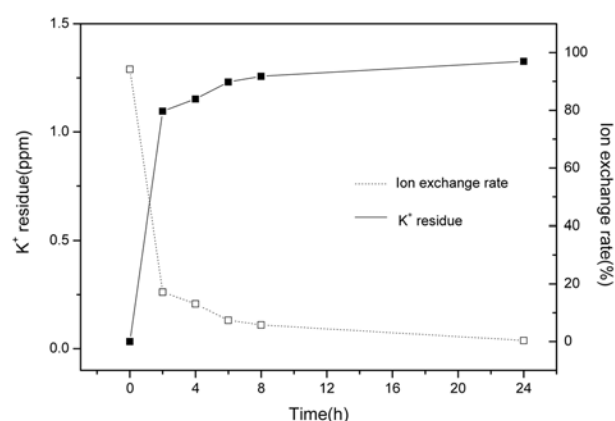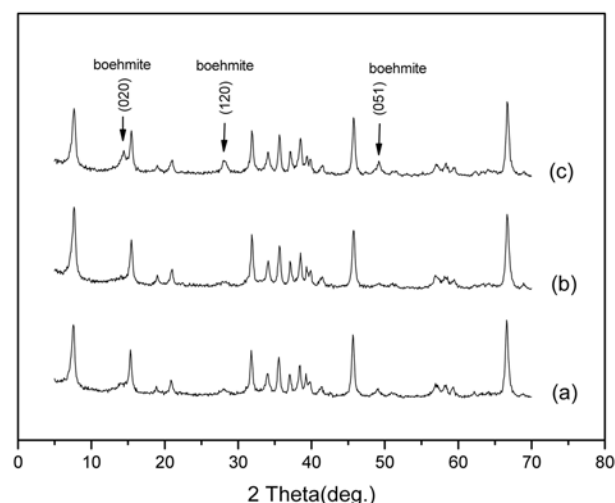
Next, to investigate the ion-exchange rate according to reaction time, the XRD of the ion-exchanged specimen that used the K^+-β''-alumina with the $K_2O\cdot6Al_2O_3$ composition and 1 M NH_4NO_3 solution at 150 °C for 24 h was performed and the results are shown in Fig. 5. Fig. 5(b)

Fig. 2. The XRD patterns of (a) γ-alumina and (b) K^+-β''-alumina.

Table 1. The remaining K^+ and ion-exchange rate according to the reaction time and the composition of $K_2O \cdot Al_2O_3$

Time (h) Molar ratio	The remaining K^+ (ppm)			Ion-exchange rate (%)		
	1 : 4	1 : 6	1 : 8	1 : 4	1 : 6	1 : 8
0 (precursor)	1.78	1.29	1.73	0	0	0
2	0.26	0.27	0.33	85.5	79.7	80.8
4	0.15	0.21	0.30	91.8	83.9	83.0
6	0.12	0.13	0.36	93.2	89.8	79.3
8	0.18	0.11	0.30	89.7	91.8	82.7

Fig. 6. ion-exchange rate according to the reaction time using K^+-β"-alumina with a 1 : 6 $K_2O \cdot Al_2O_3$ composition in a 1 M NH_4NO_3 solution at 150 °C for 24 h.

shows the maintenance of the β"-alumina structure which has the same peak as the precursor after 2 h, but AlOOH (boehmite) peaks appeared from the [020], [120] and [051] planes after 4 h. As can be seen in Fig. 5(f), the increase of AlOOH was seen due to the collapse of the β"-alumina structure. It is shown that the reaction maintains a high pressure for a long time and this transformed its crystal lattice. Fig. 6 shows the ion-exchange rate according to the reaction time for the K^+-β"-alumina with the $K_2O \cdot 6Al_2O_3$ composition and 1M NH_4NO_3 solution at 150 °C for 24 h.

The investigation of the ion-exchange rate according to the reaction temperature was performed using K^+-β"-alumina with the $K_2O \cdot 6Al_2O_3$ composition and 1 M NH_4NO_3 solution for 2 h at each temperature (130 °C, 150 °C and 180 °C). The XRD analysis at each temperature is shown in Fig. 7. As one can see, the ion exchange was completed without any phase change to the boehmite structure at 130 °C and 150 °C, but at 180 °C, boehmite appeared with the (0 2 0), (1 2 0) and (0 5 1) planes, as shown in Fig. 7(c), due to the increase of the pressure in the autoclave. The ion-exchange rate increased from 78.7%

Fig. 7. The XRD analysis according to the reaction temperature using K^+-β"-alumina with a 1 : 6 $K_2O \cdot Al_2O_3$ composition in a 1 M NH_4NO_3 solution for 2 h (a) 130 °C, (b) 150 °C, (c) 180 °C.

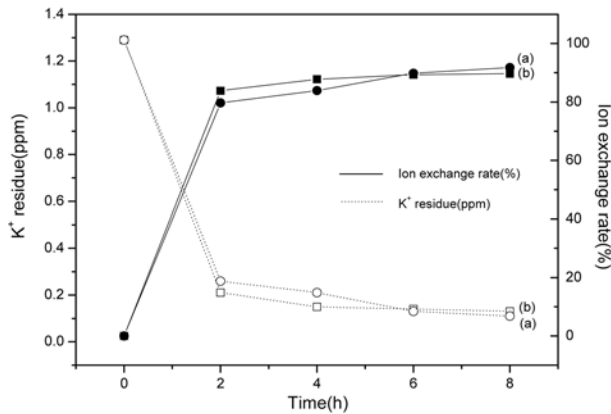at 150 °C to 85.9% at 180 °C, and the results are presented in Table 2.

Lastly, the ion-exchange rate according to the concentration of the NH_4NO_3 solution, the ion-exchange medium, was analyzed. The ion-exchange reaction was carried out using K^+-β"-alumina with the $K_2O \cdot 6Al_2O_3$ composition and 1 M and 2 M NH_4NO_3 solutions at 150 °C for 8 h. Ion-exchange rates of each specimen are shown in Fig. 8 and Table 3. The ion-exchange rate of the reaction using the 2 M NH_4NO_3 solution was higher than that using the 1 M NH_4NO_3 solution before 4 h, owing to the initial higher amount of NH_4NO_3, but not much difference was observed after 8 h.

The ion-exchange reaction in the heating mantle

The ion-exchange reaction was carried out at 180 °C and 200 °C, above the melting point of the NH_4NO_3 salts (169 °C), for 48 h, and also a 5 hour reaction was repeated up to 5 times at 180 °C. The composition of the K^+-β"-alumina precursor was $[K_2O] : [Al_2O_3] = 1 : 5$.

Fig. 5. XRD patterns of NH_4^+/H_3O^+-β"-alumina with a 1 : 6 $K_2O \cdot Al_2O_3$ composition according to the ion-exchange time; (a) precursor, (b) 2 h, (c) 4 h, (d) 6 h, (e) 8 h, (f) 24 h.

Table 2. The phase and ion-exchange rate according to the reaction temperature using K^+-β''-alumina with a 1 : 6 $K_2O\cdot Al_2O_3$ composition in a 1 M NH_4NO_3 solution for 2 h

| Temperature (^oC)	The remaining K^+ (ppm)	Ion exchange rate (%)	Phases
130	0.28	78.7	$K^+/NH_4^+/H_3O^+$-β''-alumina
150	0.26	79.7	$K^+/NH_4^+/H_3O^+$-β''-alumina
180	0.18	85.9	$K^+/NH_4^+/H_3O^+$-β''-alumina AlOOH

Fig. 8. Ion-exchange rate according to the concentration of NH_4NO_3 solution using K^+-β''-alumina with a 1 : 6 $K_2O\cdot Al_2O_3$ composition at 150 ^oC for 8 h. (a) 1 M, (b) 2 M.
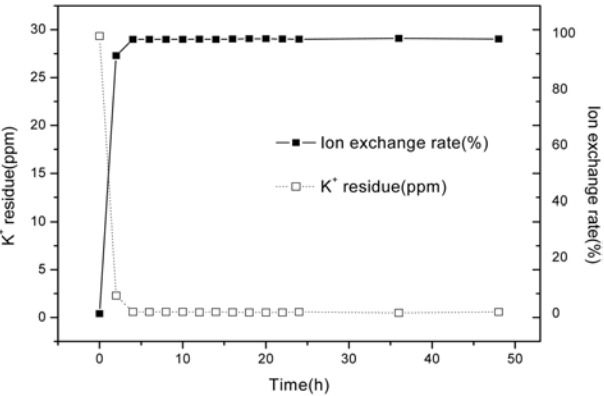
Table 3. Ion-exchange rate according to the concentration of the NH_4NO_3 solution using K^+-β''-alumina with a 1 : 6 $K_2O\cdot Al_2O_3$ composition at 150 ^oC for 8 h.

Time (h) / Molar ratio	The remaining K^+ (ppm)		Ion exchange rate (%)	
	1 M	2 M	1 M	2 M
2	0.26	0.21	79.7	83.8
4	0.21	0.15	83.9	87.8
6	0.13	0.14	89.8	89.3
8	0.11	0.13	91.8	89.7

The phase analysis of each ion-exchanged specimen and ion-exchange rate of the H_3O^+/NH_4^+-β''-alumina at 180 ^oC are shown in Fig. 9, Fig. 10 and Table 4. During all the reactions, the β''-alumina structure was maintained without any phase changes for 48 h. In addition, it is expected that the K^+ ion in the conduction plane in the K^+-β''-alumina was substituted with H_3O^+/NH_4^+ ions, based on the remaining K^+ and ion-exchange rate in Table. 4. For the ion exchange at 200 ^oC, a similar tendency to the preceding results is shown in Fig. 11, Fig. 12 and Table. 5. All specimens maintained the β''-alumina structure for 48 h. The maximum ion-exchange rate was 98% at 180-200 ^oC, and it is confirmed that most of the reaction was completed before 4 h. However, both of the samples exhibited a tendency to have slightly decreased ion-exchange rates
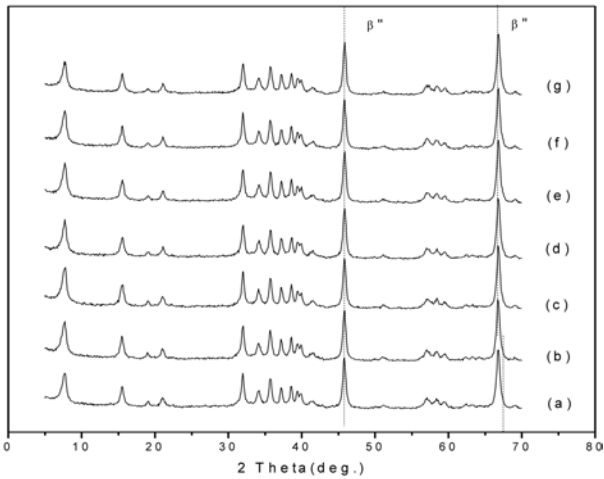
Fig. 9. The XRD analysis according to the reaction temperature using K^+-β''-alumina with a 1 : 5 $K_2O\cdot Al_2O_3$ composition in molten NH_4NO_3 at 180 ^oC for 48 h. (a) 2 h (b) 4 h (c) 6 h (d) 8 h (e) 10 h (f) 24 h (g) 48 h.
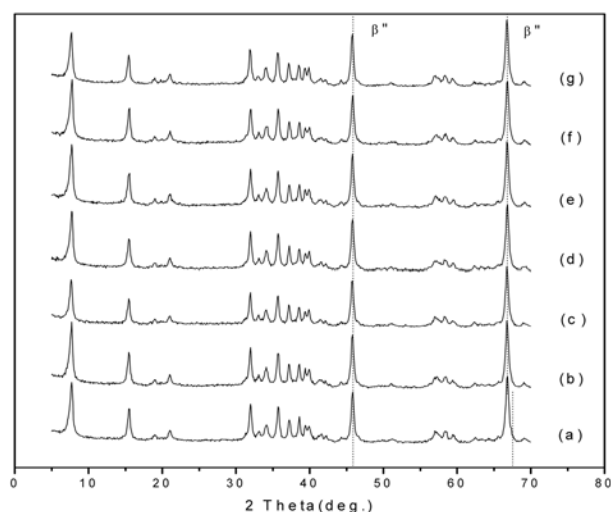

Fig. 10. Ion-exchange rate according to the reaction temperature using K^+-β''-alumina with a 1 : 5 $K_2O\cdot Al_2O_3$ composition in molten NH_4NO_3 at 180 ^oC for 48 h.

Table 4. Ion-exchange rate according to the reaction temperature using K^+-β''-alumina with a 1 : 5 $K_2O\cdot Al_2O_3$ composition in molten NH_4NO_3 at 180 ^oC for 48 h.

Time (hour)	The remaining K^+ (ppm)	Ion exchange rate (%)
precursor	29.340	0
2	2.295	92.177
4	0.583	98.013
6	0.580	98.023
8	0.583	98.013
10	0.585	98.006
24	0.568	98.064
48	0.557	98.101

after 36h. The difference is that the ion-exchange rate was 98% faster in the case of the 180 ^oC sample compared to the case of the sample prepared at 200 ^oC.

A re-ion-exchange experiment was performed several times and this yielded similar results to the preceding XRD

Fig. 11. The XRD analysis according to the reaction temperature using K$^+$-β''-alumina with a 1 : 5 K$_2$O·Al$_2$O$_3$ composition in molten NH$_4$NO$_3$ at 200 °C for 48 h. (a) 2 h (b) 4 h (c) 6 h (d) 8 h (e) 10 h (f) 24 h (g) 48 h.
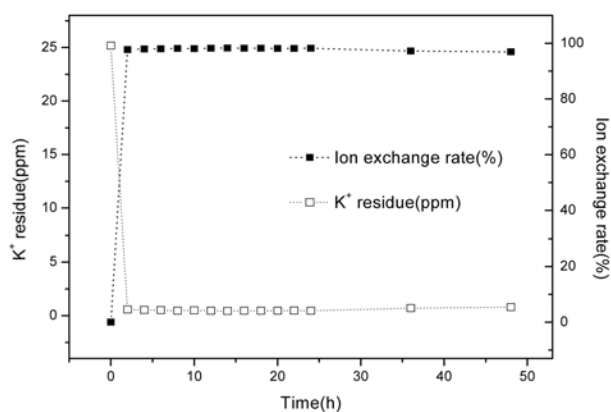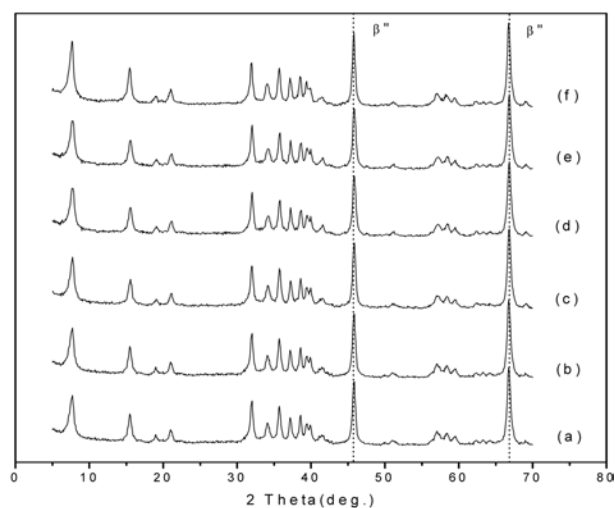

Fig. 13. The XRD analysis according to the number of re-ion exchanges using K$^+$-β''-alumina with a 1 : 5 K$_2$O·Al$_2$O$_3$ composition in molten NH$_4$NO$_3$ at 180 °C for 5 h. (a) precursor (b) 1st (c) 2nd (d) 3rd (e) 4th (f) 5th

Fig. 12. Ion-exchange rate according to the reaction temperature using K$^+$-β''-alumina with a 1 : 5 K$_2$O·Al$_2$O$_3$ composition in molten NH$_4$NO$_3$ at 200 °C for 48 h.

Fig. 14. Ion-exchange rate according to the number of re-ion exchanges using K$^+$-β''-alumina with a 1 : 5 K$_2$O·Al$_2$O$_3$ composition in molten NH$_4$NO$_3$ at 180 °C for 5 h.
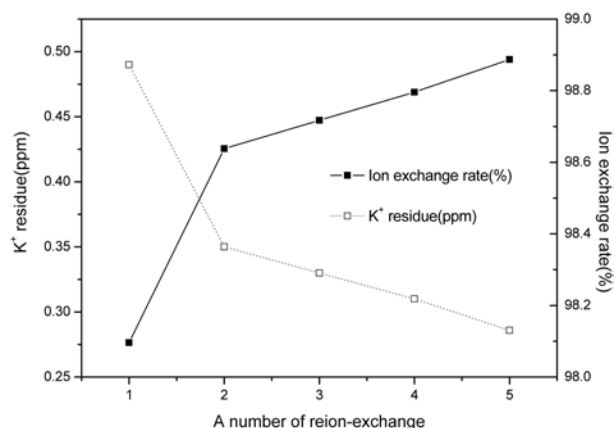
Table.5 Ion-exchange rate according to the reaction temperature using K$^+$-β''-alumina with a 1 : 5 K$_2$O·Al$_2$O$_3$ composition in molten NH$_4$NO$_3$ at 200 °C for 48 h.

Time (hour)	The remaining K$^+$ (ppm)	Ion exchange rate (%)
precursor	25.170	0
2	0.571	97.702
4	0.529	97.885
6	0.507	97.986
8	0.464	98.157
10	0.470	98.026
24	0.460	98.132
48	0.455	98.192

Table 6. Ion-exchange rate according to the number of re-ion exchanges using K$^+$-β''-alumina with a 1 : 5 K$_2$O·Al$_2$O$_3$ composition in molten NH$_4$NO$_3$ at 180 °C for 5 h.

Repetition of times	The remaining K$^+$ (ppm)	Ion exchange rate (%)
1st	0.490	98.096
2nd	0.350	98.638
3rd	0.390	98.717
4th	0.310	98.796
5th	0.286	98.887

analysis of the ion-exchanged H$_3$O$^+$/NH$_4$$^+$-β''-alumina at 180 °C and 200 °C. As one can see in Fig. 13, phase changes to other crystal structures were not observed. However, the ion-exchange rate did increase slightly by

about 1% in total for the 5th re-ion-exchange reactions performed. Here, most of ion-exchange increase was completed during the 2nd re-ion exchange. (Fig. 14, Table 6) This result corresponded to the assumption that the driving force in the high concentration is stronger than that in the low concentration.

Conclusions

This paper shows the preparation of H_3O^+/NH_4^+-β''-alumina using two types of ion-exchange mediums, an NH_4NO_3 solution and molten NH_4NO_3, with a K^+-β''-alumina precursor by an ion-exchange reaction in an autoclave and a heating mantle, respectively.

In the autoclave reaction, most of the reactions were completed within 2 h in the initial stage and the higher potassium concentration precursors yielded higher ion-exchange rates, but β''-alumina collapsed easily over short periods of time. In order to compare the effect of the concentration of the ion-exchange medium, 1 M and 2 M NH_4NO_3 solutions were used. In the initial period, the 2 M NH_4NO_3 solution had a higher ion-exchange rate than did the 1 M NH_4NO_3 solution, but there was not much difference after 6 h. The ion-exchange rate increased with the reaction temperature and time. However, when certain temperatures or times are reached, the β''-alumina structure collapses to AlOOH, which is an undesired secondary phase. The highest ion-exchange rate was about 90% in the autoclave.

In the heating mantle reaction, the β''-alumina phase was stable during all ion-exchange procedures at 180 °C and 200 °C for 48 h. The highest ion-exchange rate was 98%. In the case of the repeating re-ion exchange, the ion-exchange rate was effectively enhanced more than in the experiment where the reaction times were increased. Almost all ion-exchange reactions were completed during the 2nd re-ion exchange (98.6%) and the rate slowly increased to 98.8% by the 5th. Here, the phase transformation to AlOOH did not occur. As stated before, the ion exchange where K^+ was replaced with H_3O^+/NH_4^+ was relatively more efficient in the molten salts than in the aqueous solutions.

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