Protonic Solid Electrolytes: Thermal Stability and Conductivity of Ammonium/Hydronium β''-Alumina

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Ammonium/hydronium β-alumina, $[NH_4/H_3O]_{1.67}Mg_{0.67}Al_{10.33}O_{17}$, is an unusually stable and conductive solid electrolyte for protonic ions. Its conductivity at 200°C, for example, reaches about 10^{-2} (Ω cm)$^{-1}$. This paper describes an investigation of the composition, stability, and ionic conductivity of ammonium/hydronium β''-alumina by means of chemical analysis, TGA, DSC, and complex impedance analysis. The results demonstrate that ammonium/hydronium β''-alumina has a preferential composition of $(NH_4)_{1.0}(H_3O)_{0.67}Mg_{0.67}Al_{10.33}O_{17}$, which corresponds to a rather elegant, albeit only hypothetical at this time, ordered arrangement of ammonium ions, hydronium ions, and vacancies in the structure. Ammonium/hydronium β''-alumina decomposes below 350°C in discrete and reversible reactions that yield water and ammonia. The conductivity of single crystals of $(NH_4)_{1.0}(H_3O)_{0.67}Mg_{0.67}Al_{10.33}O_{17}$ obeys an Arrhenius relationship below 200°C with an activation energy of 0.26 eV ($\sigma = 10^{-3}$ (Ω cm)$^{-1}$ at 25°C). © 1989 Academic Press, Inc.

Introduction

Protonic electrolytes are of considerable technological interest because of their potential application as electrolytes in fuel cells and water electrolyzers. Many compounds exhibit some form of protonic conductivity; most commonly it arises from the presence of weakly bound water which is generally evolved upon heating to about 100°C. One example of a protonic solid electrolyte is hydrogen uranyl phosphate, which has a protonic conductivity of 4×10^{-3} (Ω cm)$^{-1}$ at 25°C (*1*). When it dehydrates near 80°C, its conductivity drops by several orders of magnitude (*2*). Another is antimonic acid, a particle hydrate with an appreciable protonic conductivity at room temperature which also decreases dramatically upon dehydration around 70°C (*3*).

To be truly useful in fuel cells and electrolyzers, a protonic electrolyte should have a high ionic conductivity and be stable from about 100 to 400°C. This range is high enough so that the electrokinetics of the hydrogen and oxygen reactions are fast but not so high that corrosion reactions are severe. These requirements have been summarized by Jensen (*4*), who proposed the following design criteria for protonic electrolytes: (1) structural stability at $T < 400$°C; (2) negligible electronic conductivity; and (3) ionic conductivity of greater than 10^{-3} (Ω cm)$^{-1}$ at $T > 100$°C.

One of the few hydrated solid proton conductors that is both stable and highly conductive above 100°C is ammonium/hydronium β''-alumina, which has the general composition, $(NH_4/H_3O)_{1.67}Mg_{0.67}Al_{10.33}O_{17}$. Ammonium/hydronium β''-alumina is

one of four related compounds: hydronium β-alumina, ammonium β-alumina, hydronium β''-alumina, and ammonium/hydronium β''-alumina. All are synthesized by the ion exchange of sodium β- or β''-alumina. The hydronium derivatives are prepared by exchange in aqueous acids and the ammonium forms by exchange in molten ammonium nitrate. Curiously, crystals of sodium β-alumina immersed in molten ammonium nitrate exchange to a nearly pure ammonium form, while crystals of sodium β''-alumina produce a mixed composition in which the sodium ions are replaced by what is stoichiometrically a mixture of ammonium and hydronium species. Ammonium/ hydronium β''-alumina is particularly interesting, because of all of the protonic β/β''-aluminas, it exhibits the highest conductivity.

This paper describes a study of the composition, stability, and ionic conductivity of ammonium/hydronium β''-alumina. The following questions were addressed: (1) why does a mixed ammonium/hydronium composition form when sodium β''-alumina undergoes ion exchange in ammonium nitrate?, (2) what determines the relative proportions of ammonium and hydronium ions in the structure?, (3) what is the thermal stability of the compound?, and (4) how is the conductivity of ammonium/hydronium β''-alumina influenced by composition?

The β''-Alumina Structure

The compositions and structures of sodium β and β''-alumina have been discussed extensively elsewhere (5, 6) and will not be reviewed in detail here. Briefly, the β''-aluminas are nonstoichiometric cation conductors of the general form, $M_{(1+x)/y}Mg_xAl_{11-x}O_{17}$, in which M denotes the mobile species. The value of x is typically 0.67, and y equals the charge of M.

The β''-aluminas are composed of spinel-type blocks of close-packed oxygens and

aluminums joined by aluminum–oxygen–aluminum linkages. Mobile cations reside in the loosely packed regions between the blocks. The linking oxygens form a hexagonal array within the conduction region and confine the mobile species to hexagonal pathways around the oxygens. The narrowest passage within the conduction region (approximately 3 Å) is between the oxygens linking the spinel blocks (Fig. 1).

The conduction pathways undulate slightly due to the threefold symmetry of the close-packed blocks. This symmetry creates two distinct crystallographic sites within the conduction region. The sites between the linking oxygens are appropriately called the mid-oxygen (MO) sites. They are anti-prismatically coordinated by close-packed oxygens in the blocks. Beevers–Ross (BR) type sites occur at the vertices of the hexagonal conduction pathways and are tetrahedrally coordinated by block oxygens. If all of the BR-type sites were occupied by mobile monovalent cations, the value of x in the formula for β''-alumina would be 2. However, β''-alumina appears always to be nonstoichiometric and to have a deficit of mobile cations. In the most characteristic composition for sodium β''-alumina, $x = 0.67$, and sodium ions fill only $\frac{5}{6}$ of the available BR-type sites.
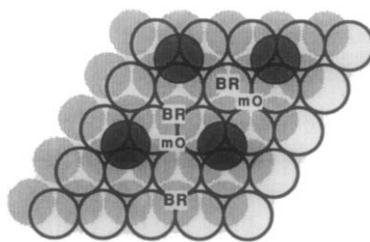

FIG. 1. Schematic diagram of the conduction plane of β''-alumina (looking down the c-axis). Open circles represent oxygen layer in the upper spinel block. Dark circles are bridging oxygens (O5), and shaded circles are oxygens in the lower spinel block. O5–mO–O5 distance is 3.0 Å.

Sample Preparation

Single crystals of ammonium/hydronium β''-alumina were prepared from Mg^{2+}-stabilized sodium β''-alumina. The crystals of sodium β''-alumina were grown in platinum crucibles in air at 1680–1700°C from a mixture of Na_2O, MgO, and Al_2O_3. Growth periods of more than 20 days at 1700°C resulted in large single crystals of typical dimensions $1 \times 1 \times 0.4$ cm. The stoichiometry of the as-grown material was determined by measuring the weight change that accompanied ion exchange with silver (7), and the crystals were found to have the general formula, $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$.

Samples of ammonium/hydronium β''-alumina were prepared by immersing sodium β''-alumina crystals in molten ammonium nitrate (NH_4NO_3; Mallinckrodt) at 195°C for several hours. The radioactive tracer, ^{22}Na, was used to monitor the extent of exchange. Prior to exchange, single crystals of sodium β''-alumina were equilibrated in molten $^{22}NaNO_3$ at 350°C for approximately 1 hr. The extent of sodium replacement in the crystal during ion exchange was measured by the loss of radioactivity. In general, small single crystals of sodium β''-alumina of approximately $2 \times 3 \times 0.2$ mm in size converted to ammonium/hydronium β''-alumina within 5 hr and resulted in samples of the general formula, $(NH_4/H_3O)_{1.67}Mg_{0.67}Al_{10.33}O_{17}$.

Determination of Sample Composition

The general formula of ammonium/hydronium β''-alumina can be written as $(NH_4)_y(H_3O)_{1.67-y}Mg_{0.67}Al_{10.33}O_{17}$. Reported values of y range from 1.0 to 1.5 (8–10). To determine the ammonium content of samples prepared in this work, we employed an evolved gas analysis (EGA) method similar to the one described by Farrington and Briant (8).

Approximately 50 mg of finely ground ammonium/hydronium β''-alumina was placed in one arm of an inverted U-tube, and approximately 10 ml of 4% boric acid solution was added to the other arm. The boric acid arm was then immersed in liquid nitrogen and the apparatus sealed under vacuum. The sample arm was heated to 500°C while the boric acid was held in liquid nitrogen. The gases evolved from the thermal decomposition of the sample condensed and froze in the cold boric acid arm of the container. After several hours, the apparatus was returned to room temperature, the seal was ruptured, and the ammonia–boric acid solution was titrated with hydrochloric acid using bromcresol green indicator. Repeated experiments demonstrated that a heating time of 1 hr at 500°C was sufficient to remove all traces of ammonia from approximately 50 mg of ammonium/hydronium β''-alumina powder.

The ammonium contents of various samples of ammonium/hydronium β''-alumina exchanged in ammonium nitrate for 3, 4, and 7 days were determined. Figure 2 illustrates the relationship between duration of exchange and ammonium-content "y." After 7 days of immersion in the exchange bath, the ammonium content reached a steady-state value of $y = 1.0$. Similar compositions were found by Farrington and Briant who reported the same composition
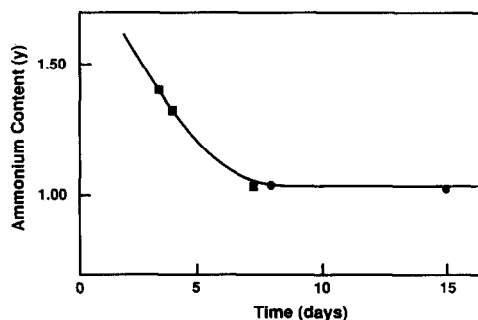

FIG. 2. Relationship of ammonium content (y) to duration of exchange in ammonium/hydronium β''-alumina.

for samples exchanged for 8, 15, and 43 days (8), but they did not recognize its relation to the duration of exchange. At the composition of $y = 1.0$, ammonium ions account for 60% of the mobile ion content and hydronium ions for the remaining 40%.

Thermal Stability

The thermal decomposition of ammonium/hydronium β''-alumina was examined using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Fine powders were used in all experiments in order to minimize errors due to slow mass and heat transfer. In addition, the amount of ammonia in the evolved gas was measured by bubbling the effluent stream of the TGA through a 4% boric acid solution and titrating with hydrochloric acid.

Previous thermogravimetric studies (9) found that ammonium/hydronium β''-alumina undergoes a single weight loss of approximately 4.8 wt% between 150 and 350°C. The evolved gases were found to contain a mixture of ammonia and water vapor, and it was difficult to separate the relative amounts of each. These earlier experiments were carried out at scan rates of 5°C/min or higher. We now have found that what previously appeared to be a single weight loss reaction resolves into two distinct reactions when the compound is
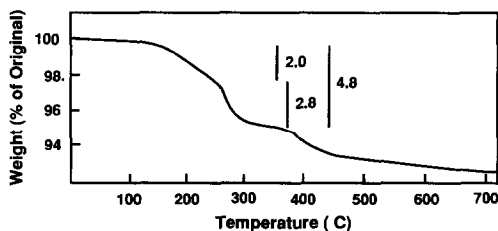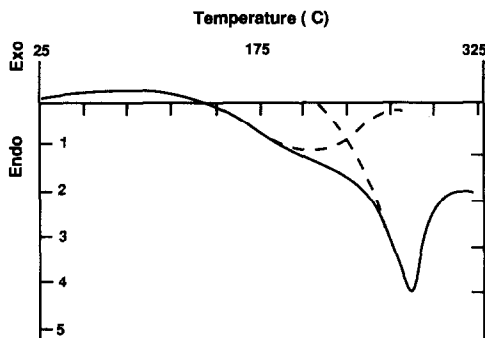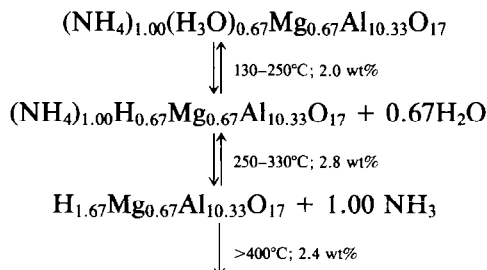
FIG. 4. Differential calorimetry scan for ammonium/hydronium β''-alumina. Dotted lines represent endothermic reactions associated with water loss (200°C) and ammonia loss (275°C). Scan rate = 5°C/min in flowing nitrogen.

heated at the slow rate of 0.5°C/min (Fig. 3).

The first thermal loss from ammonium/hydronium β''-alumina (2.0 wt%) occurs in the range 130–250°C; the second (2.4 wt%) is more distinct and takes place over a narrower temperature range, 250–300°C. Chemical analysis of the effluent stream has shown that the second transition is the result of the evolution of ammonia. We have therefore attributed the first transition (2.0 wt%) to the loss of water. Differential scanning calorimetry has confirmed the existence of two separate endothermic reactions which correspond to the TGA transitions (Fig. 4). The enthalpy of the water evolution reaction is approximately 10 kcal/mole, and the enthalpy of the ammonia loss is 19 kcal/mole.

The weight of ammonium/hydronium β''-alumina is constant from 300 to 400°C. A final weight loss occurs above 400°C, and by 900°C no further losses are observed. Frase (9) showed that all of the protonic species are evolved from ammonium/hydronium β''-alumina by 900°C and that the residue contains only Mg, Al, and O in the ratio 1.67 : 10.33 : 16.33. On the basis of this final composition and our direct mea-

FIG. 3. TGA graph for ammonium/hydronium β''-alumina. Scan rate = 0.5°C/min in flowing nitrogen. Bars indicate magnitudes of specific weight losses.

surements of the amount of ammonia evolved from samples, we propose the following thermal decomposition scheme for ammonium/hydronium β''-alumina.

$$(NH_4)_{1.00}(H_3O)_{0.67}Mg_{0.67}Al_{10.33}O_{17}$$

$\Updownarrow$ 130–250°C; 2.0 wt%

$$(NH_4)_{1.00}H_{0.67}Mg_{0.67}Al_{10.33}O_{17} + 0.67H_2O$$

$\Updownarrow$ 250–330°C; 2.8 wt%

$$H_{1.67}Mg_{0.67}Al_{10.33}O_{17} + 1.00\ NH_3$$

$\Downarrow$ >400°C; 2.4 wt%

Various Phases Formed by Mg, Al, and O

According to this set of reactions, when ammonium/hydronium β''-alumina is heated from room temperature to 300°C, hydronium and ammonium ions dissociate into water, ammonia, and protons. Water and ammonia are evolved, but the protons remain in the conduction plane to maintain charge neutrality. Neutron diffraction studies (7) have shown that some and perhaps all of the protons bond to column oxygens. Because the structural integrity of the compound is not disrupted below 300°C, it is reasonable to expect these reactions to be reversible.

The reversibility of the water loss reactions was studied by thermally cycling samples in a humid atmosphere. A sample of ammonium/hydronium β''-alumina was first transformed to hydrogen β''-alumina by slowly heating it to 325°C under dry nitrogen in the TGA. The sample was then slowly cooled to room temperature in a stream of humid nitrogen. The sample actually regained more weight than it had lost. The excess could be easily removed upon mild heating below 100°C and was therefore considered to be surface water. Subsequent thermal cycling to 325°C resulted in a single weight loss (4.8 wt%) between 100 and 250°C. DSC analysis of original and rehydrated samples also confirmed the presence of both adsorbed and absorbed water (Figs.
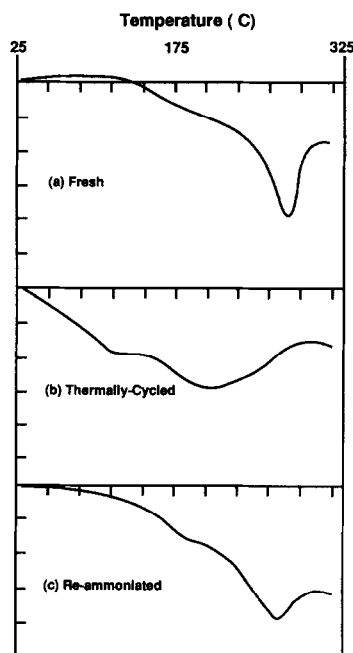

FIG. 5. Differential calorimetry scan of (a) freshly prepared ammonium/hydronium β''-alumina, (b) rehydrated sample, (c) reammoniated sample. All scans are referenced against α-alumina and recorded at a scan rate of 5°C/min in flowing nitrogen.

5a and 5b). For the rehydrated material, an endotherm attributable to absorbed water is the dominant feature in the DSC trace; adsorbed water produces a small broad endothermic peak centered around 100°C.

The reammoniation of hydrogen β''-alumina was also attempted. It was carried out in a closed, dry system, to prevent competitive absorption of water. Approximately 50 mg of ammonium/hydronium β''-alumina powder was first heated to 325°C in vacuum to produce hydrogen β''-alumina. A portion of the sample was removed from the vessel and analyzed to determine that all of the ammonium species had been decomposed. Hydrogen β''-alumina rehydrates rapidly, so the sample was reheated to 300°C under vacuum to drive off reabsorbed water. The vessel was then back-filled with approximately 1 atm of anhydrous ammonia gas

and slowly cooled to room temperature over 12 hr. DSC data indicate that ammonia reentered the structure (Fig. 5c). The sharp endotherm associated with the initial loss of ammonia reappeared at 250°C, though it was smaller than in the original sample. It is not clear why it was smaller.

Conductivity Measurements

Ionic conductivity measurements on fresh and thermally treated ammonium/hydronium β''-alumina were carried out using complex impedance analysis. The measurement system consisted of a Solartron 1174 frequency response analyzer and a programmable furnace, all controlled by a Hewlett–Packard 9845A computer. Impedance was measured over a frequency range 100–65,000 Hz with an ac perturbation of 100 mV (peak-to-peak). All measurements were made on single crystals of ammonium/hydronium β''-alumina in order to eliminate uncertainties due to grain boundary conduction processes. The crystals were contacted with sputtered gold

electrodes covered with silver paint and held between spring-loaded platinum plates.

The conductivity of ammonium/hydronium β''-alumina was measured at several temperatures during heating in dry argon. Samples were annealed for 10 min at each temperature prior to the conductivity measurement. The results are plotted in Fig. 6. Below 170°C, the data follow an Arrhenius relationship,

$$\log(\sigma T) = \log \sigma_0 - E_a/kT,$$

where σ_0 and E_a/k are best-fit parameters of the intercept and slope, respectively. The average conductivity of ammonium/hydronium β''-alumina is 1.3×10^{-3} $(\Omega \text{ cm})^{-1}$ at 30°C, with an activation energy of 0.27 eV below 170°C. The samples for which these data were measured had been exchanged for more than 5 days in ammonium nitrate. Based on the composition studies discussed previously, they were assumed to be near the "60/40" composition. Samples exchanged for 3 days (hence approximately a 84/16 composition) exhibited only slightly higher conductivities (2.8×10^{-3} $(\Omega \text{ cm})^{-1}$ at 30°C; $E_a = 0.24$ eV).

Above 170°C, the conductivity slowly decreases when the samples are held at each temperature for 4 hr (Fig. 7). Longer annealing periods might shift the onset of conductivity loss to lower temperatures. Thus, we associate this conductivity loss with the onset of thermal decomposition in powdered samples. After long periods of heating in air at 280°C, the conductivity of ammonium/hydronium β''-alumina decreases by several orders of magnitude, to as low as 10^{-6} $(\Omega \text{ cm})^{-1}$ at 25°C, and its activation energy increases to about 0.45 eV (Fig. 8). These values are very similar to the conductivity data previously reported for hydronium β''-alumina (8) in the same temperature range, suggesting that both ammonium/hydronium and hydronium β''-alu-
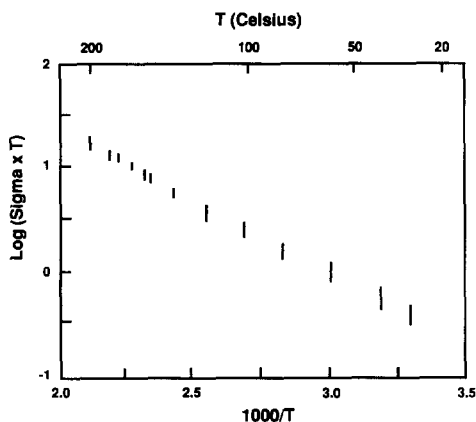

FIG. 6. Arrhenius plot of the conductivity of ammonium/hydronium β''-alumina, $(NH_4)_{1.0}(H_3O)_{0.67}Mg_{0.67}Al_{10.33}O_{17}$. Data taken during cooling from 200°C in flowing, dry argon. Each bar represents the spread of independent measurements on five different crystals.
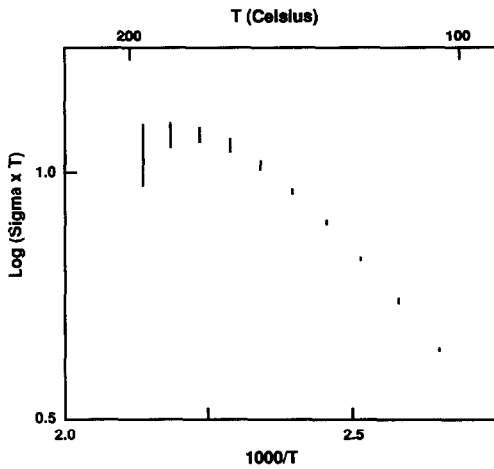
FIG. 7. Arrhenius plot of the conductivity of ammonium/hydronium β''-alumina. Data taken during heating from 25 to 200°C in flowing, dry argon. The sample was heated at each temperature for 4 hr. Each bar represents the spread of four conductivity measurements during the time the sample was at each temperature. At the six highest temperatures, the conductivity values decreased steadily during the heating process.

dence that it contains traces of water (*11*). Infrared spectroscopy (*12*) and neutron diffraction studies (*10*) have confirmed the existence of both ammonium and hydrated protonic species in ammonium/hydronium β''-alumina. These hydrated protonic species have been generally referred to as hydronium ions, because the stoichiometry of the material is consistent with the presence of hydronium ions. However, it must be emphasized that none of the experiments carried out to date have differentiated between the presence of true hydronium ions and of hydrated protons, such as water molecules closely associated with protons bonded to another electronegative species. The term, hydronium, is conveniently used, but the demonstration that hydronium ions actually do or do not exist in the β-aluminas awaits the results of further investigations.

The most likely source of the hydronium ions that enter sodium β''-alumina is the decomposition of the ammonium nitrate exchange bath to nitrous oxide and water at the exchange temperature of 200°C.

mina slowly transform into the same composition upon heating at 200°C.

Discussion

The data presented have provided insight into three central issues concerning ammonium/hydronium β''-alumina: (1) the reason hydronium ions are found in the material along with ammonium ions; (2) the general thermal stability of the compound; and (3) the relationship between its composition and conductivity.

In considering the question of why the ion exchange of sodium β''-alumina in molten ammonium nitrate produces a mixed ammonium–hydronium composition, it is useful to recall that this result occurs with sodium β''-alumina but not with sodium β-alumina. The latter readily undergoes ion exchange in molten ammonium nitrate but transforms into nearly anhydrous ammonium β alumina, although there is some evi-
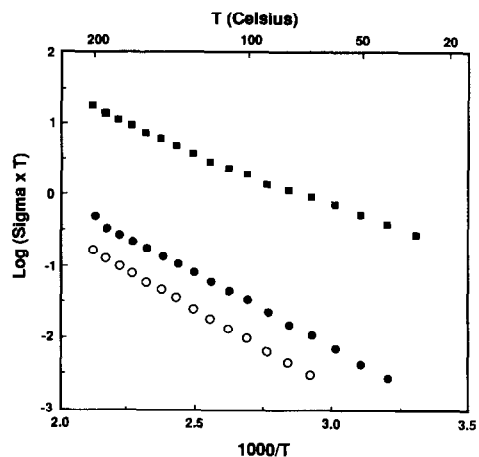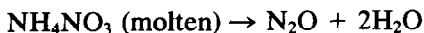
FIG. 8. Arrhenius plots illustrating the change in the conductivity of ammonium/hydronium β''-alumina upon long-term heating at 200°C in water vapor. ■, Fresh sample; ●, heated for 10 days; ○, heated for 36 days.

$$NH_4NO_3 \text{ (molten)} \rightarrow N_2O + 2H_2O$$
$$NH_4^+ \text{ (molten salt)} \rightarrow NH_3 + H^+$$

The most reasonable explanation for the absence of hydronium species in ammonium β alumina is that they diffuse too slowly to accumulate beyond trace amounts. Based on conductivity data for hydronium β-alumina (13) and ammonium β-alumina (11), hydronium ions are only 10^{-3} times as conductive as ammonium ions at 200°C. However, the estimated conductivities of hydronium β''-alumina and ammonium/hydronium β''-alumina are within an order of magnitude of each other at 200°C. Thus, hydronium ions clearly are far more mobile in β''-alumina than β-alumina, and thus it is not surprising to find both hydronium and ammonium species in ammonium/hydronium β''-alumina.

Long periods of exchange in ammonium nitrate lead to the steady-state composition $(NH_4)_{1.0}(H_3O)_{0.67}Mg_{0.67}Al_{10.33}O_{17}$. This is referred to as the "60/40" composition, because ammonium ions account for 60% of the mobile species and hydroniums account for 40%. The ammonium concentration was determined from an analysis of the gases evolved during thermal decomposition, and the hydronium content was assumed on the basis of charge neutrality. The slow exchange kinetics which lead to a relatively slow approach to the apparent 60/40 equilibrium would explain why a number of different compositions of ammonium/hydronium β''-alumina have been reported in the literature (8–10).

The thermal decomposition of ammonium/hydronium β''-alumina occurs in three steps. The first two steps ($T < 350°C$) reflect the loss of water and ammonia, and the final weight loss ($T > 400°C$) signals the irreversible collapse of the structure. Water and ammonia evolve separately below 350°C, and these losses are reversible. These transitions can be resolved only at very slow scan rates ($\leq 0.5°C/min$). Al-though it was difficult to control the proportion of ammonium and hydronium species in the structure during rehydration and reammoniation, TGA and DSC results confirmed the reversibility of these processes.

The conductivity of single crystals of ammonium/hydronium β''-alumina follows Arrhenian behavior below 170°C. When samples are heated for long times at 200–250°C, the conductivity decreases dramatically. Ultimately, the conductivity of such samples achieves what appear to be stable values comparable to those observed for hydronium β''-alumina at similar temperatures. This loss in conductivity appears to result from the formation of dehydrated regions near the edges of the crystals. Scanning micro-Raman results (14) have shown that, during heating at higher temperatures around 280°C, ammonium-deficient regions begin to form at the edges of single crystals and grow into the crystals very slowly.

Taken together, these experimental results suggest that the 60/40 proportion of ammonium and hydronium ions in ammonium/hydronium β''-alumina is not accidental and is, in fact, more stable than other compositions. From the composition and stability data presented in this work and the results of previous structure studies, it is possible to speculate about the critical structure/property relationships in ammonium/hydronium β''-alumina which favor the establishment of this particular composition.

A single crystal neutron diffraction study of the structure of ammonium/hydronium β''-alumina reported by Thomas and Farrington (10) has shown that ammonium ions occupy BR sites and hydronium ions reside between mO and BR sites (Fig. 9). The major axis of each ammonium ion is aligned along the c-direction of the crystal, and its three remaining N–H bonds extend toward the nearest bridging oxygens. Hydronium ions are centered between mO and BR sites
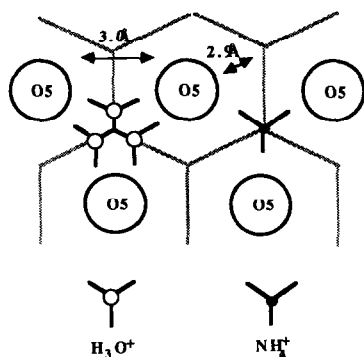
FIG. 9. The arrangement of ammonium and hydronium ions in the conduction plane of ammonium/hydronium β''-alumina according to Thomas and Farrington (10). The ammonium ions are situated in the BR sites, and the hydronium ions occupy three equivalent sites near the BR site.

with one O–H bond directed toward the BR site and the other two toward adjacent bridging oxygens. Hydroniums occupy three equivalent positions around each BR site, and there is extensive hydrogen bonding between hydroniums and bridging oxygens. Thus, the hydronium ion location can be represented by three hydrogen bonds extending from the center (the BR site) of the equivalent positions occupied by hydronium ions to the three surrounding bridging oxygens. If this arrangement of ammonium and hydronium species is extended to many unit cells and the population of ions constrained to the 60/40 composition, a rather elegant ordered structure is produced (Fig. 10). The 60/40 composition is essential for the formation of this ordered structure, and we propose that it may be the formation of this ordered structure which enhances the stability of the 60/40 composition.

The stability of this proposed arrangement of mobile ions in the conduction plane of ammonium/hydronium β''-alumina arises from its extensive hydrogen bonding and ammonium-vacancy interactions. First, a minimum of 40% hydronium occupancy in the conduction plane is necessary for all of the bridging oxygens to join in the hydro-

gen-bonded network. Second, when 60% of the cationic charge is the result of ammonium ions, each vacancy in the conduction plane is surrounded by three ammoniums.

The proposed structure also leads to intriguing speculation about the conduction mechanism is ammonium/hydronium β''-alumina. It is possible that conduction in the material actually occurs by Grotthus-like proton transfer through the extensive hydrogen-bonded network of ions and lattice oxygens. Whether or not Grotthus-like transport actually occurs in ammonium/hydronium β''-alumina has long been a tantalizing question. This work does not resolve the issue, but it does provide a structural model which may make such transport seem more likely.

Summary and Conclusions

In summary, we have presented data which demonstrate that the composition, thermal stability, and ionic conductivity in ammonium/hydronium β''-alumina are
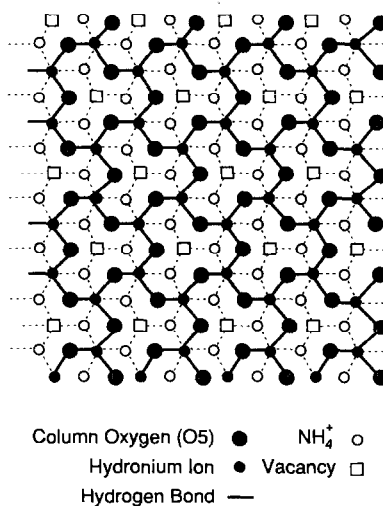

Column Oxygen (O5) ●   NH$_4^+$ ○
Hydronium Ion ●   Vacancy □
Hydrogen Bond —

FIG. 10. Proposed ordered structure of the conduction plane of the 60/40 composition of ammonium/hydronium β''-alumina, $(NH_4)_{1.0}(H_3O)_{0.67}Mg_{0.67}Al_{10.33}O_{17}$. The hydronium ions form hydrogen bonds with the column oxygens, and the vacancies are stabilized by the ammonium ions.

closely interrelated. The proportions of ammonium and hydronium ions vary from sample to sample, depending on the duration of the ion exchange process. Eventually, however, a steady-state composition is achieved: $(NH_4)_{1.0}(H_3O)_{0.67}Mg_{0.67}Al_{10.33}O_{17}$. This composition corresponds to a rather elegant ordered arrangement of ammonium ions, hydronium ions, and vacancies in the structure.

We have also found that water and ammonia evolve from ammonium/hydronium β''-alumina in discrete steps below 350°C. Water is lost from the structure between 150 and 250°C with an enthalpy of 10 kcal/mole. The loss of ammonia occurs at 250–300°C with an enthalpy of 19 kcal/mole. Below 300°C, the thermal decomposition of ammonium/hydronium β''-alumina is reversible.

The conductivity of single crystals of ammonium/hydronium β''-alumina (steady-state composition) obeys an Arrhenius relationship below 200°C with an activation energy of 0.26 eV ($\sigma = 10^{-3}$ (Ω cm)$^{-1}$ at 25°C). Heating at 280°C causes the conductivity to fall into the range observed for samples of hydronium β''-alumina ($\sigma = 10^{-6}$ (Ω cm)$^{-1}$ at 25°C; $E_a = 0.45$ eV).

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