JOURNAL OF SOLID STATE CHEMISTRY **24**, 311–319 (1978)

Ionic Conductivity in H_3O^+ Beta Alumina

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Received June 6, 1977; in final form July 25, 1977

The first detailed conductivity measurements on single crystals of H_3O^+ beta alumina are discussed in this paper. The conductivity of single crystal H_3O^+ beta alumina at 20°C is 10^{-11} (ohm cm)$^{-1}$. From 20 to about 200°C it increases in an Arrhenius relationship with an activation energy of 18 kcal/mole. Between 200 and 300°C H_3O^+ beta alumina undergoes a partial and reversible dehydration in which approximately 50% of its H_3O^+ content is converted to H^+. The resulting composition, H^+–H_3O^+ beta alumina has a much lower conductivity at 300° than H_3O^+ beta alumina. H^+–H_3O^+ beta alumina has a conductivity of 10^{-6} (ohm cm)$^{-1}$ at 500°C, which varies between 300 and 550° in an Arrhenius expression with an activation energy of 29 kcal/mole.

Introduction

Proton conduction in solids is important in a variety of physical, biological, and chemical processes (*1*). It proceeds in many natural and synthetic organic polymer networks through a series of interconnected hydrogen bonds linking a relatively immobile framework of oxygen atoms. This study focuses on H^+ and H_3O^+ conduction in the inorganic structural framework, beta alumina. Unlike organic polymers, beta alumina, which in the sodium form has the composition $(1 + x)Na_2O \cdot 11Al_2O_3$, $0 < x < 0.3$, is stable at high temperatures in aggressive chemical environments. Na^+ beta alumina has a two-dimensional layer structure (*2*, *3*) in which tightly packed aluminum-oxygen "spinel" blocks are separated by relatively open conducting planes in which the sodium ions are located. Also in the conducting planes are "spacer" oxygens which bind together the alternating spinel blocks. Within the conducting planes, Na ions are mobile in two dimensions. Single crystal Na^+ beta alumina has an ionic conductivity of about 10^{-2} (ohm cm)$^{-1}$ at 25°C.

Saalfeld *et al.* (*4*) first demonstrated that the entire Na^+ content of Na^+ beta alumina can be replaced with H_3O^+ by equilibrating single crystals of Na^+ beta alumina with concentrated H_2SO_4 at 290°C. Complete exchange of Monofrax Na^+ beta alumina crystals of about 2 mm in diameter required about 14 days and several changes of H_2SO_4.

As Saalfeld *et al.* (*4*) and Breiter *et al.* (*5*) have shown, two forms of hydronium beta alumina exist over the temperature range of 20 to 550°C. The composition of the low temperature form may be represented as $n_A H_2O \cdot 11Al_2O_3$, that of the high temperature form as $n_B H_2O \cdot 11Al_2O_3$. These two compositions reversibly interconvert by a process of water desorption/absorption in the range of 200 to 300°C. Above about 700°C, hydronium beta alumina irreversibly decomposes into alpha alumina and water. Equation [1] summarizes these reactions:

$$n_A H_2O \cdot 11Al_2O_3 \underset{200-300°C}{\rightleftharpoons} n_B H_2O \cdot 11Al_2O_3 + H_2O \underset{>700°C}{\longrightarrow} \alpha Al_2O_3 + H_2O. \quad [1]$$

The composition of the low temperature

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0022-4596/78/2434-0311$02.00/0

form, $n_AH_2O \cdot 11Al_2O_3$, in the crystals used for the present conductivity measurements was $(3.8 \pm 0.2)H_2O \cdot 11Al_2O_3$, which corresponds to the composition in which every sodium ion has been replaced by an hydronium ion. In the high temperature form, $n_BH_2O \cdot 11Al_2O_3$, the value of n_B is 2.4 ± 0.1. The high temperature composition contains about one water molecule for every two protons in the conducting plane. In this paper, the low temperature composition will be designed as H_3O^+ beta alumina and the high temperature form as H^+–H_3O^+ beta alumina.

Conductivity in hydronium beta alumina may occur by several different mechanisms, such as proton exchange among water molecules and hydronium ions within the conducting plane, proton exchange among lattice oxygens bounding or located in the conduction plane, and hydronium ion migration. The conductivity of H^+–H_3O^+ beta alumina is of particular interest, since H^+–H_3O^+ beta alumina is analogous to Li^+–Na^+ beta alumina. In both of these compounds, an unexpectedly stable beta alumina composition containing two different ions is formed. This has previously been termed "co-ionic" behavior and may be a general phenomenon with solid ionic conductors (*6*, *7*).

No definitive conductivity or diffusion measurements on hydronium beta alumina have been reported. The object of the present experiments was to determine the conductivity of well-characterized hydronium beta alumina crystals as a function of temperature from 20 to 550°C. Single crystals were studied in order to eliminate uncertainties that might have arisen from grain boundary effects or porosity within polycrystalline material. Single crystals of beta alumina cleave readily along the conducting planes, and therefore are typically found as thin platelets. In order to measure conductivity parallel to the conducting planes, contact is made to the edges of the platelets. No determinations of conductivity in the direction normal to the conducting planes were carried out.

Preparation of H_3O^+ Beta Alumina Crystals

Good quality single crystals, approximately 2 mm × 2 mm × 0.1 mm were carefully selected from crushed Monofrax Na^+ beta alumina. Groups of crystals were suspended in Pt screen baskets in a quartz beaker containing concentrated H_2SO_4 (96–98%). The acid was heated to about 290°C, just below its boiling point, and exchange allowed to proceed for about 14 days during which the H_2SO_4 was changed once.

As the exchange progressed, considerable degradation of the crystals took place. Saalfeld *et al.* (*4*) have also observed that H_2SO_4 attacks beta alumina at a slow rate. However, after washing in distilled water, a satisfactory quantity of small, thin, and clear crystals remained. Analysis by X-ray diffraction confirmed that they had the beta alumina structure. Chemical analysis for Na^+ by atomic absorption of a sample dissolved in aqueous HF revealed that greater than 98% of the Na^+ content initially present in the crystals had been exchanged. Separate analysis for Na^+ in the unexchanged crystals found them to contain 6.2% Na^+ (wt% as Na_2O). These results are consistent with the chemical composition of $1.32\ Na_2O \cdot 11Al_2O_3$ given previously by Breiter *et al.* (*5*) on the basis of the weight increase accompanying complete Ag^+ exchange of Na^+ beta alumina crystals from the same source as those used here.

In order to determine the extent of H_2O loss resulting from partial dehydration of H_3O^+ beta alumina, a sample of millimeter-sized H_3O^+ beta alumina crystals was weighed into a small Pt cup. The crystals were heated to 300°C, above the temperature range of 180° to 250°C in which Saalfeld *et al.* (*4*) observed partial dehydration. After 3 hr, the sample had lost 1.55% in weight. Continued heating at 300°C for 24 hr produced no further weight decrease. The magnitude of the weight loss agrees closely with data reported by Breiter *et al.* (*5*) for powdered samples of Monofrax H_3O^+ beta alumina prepared as in this procedure. Considering the initial composition of the Monofrax Na^+ beta alumina to be 1.32 $Na_2O \cdot 11Al_2O_3$, and the composition of fully hydrated H_3O^+ beta alumina prepared from the same material to be 3.8 ± 0.2 $H_2O \cdot 11Al_2O_3$, as determined earlier from the weight change upon complete conversion of H_3O^+ beta alumina to Al_2O_3 at 1000°C, the composition of the partially dehydrated hydronium beta alumina at 300°C is 2.4 ± 0.1 $H_2O \cdot 11Al_2O_3$.

Conductivity Experimental Procedure

Selected H_3O^+ beta alumina crystals were mounted on polished alpha alumina disks with insulating varnish. Separate experiments demonstrated that the surface conductivity of the disks was undetectable between 20 and 500°C. The conductivity of the varnish is insignificant below 300°C, but it increases upon carbonization at 300 to 500°C in air. The varnish completely pyrolyzes within 45 min at 550°C in air. So experiments on H_3O^+ beta alumina crystals could be carried out between 20 and 300°C without interference from the varnish, and experiments at higher temperatures could be performed if the varnish was first allowed to pyrolyze. Varnish was not essential for holding the samples in place. Satisfactory if fragile bonds were also formed by the electrodes.

Several types of electrodes were used for conductivity experiments. Measurements at 25°C were made with two- and four-probe contacts using Ag electrodes, applied as a suspension of finely divided Ag particles in a volatile organic solvent, and with electrodes formed of a paste of carbon black and concentrated H_2SO_4. The H_2SO_4 electrodes were only suitable for room temperature measurements because of the acid's tendency to creep with increasing temperature. Experiments at higher temperatures were carried out both with Ag electrodes and with C electrodes, applied as a colloidal suspension (Aquadag).

Initial observations indicated that the conductivity of H_3O^+ beta alumina is quite small. It was not possible to use multifrequency ac impedance measurements. Therefore, a dc technique was adopted in which a Keithley digital electrometer (Model 616) was used to compare the voltage across a sample with that across a (1×10^6) or a (10×10^6)-ohm resistor in series with the sample. Current was supplied with a 22-V battery. Figure 1 details the simple measuring circuit.

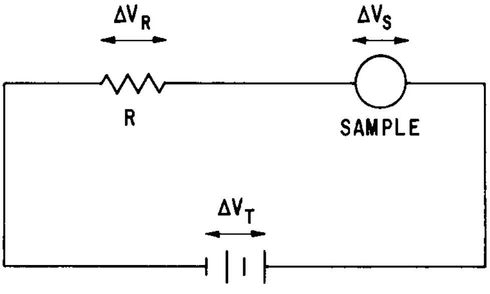

FIG. 1. Circuit for conductivity measurements.

One uncertainty affecting all the conductivity experiments is the question of whether the two-probe, Ag and C interfaces contributed significantly to the observed resistivities of the crystals. To demonstrate that Ag/beta alumina and, by extension, C/beta alumina interfaces could support adequate ionic current for these measurements, two comparable single crystals, one of Na^+ beta alumina and the other of H_3O^+ beta alumina, were mounted on a single alpha alumina disk. Two-probe contacts were made to each with Ag paint. The current through each crystal was then measured as a function of temperature from 20 to 500°C. Over the entire temperature range, the current through the Na^+ beta alumina sample was 10^4 to 10^6 times greater than that through the H_3O^+ beta alumina sample. The level of current was not sufficient at lower temperatures to yield an accurate determination of the conductivity of Na^+ beta alumina. For this compound the electrode/electrolyte interfaces still dominated the crystal resistivity. But, the current that flowed through the Na^+ beta alumina crystal, on the assumption that changing the crystal composition does not affect electrode behavior, was more than sufficient to demonstrate that the electrode impedance was insignificant in measuring the much lower H_3O^+ beta alumina conductivity. These observations, combined with the reproducibility of conductivity results with multiple H_3O^+ beta alumina crystals, argue that the two-probe approach used in these experiments truly measured crystal conductivity.

Results

Conductivity of H_3O^+ Beta Alumina at 20°C

Conductivity results obtained for single crystal samples of H_3O^+ beta alumina at 20°C are summarized in Table I. No significant difference was observed between experiments using Ag and H_2SO_4 electrodes, or between two- and four-probe measurements. Specific conductivities of about 10^{-11} (ohm cm)$^{-1}$ are observed regardless of technique. This value is probably an upper limit on conductivity; data obtained at higher temperatures indicate that surface conductivity may increase the observed conductivity measurements between 20 and 80°C. An estimate of the conductivity of H_3O^+ beta alumina at 20°C calculated by extrapolating data observed at temperatures between 20 and 200°C is 10^{-12} (ohm cm)$^{-1}$.

TABLE I

CONDUCTIVITY OF HYDRONIUM BETA ALUMINA AT 20°C

Crystal	σ (Ω^{-1} cm^{-1})	Technique[a]
1	$<1 \times 10^{-8}$	$2/H_2SO_4$ + C
2	$<5 \times 10^{-10}$	$2/H_2SO_4$ + C
3	3×10^{-11}	$2/H_2SO_4$ + C
4	$<1 \times 10^{-9}$	$4/H_2SO_4$ + C
5	5×10^{-10}	$2/H_2SO_4$ + C
6	1×10^{-9}	2/Ag
7	5×10^{-10}	$2/H_2SO_4$ + C
8	8×10^{-11}	2/Ag
9	3×10^{-10}	2/Ag
10	2×10^{-10}	2/C
11	1×10^{-10}	2/C

[a] Lists number of electrodes on sample as well as type of electrodes.

Conductivity of H_3O^+ Beta Alumina From 20 to 200°C

The conductivity of H_3O^+ beta alumina increases with temperature from 20° to 200°C as is shown in Fig. 2. Eleven crystals were measured in this temperature range. Some were contacted with C electrodes, others with Ag electrodes. All showed behavior consistent with that in Fig. 2. All readings were steady with time and repeatable regardless of the direction in which temperature was changed. Between 20° and 200°C, the conductivity of H_3O^+ beta alumina obeys an Arrhenius relationship (Eq. [2]). Deviation from a straight line Arrhenius plot is observed between 20 and 80°C and probably arises from surface conductivity. Table II lists the conductivity at 100°C and activation energy observed for each of the eleven samples measured. An average activation energy of 18 kcal/mole (0.78 eV) was used to calculate the preexponential factor (σ_0) and estimated con-

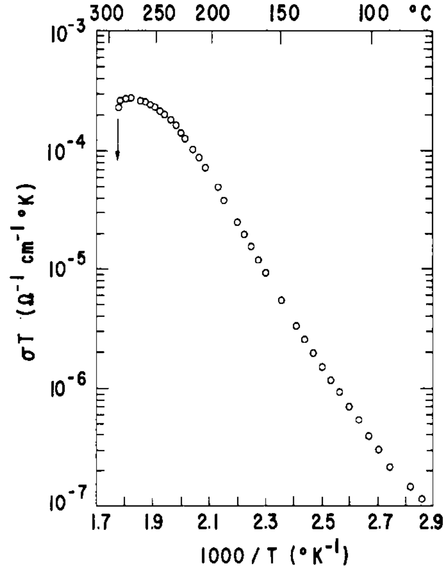

FIG. 2. Arrhenius plot of relationship between conductivity of single crystal H_3O^+ beta alumina and temperature; region between about 25 and 225°C follows a straight line from which an activation energy of 18 kcal/mole is calculated.

TABLE II

CONDUCTIVITY OF HYDRONIUM BETA ALUMINA—LOW TEMPERATURE FORM

Sample	E_a [kcal/mole]	$\sigma(100°C)_{obs}$ $[(\Omega\,cm)^{-1}]$	$\sigma_0{}^a$ $[(\Omega\,cm)^{-1}]$	$\sigma(20°C)^a$ $[(\Omega\,cm)^{-1}]$
11	18	1.2×10^{-8}	420	1.6×10^{-11}
12	15	8×10^{-9}	200	7.5×10^{-12}
10	17	1.9×10^{-8}	730	2.7×10^{-11}
9	20	2.2×10^{-9}	65	2.4×10^{-12}
13	19	1.6×10^{-9}	52	1.9×10^{-12}
8	16	5.4×10^{-9}	180	6.7×10^{-12}
14	20	1.1×10^{-9}	39	1.5×10^{-12}
6	18	1.5×10^{-8}	530	2.0×10^{-11}

[a] Calculated assuming $E_a = 18$ kcal/mole.

ductivity at 20°C listed for each sample in Table II.

$$\sigma = \sigma_0 \exp(-E_a/RT). \qquad [2]$$

Conductivity of H^+–H_3O^+ Beta alumina From 200 to 500°C

Between 200 and 300°, H_3O^+ beta alumina undergoes partial dehydration. This conversion is accompanied by a decrease in conductivity, as Fig. 3 shows. Individual conductivity values between 200 and 300°C decrease with time until equilibrium is attained. If a fresh H_3O^+ beta alumina crystal is rapidly heated to 300°C and maintained at that temperature while its conductivity is monitored, a plot of the change in conductivity vs $(\text{time})^{1/2}$ is a straight line, indicating that the decrease in conductivity is diffusion controlled. After approximately 3 hr, the rate of the conductivity decrease approaches zero. The process is slowly reversible upon cooling to 160°C. Figure 4 is an Arrhenius plot for a sample that first was heated slowly from 20 to 180°C (A–B). Partial dehydration commenced and continued as the temperature was slowly increased to 300°C (B–C). The sample was held at 300°C for approximately 45 min, cooled slowly to 160°C (C–D), and held at 160°C for 24 hr. The conductivity at 160°C initially increased rapidly. But, the rate of increase became small after 24 hr, although the actual conductivity was still an order of magnitude less than that observed initially at 160°C.

The conductivity of partially dehydrated beta alumina at temperatures up to 550°C was determined for three separate single crystal samples. In each case, the conductivity of a fresh H_3O^+ beta alumina crystal was

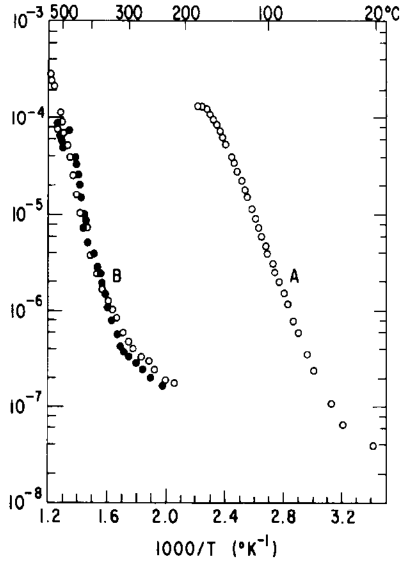

FIG. 3. Arrhenius plot for single crystal hydronium beta alumina from 20 to 580°C; curve A corresponds to an activation energy of 18 kcal/mole; straight portion of curve B corresponds to an activation energy of 29 kcal/mole. Open circles denote rising temperature, solid circles falling temperature.

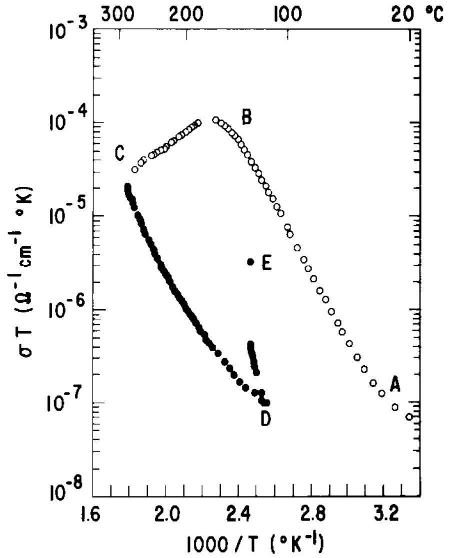

FIG. 4. Arrhenius plot for single crystal hydronium beta alumina showing influence of partial water desorption (B–C) and absorption (D–E) on conductivity. Open circles denote rising temperature, solid circles falling temperature. Total time between D and E was 18 hr.

measured as the temperature was slowly increased from 20 to approximately 200°C. Then the temperature was rapidly increased to 550°C at which point pyrolysis of the varnish used to mount the sample and dehydration occurred simultaneously. After 60 min the temperature was slowly decreased to 350°C and then increased slowly to 550°C while additional conductivity data were recorded. Curve B, Fig. 3 is representative of the behavior of all three crystals. Table III summarizes the individual results. The conductivity of hydronium beta alumina above 315°C is described by an Arrhenius plot with an activation energy of 29 kcal/mole (1.3 eV). Deviation from Arrhenius behavior is seen between 210 and 315°C. Its source is probably gradual reabsorption of water into the crystal structure.

TABLE III

CONDUCTIVITY OF HYDRONIUM BETA ALUMINA—HIGH TEMPERATURE FORM

Sample	E_a (kcal/mole)	σ (500°C)$_{obs}$ ((Ω cm)$^{-1}$)	σ_0[a] ((Ω cm)$^{-1}$)
11	29	1.1×10^{-7}	17
13	29	1.2×10^{-6}	200
14	27	1.2×10^{-6}	60

[a] Calculated assuming $E_a = 29$ kcal/mole.

The conductivity of H^+–H_3O^+ beta alumina between 300 and 400°C appears to be influenced greatly by a small change in the H_2O content of the crystal. For example, 3 hr is apparently ample time for complete conversion of H_3O^+ beta alumina to H^+–H_3O^+ beta alumina at 300°C based on weight change measurements. If a H_3O^+ beta alumina crystal is heated to 300°C for 3 hr, it has a conductivity at 300°C after dehydration about eight times greater than that at 100°C before dehydration. In contrast, the conductivity at 300°C of a sample of H^+–H_3O^+ beta alumina produced by dehydration at 550°C is at least ten times less than its initial conductivity at 100°C. The small additional water concentration in the crystal present at 300°C, either because of incomplete attainment of equilibrium or because of a real difference in the equilibrium conditions at 300 and 550°C, is sufficient to increase the ionic conductivity by almost two orders of magnitude.

Discussion

Our experiments indicate that the ionic conductivity of H_3O^+ beta alumina is very small, about 10^{-11} (ohm cm)$^{-1}$ at 20°C. It increases from 20 to 200°C in an Arrhenius expression having an activation energy of 18 kcal/mole. Partial dehydration of H_3O^+ beta alumina between 200 and 300°C, forming H^+–H_3O^+ beta alumina, is accompanied by a decrease in conductivity of several orders of magnitude.

These observations are consistent with several indirect reports of H_3O^+ beta alumina conductivity in the literature. For example, Lundsgaard and Brook (*8*) examined the potentiometric response of a Pt/Na^+ beta alumina/Pt cell with different concentrations of dilute HCl and H_2SO_4 in each half cell. They found the conductivity of the cell to be very small. Although they chose to conclude that this stemmed from surface blocking at the Pt/Na^+ beta alumina interfaces, it can also be explained by the formation of H_3O^+ beta alumina as the result of spontaneous ion exchange at the interfaces assuming the conductivity of H_3O^+ beta alumina to be less than 10^{-9} (ohm cm)$^{-1}$ at 25°C. Kummer (*9*), in studying the ion exchange reactions of Na^+ beta alumina in aqueous solutions of other cations, found that the rate of ion exchange is rapidly inhibited by water. Faster inhibition was observed in acidic solutions than in basic solutions. Crystals exposed to moist air before ion exchange was attempted showed slower initial exchange than crystals that had been carefully dried. One explanation for this behavior, as pointed out by Kummer, is that ion exchange in aqueous solutions is inhibited by the formation of poorly conducting H_3O^+ beta alumina. Will (*10*) examined the rate of Na^+ exchange with H_3O^+ in a sample of polycrystalline Na^+ beta alumina immersed in water. He also reported that the ion exchange was accompanied by a large and progressive increase in sample resistivity. Will interpreted this as indicating that H_3O^+ ions substitute in the grain boundaries of Na^+ beta alumina and greatly increase the grain boundary resistivity. However, these data can also be explained by the formation of bulk H_3O^+ beta alumina within the grains of Na^+ beta alumina exposed to H_2O, if the bulk conductivity of H_3O^+ beta alumina is less than 10^{-9} (ohm cm)$^{-1}$ at 25°C. Farrington (*11*) found that H_3O^+ ions electrochemically injected into Na^+ beta alumina at a Pt/Na^+ beta alumina interface exposed to H_2O vapor produced a large conductivity decrease. None of these reported experiments directly measured the conductivity of H_3O^+ beta alumina, but all can be explained by our finding that it has an ionic conductivity very low in comparison to Na^+ beta alumina. So, the conclusion that H_3O^+ beta alumina has a very low ionic conductivity seems soundly based.

The great difference in the room temperature conductivities of Na^+ and H_3O^+ beta alumina arises from the disparity in their activation energies, E_a for H_3O^+ beta alumina being 18 kcal/mole and for Na^+ beta alumina being 3.7 kcal/mole, and not from a large difference in their preexponential factors (σ_0 in Eq. [2]). Table IV summarizes the activation energies and preexponential factors for ionic conductivity in beta alumina containing various monovalent cations including the two forms of hydronium beta. The preexponential factors for both compositions of hydronium beta alumina are the averages of those already

TABLE IV

CONDUCTIVITY OF BETA ALUMINA ISOMORPHS

Ion	Radius (Å)	E_a (kcal/mole)	σ_o $((\Omega\ \mathrm{cm})^{-1})$	σ298°K $((\Omega\ \mathrm{cm})^{-1})$	σ473°K $((\Omega\ \mathrm{cm})^{-1})$
Na^a	0.97	3.81	8.6	1.4×10^{-2}	1.5×10^{-1}
Ag^b	1.26	4.05	41	4.4×10^{-2}	5.5×10^{-1}
H_3O^a (low)	1.32	18	280	1.7×10^{-11}	1.3×10^{-6}
H_3O^a (high)	—	29	90	—	5.8×10^{-7} (500°C)
K^b	1.33	5.36	8.3	9.7×10^{-4}	2.8×10^{-2}
Rb^b	1.47	7.18	2.5	1.3×10^{-5}	1.2×10^{-3}
Tl^b	1.47	8.22	6.8	6.4×10^{-6}	1.1×10^{-3}

[a] Single crystal conductivity measurement.

[b] Tracer diffusion using Nernst–Einstein equation with correlation factor of 3 (*9*).

shown in Tables II and III. Neither pre-exponential factor is significantly beyond the range defined by the other ions.

An intriguing question is why the activation energies for conduction in H_3O^+ and H^+–H_3O^+ beta alumina are so high. Also, the nature of the ionic species that diffuse in these compositions and the proportion with which each carries charge are unknown. One characteristic that distinguishes beta alumina isomorphs containing hydronium ions and protons from those in which monovalent metal cations are present is the possibility in the former of charge transport by multiple species and multiple pathways. For example, charge transport in H_3O^+ or H^+–H_3O^+ beta alumina may occur by the motion of hydronium ions or by proton exchange among hydronium ions and other species, such as structural oxygen atoms, within the conducting plane. Thus, H_3O^+ or H^+–H_3O^+ beta alumina might be a good proton conductor without being a good hydronium conductor.

Figure 5 depicts the beta alumina conducting plane with one layer of close-packed oxygens that define the conducting plane removed. The second layer of close-packed oxygens is shown by light circles. Column or "spacer" oxygens around which the mobile ions diffuse are shown in dark circles. Peters *et al.* (*2*) and Roth *et al.* (*3*) have shown, on the basis of X-ray and neutron diffraction studies, that sodium ions are primarily found in the Beevers–Ross (d) and mid-oxygen (M.O.) sites at 20°C.

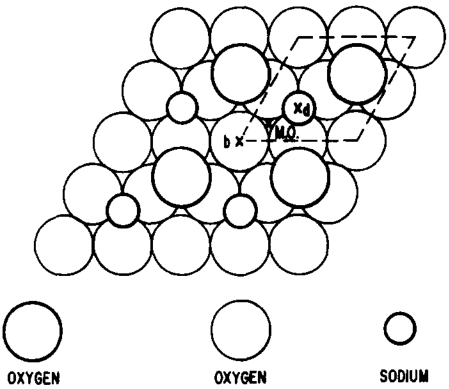

FIG. 5. Na^+ beta alumina conducting plane. Three available sites for mobile ion occupation are shown: "d" is Beevers–Ross, "M.O." is mid-oxygen, and "b" is anti-Beevers–Ross. "Spacer" oxygens are located in the conducting plane.

A factor which may alter this ionic distribution in H_3O^+ and H^+–H_3O^+ beta alumina is the ability of protons and hydronium ions to form hydrogen bonds with oxygen ions within the conducting plane. The ionic distribution and ionic transport mechanism will then be influenced by the formation of hydrogen bonds to column oxygens, interstitial oxygens (*3*), or oxygens in the close-packed layers defining the conduction plane. Hydrogen bonding among hydronium ions and structural oxygens in a variety of solid organic and inorganic compounds has been reviewed by Pimentel and McClellan (*12*). In the solid state, the most probable O–H–O distance found is 2.8 Å; few bonds are less than 2.4 Å or greater than 3.1 Å in length. Typical bond energies are 5 to 9 kcal/mole. On this basis, a favorable site for hydronium ion occupation in beta alumina is the mid-oxygen site. The center of the mid-oxygen site is 2.8 Å from the centers of two oxygen atoms within the conduction plane and six additional oxygen atoms above and below the conduction plane. Hydrogen bonding to several of these oxygen atoms seems possible. Alternatively, hydronium ions may be found in the Beevers–Ross site which is 2.8 Å from each of six oxygen ions above and below the conduction plane and 3.2 Å from three oxygen ions within the conduction plane. In this site, hydronium ions would be most favorably bonded to the close-packed oxygen ions. Least probable is hydronium occupation of the anti-Beevers–Ross site which is only 2.4 Å from each of two oxygen ions above and below the conduction plane. This spacing is small in comparison to the sum of the radii of an oxygen and a hydronium ion, about 2.6 Å. Migration through the anti-Beevers–Ross site is, therefore, on the basis of ionic size considerations the most difficult transition for hydronium ion diffusion. Kato (*13*) determined the structure of H_3O^+ beta alumina by X-ray diffraction and found that indeed the anti-Beevers–Ross site is the least favorable for hydronium ion occupation and that hydronium ions are principally found in the vicinity of the Beevers–Ross site.

The additional stability afforded by hydrogen bond formation is most likely the basis of the higher activation energies observed for conduction in H_3O^+ and H^+–H_3O^+ beta alumina compared to alkali-ion-substituted isomorphs. It is not possible from the data presented here to distinguish among various conductivity mechanisms that potentially occur in H_3O^+ and H^+–H_3O^+ beta alumina. There is no clear evidence for the existence of rapid proton motion or delocalization throughout the structure independent of hydronium ion motion, although such exchange may occur on the unit cell level. The large decrease in conductivity that accompanies the conversion of H_3O^+ beta alumina to H^+–H_3O^+ beta alumina does imply that the protons resulting from the dissociation and dehydration are strongly hydrogen bonded within the conducting plane and not rapidly mobile.

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