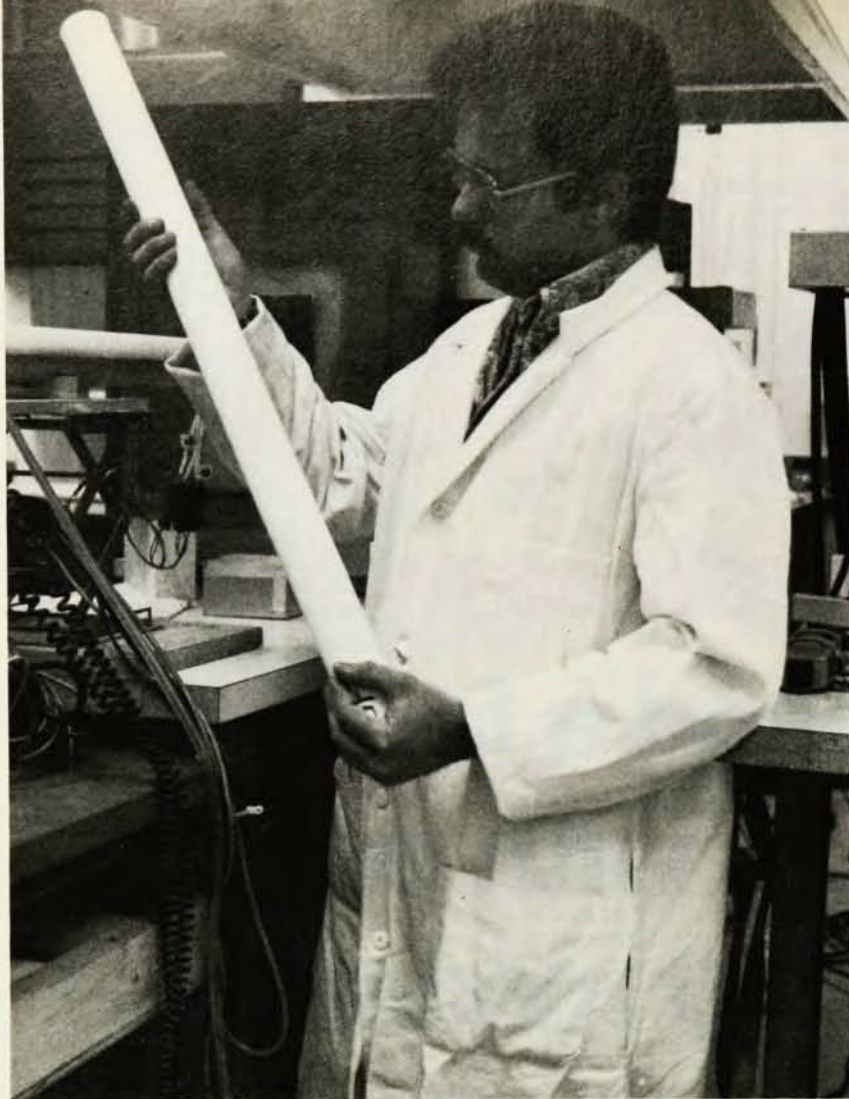




Solid-electrolyte tube and crystals. The photo below shows large crystals of sodium β -alumina sitting in a platinum crucible 2.5 cm in diameter after forming at 1700 °C. At left, technician Paul Gallo holds a beta-alumina tube designed to be the electrolyte of a sodium-sulfur battery. (Crystals were grown by Bill Brundage, Oak Ridge National Laboratory; tube was made at General Electric Research and Development Center, Schenectady, New York.)

Figure 1



Solid electrolytes— the beta aluminas

Materials in which lattice defects allow ions to flow rapidly have interesting physical properties and important applications in new electrochemical devices such as sodium-sulfur batteries.

John B. Bates, Jia-Chao Wang and Nancy J. Dudney

Electrolytes conduct electricity by the movement of ions, whereas metals conduct by the flow of electrons. Until recently, almost all electrolytes known to have high conductivities were liquids, such as molten salts or aqueous solutions of salts. But research over the last twenty years has uncovered many solid electrolytes—substances that have a high ionic conductivity

even though they are insulators to the flow of electrons. Physicists often call these solids “superionic conductors” because a number of the compounds have electrical conductivities comparable with those of liquid electrolytes. (But we will avoid this term to prevent a possible mistaken identification with superconductors.)

A major factor motivating the devel-

opment of solid electrolytes, besides their interesting physical properties, is their application in fuel cells, batteries, ion-selective membranes, gas sensors and other electrochemical devices. As a result, in the last decade we have seen the study of solid electrolytes develop into a broad interdisciplinary field involving physics, chemistry, materials science and engineering.¹⁻⁷

Much of the research effort is aimed at developing rechargeable batteries that have high energy and power densities. These batteries could reduce oil consumption by powering electric vehicles and storing electricity from generating plants for use during periods of peak demand.^{1,7}

A leading candidate for such a battery is based on the sodium-sulfur cell, which uses an aluminate as its electrolyte. In this article we will discuss some of the research aimed at understanding the mechanisms of high ionic conductivity in a family of aluminates known as beta-alumina and beta"-alumina (figure 1). We focus on these materials because of their interesting properties and their technological importance, and because they are probably the most extensively investigated group of solid electrolytes. Studies of the mechanisms of high ionic conductivity in solids are crucial to the development of new electrolyte and electrode materials. Accordingly, there have been many books and conferences on solid electrolytes.¹⁻⁷ Most of the research on the aluminates that we will discuss here was taken up at a recent conference hosted by Oak Ridge National Laboratory.⁷

Before we examine the beta aluminas, let us briefly survey the various types of ionic conductors and look at the nature of ionic transport in solids.

Materials and applications

Solid electrolytes generally fall into three categories:

- ▶ inorganic crystalline solids
- ▶ glasses
- ▶ polymers

Table 1 compares the room-temperature conductivities of examples from each of these groups, with conductivities of other substances. The first category, inorganic crystalline solids, is by far the largest and includes both cation and anion conductors, as table 2 shows.

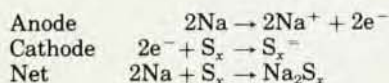
For some compounds, such as sodium beta-alumina, the conductivity increases continuously with temperature (figure 2). In other solids, such as silver iodide, the conductivity increases abruptly at a first-order phase transition. A similar sharp increase in conductivity also occurs on melting of an ionic crystal such as sodium chloride, which is an electrical insulator in the solid phase. As can be seen from figure 2, the term "solid electrolyte" is quite appropriate; for example, the conductivity of RbAg₄I₅ at 30 °C is only about a factor

of 10 less than that of molten NaCl at 900 °C.

In recent years, researchers have worked to improve the conductivity of glasses and have discovered⁷ several promising Li⁺, Na⁺ and Ag⁺ conductors. Polymeric materials prepared from polyethylene and alkali-metal salts also turn out to have high conductivities.⁷ Although the conductivities of glasses and polymers are generally much lower than those of inorganic solids, they have important advantages because of their greater plasticity, isotropic conductivity and absence of grains.³

Electrolytes play a major role in batteries and fuel cells, which both operate on the same principle: Energy released in a chemical reaction is converted directly into electricity. In a fuel cell, the reactants are usually supplied continuously to the electrodes and electrolyte from an external source. In a battery, the reactants are stored as part of the electrode or electrolyte material.

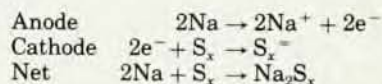
Figure 3a is a schematic diagram of a high-temperature fuel cell that uses stabilized zirconia as the electrolyte.³ In this cell, the energy released during the reaction of hydrogen and oxygen to form water drives electrons from the hydrogen or fuel electrode (the anode) through an external load *R* to the air electrode (the cathode). Oxygen ions produced at the cathode diffuse through the zirconia electrolyte to combine with hydrogen ions produced at the anode. The reactions are



The direct conversion of chemical energy to electrical energy in a fuel cell is in principle much more efficient than the conventional method of producing electricity with steam-driven turbine generators. In the latter, the fuel's heat of combustion is converted to mechanical energy in a process whose efficiency can never exceed that set by the Carnot limit.

The sodium-sulfur cell, shown schematically in figure 3b, is a battery because there is no external source of fuel. This cell uses either sodium beta-alumina or sodium beta"-alumina as its electrolyte. In the discharge reaction, sodium ions diffuse through the electrolyte and react with polysulfide ions to produce Na₂S_x, where *x* ranges from

3 to 5. Electrical work is done as the reaction drives electrons through an external circuit from the negative to the positive electrode. The reactions are:



One can recharge the cell by applying an external voltage to the electrodes to reverse the flow of electrons. Some of the problems hindering commercial application of the sodium-sulfur battery concern the behavior of the electrolyte after many charge-discharge cycles.⁷

True solid electrolytes are electronic insulators, which is important for the applications just described. Some of the solids listed in table 2 are good conductors of both ions and electrons. These mixed conductors are useful as electrodes.

Ionic conductivity in solids

Ionic conduction in solids is the result of the diffusion of ions under an applied voltage. For an ion to diffuse there must be sites available that it can occupy as it moves through the lattice, and there must be sufficient energy available to cause it to move. Diffusion cannot occur on a reasonable time scale in an ideal solid in which all ions occupy regular lattice positions and no regular sites are vacant. High ionic conductivity is therefore associated with defects.

We are interested in two important types of defects: those involving vacant lattice sites, and those involving ions located between regular sites, in "interstitial" positions.

▶ An ion in an interstitial position can move in two ways: It can jump into a neighboring interstitial site, or it can push a neighboring ion out of a regular lattice site into an interstitial position. The latter, known as the "interstitialcy mechanism," requires the cooperative motion of two ions, as shown in figure 4.

▶ In solids containing vacancies, an ion can move by jumping into a neighboring vacant site. We can view this type of diffusion as the motion of vacancies.

As we will see later, conduction in beta-alumina involves an interstitialcy

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mechanism, while a vacancy mechanism is responsible for the flow of ions in β'' -alumina.

For the simple example of particles in a one-dimensional periodic potential, the probability that a particle will jump from one potential well to another in unit time is proportional to $\nu e^{-E/kT}$, where ν is the frequency at which the particle approaches the barrier, and E is the barrier height. If l is the distance between potential minima, then the diffusion coefficient for a random-walk process is given by

$$D = l^2 \nu e^{-E/kT} \quad (1)$$

where k is Boltzmann's constant and T is the absolute temperature. If l and ν are constants, D has the familiar Arrhenius form, $D = D_0 e^{-E/kT}$. If n is the number of particles per unit volume, then, from the Nernst-Einstein relation between mobility and diffusivity,^{2,3} the ionic conductivity is

$$\sigma = (nq^2/kT)D \quad (2)$$

where q is the effective charge of each ion. Thus we can write the product σT in the same form as D :

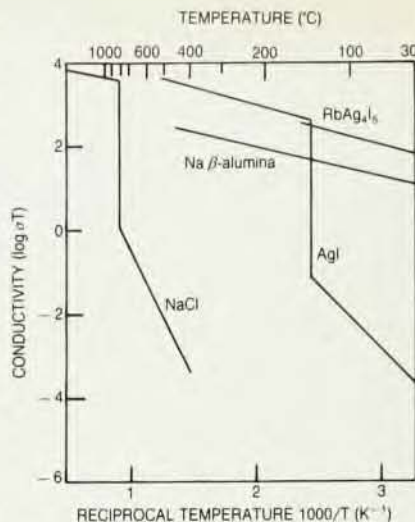
$$\sigma T = \sigma_0 e^{-E/kT} \quad (3)$$

It is evident from equations 2 and 3 that high conductivity is associated with high particle density and low barrier height. One obtains the values of E and σ_0 experimentally from the slope and intercept, respectively, of the graph of $\log \sigma T$ versus $1/T$. Measurements of the resistance of a sample give its conductivity.

Equations 1 and 2 show how conductivity is related to the microscopic properties of the lattice. The barrier height or activation energy, E , depends on the nature and arrangement of ions surrounding the mobile species and on the lattice structure in general. The jump distance l is determined by the structure, and the attempt frequency ν is related to a particular vibrational mode of the mobile ion. Thus, in addition to conductivity data, knowledge about structure and dynamics is important for understanding the mechanisms of fast ionic transport in solids.

Aluminate composition

Sodium β -alumina and sodium β'' -alumina are the end members of a



Electrical conductivities of several ionic solids. Sodium chloride's ionic conductivity increases sharply when it melts. Figure 2

family of sodium aluminates whose composition ranges⁸ from approximately $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ to $\text{Na}_2\text{O} \cdot 0.5\text{Al}_2\text{O}_3$. (The term "beta-alumina" is actually a misnomer that originated when these compounds were believed to be a modification of alumina, Al_2O_3 .) Sodium β -alumina has a nonstoichiometric composition represented by $(1+x)\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$, where x ranges from about 0.15 to about 0.3. By using a particular series of ion-exchange and decomposition reactions one can prepare^{3,7} nearly stoichiometric β -alumina, that is, the compound for which x is approximately zero. The electrical properties of the stoichiometric β -aluminas are not well known, but it is clear that they have a much higher activation energy and a lower conductivity than the nonstoichiometric materials.

No one has reported the preparation of sodium β'' -alumina as a stable binary compound of Na_2O and Al_2O_3 . For stability, the sodium β'' -alumina structure requires the addition of some divalent or monovalent cations such as magnesium or lithium, which replace a fraction of the Al^{3+} ions. The composition of the magnesium-stabilized compound is represented by $\text{Na}_{1+x}\text{Mg}_x\text{Al}_{11-x}\text{O}_{17}$, where x is typically about

0.67. Mixtures of Na_2O and Ga_2O_3 yield⁵ gallium analogs of sodium β - and β'' -alumina; the gallates have properties similar to the aluminates.⁴⁻⁷

The commercial availability several years ago of large single crystals of sodium β -alumina was instrumental in promoting extensive research on the properties of this material. These crystals were grown⁹ from a melt at 1900 °C. Large single crystals of sodium β'' -alumina grow⁸ when Na_2O evaporates from a mixture of Na_2O , Al_2O_3 and MgO or ZnO at temperatures above 1600 °C. Figure 1 shows single crystals of magnesium-stabilized sodium β'' -alumina that grew in a platinum crucible at 1700 °C. Sodium-sulfur batteries use tubes of polycrystalline β - and β'' -alumina, which are prepared by sintering or hot-pressing. The technician in figure 1 is holding such a tube.

Although there have been many studies of the technologically important polycrystalline materials, measurements on single crystals are essential to characterize accurately the bulk properties of β - and β'' -alumina, so we will discuss only these kinds of measurements.

The high mobility of sodium ions in β - and β'' -alumina allows them to be exchanged for other alkali-metal ions or silver ions by treatment in molten salts.¹⁰ Researchers recently found that one can replace^{7,11} the Na^+ ions in $\text{Na } \beta''$ -alumina with divalent cations such as Ba^{2+} and Pb^{2+} . Also, polyatomic ions such as H_3O^+ , NH_4^+ and other protonated species can replace sodium in β - and β'' -aluminas. This is done with ion-exchange and hydration reactions, and the result can be a good proton conductor.⁵

Aluminate structure

Figure 5 is a drawing of the unit cell of sodium β -alumina. The structure consists of densely packed layers of Al^{3+} and O^{2-} ions, about 11 Å thick, separated by loosely packed layers containing Na^+ and O^{2-} ions.¹² The dense layers are known as spinel blocks because the arrangement of Al^{3+} and O^{2-} ions is similar to the structure of spinel, MgAl_2O_4 . In beta-alumina the Al^{3+} ions occupy both tetrahedral and octahedral interstices formed by the O^{2-} ions.

The O^{2-} ions in the loosely packed layers form a bridge between adjacent spinel blocks, so they are called "bridging oxygen ions." The plane of these oxygen ions is commonly referred to as the conduction plane because it contains the sodium ions. The conduction plane is bounded above and below by close-packed oxygen layers in the adjacent spinel blocks.

The structure of β'' -alumina is similar¹² to that of β -alumina, one distinction being the relative orientation of adjacent spinel blocks along the c axis.

Table 1. Typical conductivities

Type of substance	Substance (charge carrier)	Conductivity at 25 °C σ ($\Omega^{-1} \text{ cm}^{-1}$)
Metal	Copper (electrons)	10^6
Crystalline solid	K β'' -alumina (K^+)	10^{-1}
Aqueous solution	0.1 M KCl (K^+ and Cl^-)	10^{-2}
Glass ⁷	0.75 AgI-0.25Ag ₂ MoO ₄ (Ag^+)	10^{-2}
Polymer ⁷	4.5 PEO-NaBF ₄ (Na^+)	10^{-7}

PEO: polyethylene oxide.

In β'' -alumina the Mg^{2+} or other stabilizing ions are located on tetrahedral sites near the middle of the spinel blocks.

A key to understanding ion transport in β - and β'' -alumina is found in the structure of the conduction layers, which includes the conduction plane and the close-packed oxygen layers above and below this plane. The schematic drawings in figure 6 show the conduction layers of both structures as viewed along the c axis. The special sites in the conduction plane designated 1, 2 and 3 are positrons on or near which the mobile ions are located. These sites are characterized by the arrangement of neighboring oxygen ions around them.

There are three special sites for mobile ions in beta-alumina. We know the distribution of sodium ions on these sites from x-ray and neutron diffraction studies.^{1,6,7,12} At or below room temperature, the "Beevers-Ross" sites have the highest population of mobile ions and are therefore the most favored locations. These are followed by the "mid-oxygen" sites and the "anti-Beevers-Ross" sites, which are least favored. (In figure 6a, the numbers 1, 2 and 3 identify the locations of the BR, mO and aBR sites, respectively.) Researchers have found that at 300 K, the respective probabilities¹ for occupation of these sites are 0.66, 0.30 and 0.04.

Potential-energy calculations indi-

cate¹³ that the mobile ions would occupy only the deep potential wells at the BR sites if enough were available. However, because there are 15 to 30% more ions than BR sites, each excess ion forms an interstitial pair with another ion such that each member of the pair is located on a mO site. Thus, the paired ions share a BR site.

The extra charge contributed by the positive sodium ions in excess of the stoichiometric number of two per formula unit is compensated¹ by extra O^- ions, which are also located in the conduction plane. Figure 6a shows the excess Na^+ and O^- ions at their calculated minimum energy locations.

In contrast to β -alumina, the close-packed oxygen layers adjacent to the conduction plane in β'' -alumina are shifted with respect to each other, as illustrated in figure 6b. As a consequence, the sodium ions are coordinated by three oxygen ions in one layer and one oxygen ion in the opposite layer. The relative numbers of sodium ions and sodium-ion vacancies shown in the figure correspond to the composition $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$, as observed experimentally.

The presence of interstitial ions pairs in β -alumina, and vacancies in β'' -alumina, causes the cations to relax away from the locations they would occupy in the absence of these defects. This introduces disorder into the conduction planes, and the effect of this disorder appears clearly in Fourier density maps calculated from neutron or x-ray diffraction data. The difference map in figure 6c was computed⁷ for the middle of the conduction layer of potassium β'' -alumina. The contours show that the potassium nuclear density is smeared out along the honeycomb lattice connecting the "preferred" sites. In addition to the static disorder caused by vacancies, the thermal motion of potassium ions within the conduction layers also contributes to the smearing of nuclear density. This thermal smearing indicates that the ions are highly mobile at room temperature, and indeed the conductivity of potassium β'' -alumina at 25 °C is high. In general, such density maps are characteristic of solid ionic conductors.

Mechanisms of conduction

Because of the layered structure of β -alumina and β'' -alumina, the conductivity is two-dimensional. The ion mobility is high within loosely packed conduction layers along directions perpendicular to the c axis, but it is essentially zero parallel to the c axis. Therefore standard conductivity measurements are made with the electric field perpendicular to the c axis.

Figure 7 gives some conductivity data for sodium β -alumina and sodium β'' -alumina. Table 3 shows activation energies and conductivities at room

Table 2. Some solid electrolytes

Solid electrolyte	Mobile species
Cation conductors	
AgI	Ag^+
X beta-alumina	$X (Li^+, Na^+, K^+, Ag^+, H^+)$
Cu_2S	Cu^+
Li_3N	Li^+
$LiBr \cdot H_2O$	Li^+
$RbAg_4I_5$	Ag^+
Anion conductors	
BaF_2	F^-
$CeO_2 \cdot Y_2O_3$	O^{2-}
$ZrO_2 \cdot CaO$	O^{2-}
Mixed ion/electron conductors	
Li_xMoO_3	Li^+, e^-
$Li_xV_2O_5$	Li^+, e^-
Na_xTiS_2	Na^+, e^-

temperature for several β - and β'' -aluminas. It is clear from equation 3 that the graph of $\log \sigma T$ versus $1/T$ will be linear if the activation energy and the σ_0 term are constants. This is the case for beta-alumina and most other ionic conductors. However, for sodium and several other β'' -aluminas, the graphs are curved at temperatures above about 200 °C. We will discuss this peculiar behavior below. The activation energies for the β'' -aluminas listed in table 3 were measured from the linear portions of the conductivity curves.

Potential-energy models^{7,13} of β - and β'' -alumina are helpful in understanding the reasons for the high conductivities of these materials. Using these models, we calculate the total potential energy (the Coulomb, core repulsion and polarization energies) for various configurations of the mobile ions, and we obtain values for physical parameters such as activation energies, vibrational frequencies and equilibrium positions of the mobile cations.

According to these calculations, the formation of interstitial ion pairs in β -alumina causes the barrier height for ion motion to be greatly reduced over that for single ions. In Na β -alumina for example, the calculated energy required to move a single Na^+ ion out of a BR site is about 2 eV. By contrast, the calculated energy for the correlated movement of ion pairs (figure 4) is only 0.14 eV, in good agreement with the observed activation energy of 0.15 eV.

As the size of the alkali ion increases, the activation energy increases because it becomes more difficult for the ions to squeeze between the oxygen ions located above and below the aBR sites (table 3). On the other hand, lithium ions are so small that they relax away from the conduction plane toward the oxygen ions above and below the BR sites. This effectively pins the lithium ions and makes their activation energy for con-

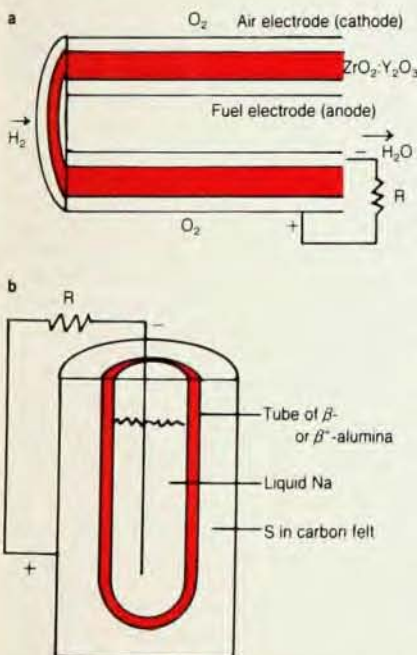
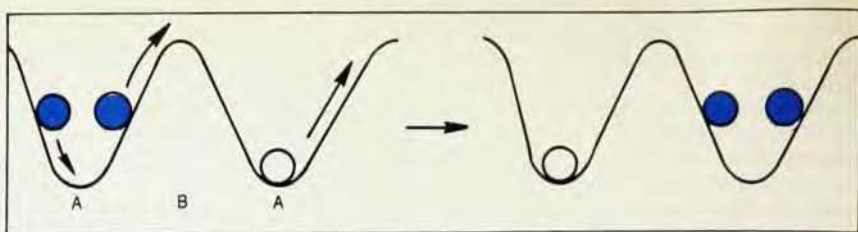
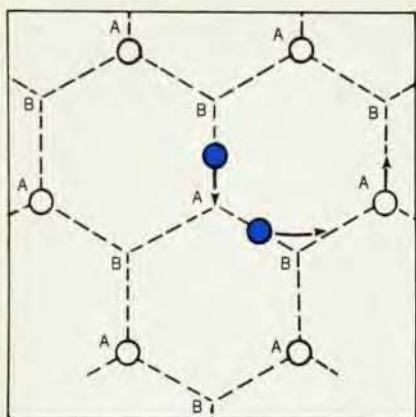


Figure 3. Fuel cell and battery, in schematic representation. Both electrochemical devices use a solid conductor of ions as an electrolyte. a: Longitudinal cross-section of a tubular fuel cell, which operates at about 1000 °C. b: Sodium-sulfur cell, which operates at about 300 °C.



Ionic diffusion. Ions can move through solids in a number of ways, one of which is represented here. The interstitial mechanism of diffusion involves the cooperative motion of two ions that make up an interstitial pair. One of the ions falls into a lattice site, while the other forms a new interstitial pair with an ion that moves out of a lattice site. This lowers the barrier for ionic motion.

Figure 4

duction larger than that for sodium ions.

Whereas the interstitial mechanism accounts for the high ionic conductivity in β -alumina, conduction occurs in β'' -alumina through the movement of cation vacancies. In most solids there is less than one vacancy for every 10^4 atoms, so the ionic conductivity is low. In β'' -alumina, approximately 17% of the available mobile cation sites are vacant, which partly accounts for the high conductivity.

Superlattice ordering. The conduction mechanism of β'' -alumina, however, involves more than just the independent hopping of cation vacancies. The high concentration of these very mobile vacancies—and the Coulomb interaction among them—leads to ordering of both the sodium ions and the vacancies on a superlattice, which, as we will see, affects the ionic conductivity.

Researchers using diffuse x-ray scattering techniques have found^{5,16} evidence of superlattice ordering in β'' -alumina. In general, if there is local order or positional correlation among atoms in a material, peaks will appear^{1,7} in the diffuse x-ray or neutron scattering background in reciprocal space. The width of the diffuse scattering peaks is inversely proportional to the correlation length, which one can take as a measure of the extent of superlattice ordering. Researchers have interpreted^{5,16} the diffuse scattering pattern from Na β'' -alumina with a model in which the ions and vacancies are locally ordered on a two-dimensional trigonal superlattice (dashed outline in figure 6b) with a unit cell of dimensions $\sqrt{3}a \times \sqrt{3}a$, where a is the lattice parameter of the Bragg cell (solid outlines in figures 6a, b and c). The correlation length at room temperature is about 70 Å. On increasing the temperature of the sample, the correlation length, or extent of superlattice ordering decreases^{5,16} (figure 7), with a rapid change occurring between 100 and 300 °C. The activation energy also decreases with increasing temperature, and there is a change in the slope of

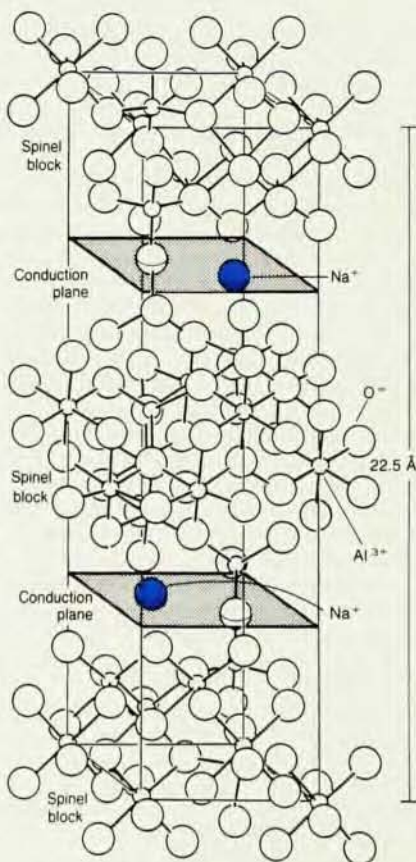
$\log \sigma T$ near 200 °C. Both the correlation length and the activation energy approach constant values at high temperature.

We can understand the x-ray and conductivity results at least qualitatively. Because of the Coulomb interaction among the ordered vacancies on the superlattice, the activation energy

is larger than it would be in the absence of this ordering. According to the potential-energy calculations,⁷ the activation energy for diffusion of a single sodium-ion vacancy in sodium β'' -alumina should be about 0.02 eV. While at high temperatures the activation energy determined from the conductivity data is about 0.03 eV, it increases to 0.33 eV near room temperature. The difference between the calculated and experimental activation energies is a measure of the effect of vacancy ordering at low temperatures.

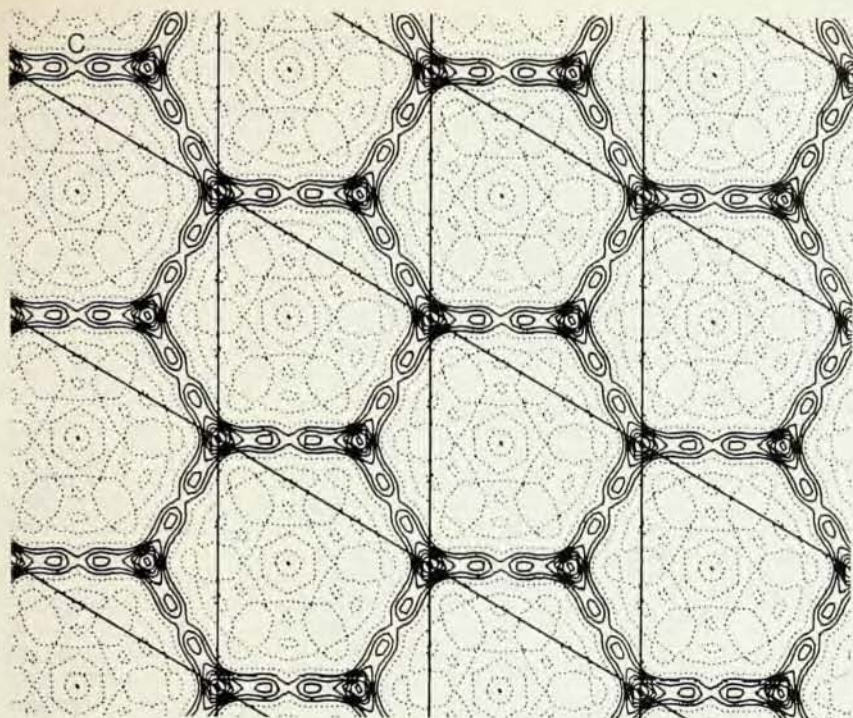
We can view² the ordered vacant sites as special positions for which the binding energy is larger than at other sites. The vacancies are effectively trapped at these sites, so it requires more energy for a vacancy to hop to a neighboring position than would be required if there were no superlattice ordering. With increasing temperature, increased thermal agitation of the cations causes a disordering of the superlattice. This reduces the contribution to the activation energy arising from the periodic arrangement of ions and vacancies. The variation in the extent of superlattice ordering with temperature introduces a temperature dependence into the activation energy and causes the curvature in the graphs of $\log \sigma T$ versus $1/T$.

Beta-alumina and its gallium analogs show some interesting changes in conductivity when two different alkali ions are introduced into their conduction layers. When experimenters put a second alkali ion into the structure by ion exchange, they found^{5,7,17} a decrease in the conductivity and an increase in the activation energy. Although this so-called mixed-alkali effect has been well known in glasses for some years, there is still no model or theory that can explain all of the observations. Because we can determine the location, vibrational frequencies and mobility of the alkali ions in the mixed-ion β - and β'' -aluminas, studies of these compounds may offer the best possibility for understanding the mixed-alkali effect.



A single unit cell of beta-alumina is outlined by the solid lines in this diagram. The cell contains one formula unit of $(1+x)\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$, with x equal to zero in this illustration. The shaded areas, containing the sodium ions and bridging oxygen ions, are the conduction planes.

Figure 5



Conduction layers of β -alumina (a) and β'' -alumina (b). In the upper left corners of these schematic diagrams we show the oxygen layers above and below the plane of the bridging oxygen ions. The numbers 1, 2 and 3 in **a** denote possible locations for mobile ions. In **b**, the numbers 1 and 2 denote equivalent sites. The Fourier difference map of potassium β'' -alumina shown in **c** was computed for the middle of the conduction layer from neutron diffraction data taken⁷ at 25 °C. The potassium ions show a liquid-like distribution. The corners of the planar Bragg cells are located at one of the two potassium-ion sites, as in **b**. (Fourier map courtesy of George Brown, ORNL.) **Figure 6**

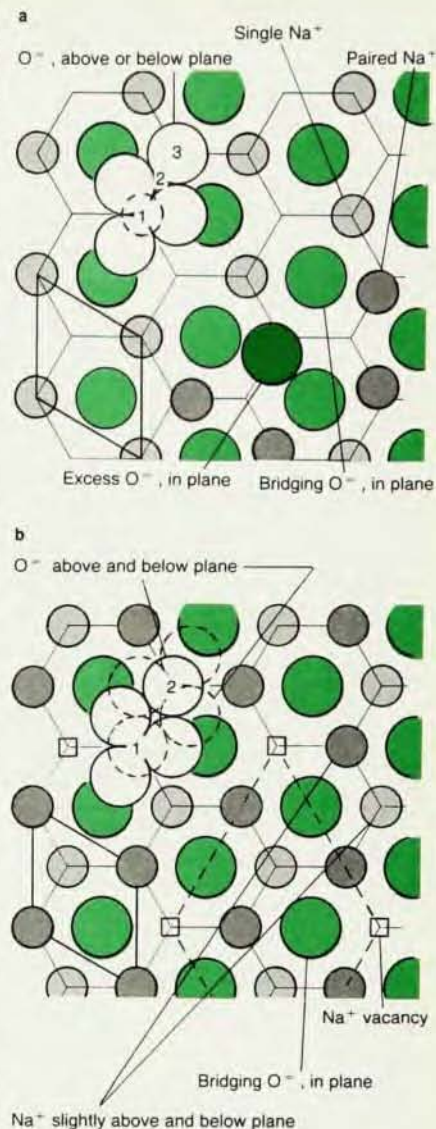
By way of the mixed-alkali effect, impurities in the form of a second ion in the conduction plane can degrade the conductivity of β - and β'' -alumina. Water is another type of impurity that can enter the conduction layers and degrade the conductivity. We will conclude our survey of β - and β'' -alumina with a discussion of the hydration reactions of these materials and the effect of water on their properties.

Water as an impurity

Early investigations revealed that water is absorbed⁸ into the conduction layers of sodium and lithium beta-alumina when single crystals are exposed to room-temperature air. Later research showed¹⁸⁻²¹ that the absorption of water decreases the conductivity of

Na β - and β'' -alumina. This is a potentially serious problem for device applications. Our present research effort is aimed at understanding the hydration reactions of β - and β'' -alumina and at measuring the effect of water on ionic conductivity. We have made most of our measurements⁷ on lithium β -alumina because it absorbs significant amounts of water much more rapidly than sodium or other alkali-metal β -aluminas.

At Oak Ridge, George Brown recently determined the structure of a hydrated crystal of lithium β -alumina using neutron crystallography. He found that water molecules in the conduction layers occupy one of three equivalent positions, each about 1 Å from an aBR site. Hydrogen bonds form



with the O^- ions directly above and below the aBR sites so that the plane of the H_2O molecule is perpendicular to the plane of the conduction layer. In Brown's experiments the hydrated crystal contained about 1.6 water molecules per unit cell. In absorbing this quantity of water, the crystal expanded by about 0.7% along the c axis.

We have not observed distinct hydration compounds of β -alumina or β'' -alumina; the equilibrium concentration of water varies continuously up to a saturation limit. Judging from the space available in the conduction layer of lithium β -alumina, the maximum amount of water that the structure can absorb is apparently the number of aBR sites (two per unit cell) less the number of extra oxygen ions. The predicted saturation limit for our crystals is about 1.8 water molecules per unit cell, and we have seen water concentrations as high as 1.7.

Table 3. Activation energies and conductivities

Beta-Alumina			Beta''-alumina		
Cation	Activation energy	Conductivity	Cation	Activation energy	Conductivity
	E_a (eV)	σ ($\Omega^{-1} \text{cm}^{-1}$) $\times 10^4$		E_a (eV)	σ ($\Omega^{-1} \text{cm}^{-1}$) $\times 10^4$
Na	0.15	358	K	0.15	1000
Ag	0.16	130	Na	0.33	250
Li	0.24	30	Li	0.30	50
K	0.28	1.6	Ag	0.19	40
Rb	0.39	0.12	$H_2^+ O-NH_4^+$	0.30	1
			Cd^{2+}	0.61	0.01

Data from references 5, 7, 11, 14, 15.

The reaction of water with the β - and β'' -aluminas is exothermic. The major contributors to the hydration enthalpies, which are on the order of -1 eV, are the strong ion-dipole attraction between the alkali ions and water molecules, and the hydrogen bonding of water molecules to the oxygen ions above and below the conduction layers. In addition to water, there are other protonic species in hydrated lithium β -alumina. These include OH^- and H_3O^+ ions from the dissociation of H_2O in the conduction layers. The concentration of these species is typically less than 25% of that of H_2O .

Diffusion by dissociation. The rates of the hydration reactions are controlled by the diffusion of water in the conduction layers. In lithium β -alumina, water diffuses very rapidly. At 350°C , for example, the diffusion coefficient is about $6 \times 10^{-7} \text{ cm}^2/\text{sec}$, which is comparable to that of lithium ions at the same temperature.⁸

Judging from the diagram in figure 8a, it would appear to be difficult for water molecules to squeeze through the channels in the conduction layer without a large displacement of the lithium ions. To account for the rapid diffusion, we recently proposed²² a mechanism suggested by measurements with water made from oxygen-18. According to this mechanism, illustrated in

figure 8b, diffusion occurs when protons jump from the water molecule's parent oxygen atom to nearby oxygen ions. The parent oxygen atom, now an ion, moves into the bridging oxygen-ion position, while the bridging ion moves into an interstitial position and combines with the protons. The diffusion of water thus consists of dissociation of H_2O , interstitial motion of oxygen ions and reformation of H_2O . This results in the net transport of water through the conduction layers without requiring major displacement of lithium ions.

A key step in this rapid diffusion process is, of course, the dissociation of H_2O . There is no evidence for the dissociation of water in sodium β -alumina, which might explain water's much lower rate of diffusion in this material. The reaction of water with the β'' -aluminas is not as well characterized. It is clear from the data available, however, that water diffuses much more rapidly in sodium β'' -alumina than in sodium β -alumina.

Quantitative measurements of the effect of water on the ionic conductivity of the β - and β'' -aluminas are in progress. From some preliminary work we know that the conductivity of lithium β -alumina at 350°C decreases by about a factor of six as the water concentration increases from 0 to 1.8 molecules

per unit cell. It appears that the major effect of water is to increase the activation energy for conduction.

Future research

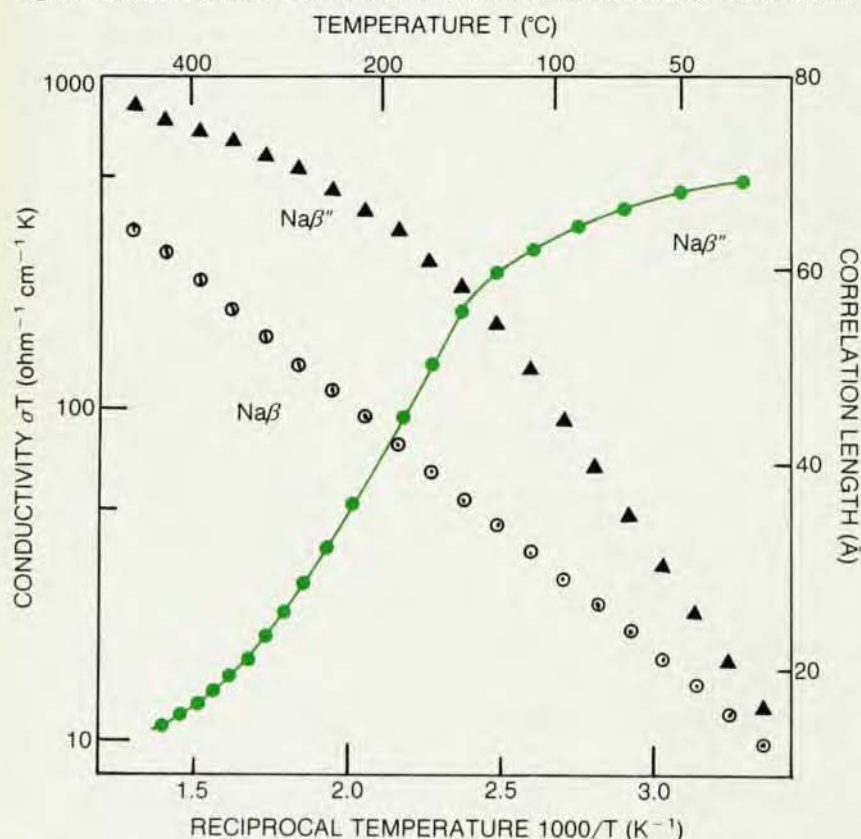
In this article we have discussed just some of the work of many researchers that has brought us to our present level of understanding of high ionic conductivity in β -alumina and β'' -alumina. It is fair to say that research on these materials has improved our general concepts of ion transport in solids. In spite of the advancements, however, there remain some important unsolved problems. For example, we do not understand how the activation energy and conductivity of β'' -alumina depend on composition. Pursuit of this problem might lead to a significant improvement in conductivity at low temperatures and, therefore, to possibilities for a new battery design based on a different cell reaction.

Beta-alumina and beta''-alumina, in spite of their complex structure, are well suited to serve as model compounds for the study of important phenomena such as the mixed-alkali effect mentioned earlier. And they are excellent media for investigating the properties of isolated water molecules in a solid. Studies of the diffusion of water in β - and β'' -alumina might give us some new ideas about the mechanism of proton transport in solids. Because of the remaining problems and opportunities for research, we expect that scientific and technological interest in the β - and β'' -aluminas will remain high over the next several years.

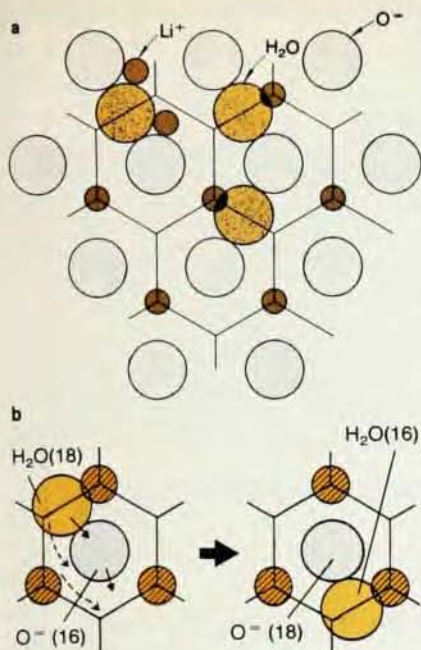
The topics discussed at recent international conferences are indicative of the course of future research on solid electrolytes. The last few years have seen an increased emphasis on intercalation and insertion compounds,²³ such as Li_xTiS_2 and $\text{Li}_x\text{V}_2\text{O}_5$. These materials, which are mixed ionic-electronic conductors, have important applications as solid-state electrodes in rechargeable ambient-temperature lithium batteries. There is also increased interest in solids that are good conductors of lithium ions at room temperature. These materials—composites of LiI and Al_2O_3 , for example—can be used as the electrolyte in an all solid-state lithium battery.

Research on glasses and polymers has also increased markedly in recent years. As electrolytes, glasses and polymers have some important properties, such as the ease with which they can be cast or molded into desired shapes. Although there has been considerable progress,^{5,7} further effort is needed to improve the conductivities of these materials.

Theoretical models have been critically important in understanding high ionic conductivity in solids. The high



Conductivities of sodium β -alumina and sodium β'' -alumina. Data are based on impedance measurements made¹⁴ at each temperature. The scale at the right is for the dashed line, which represents the correlation length of sodium β'' -alumina.^{5,16} Figure 7



Mechanism by which water moves through lithium β -alumina may involve dissociation and reformation of H_2O , as these schematic diagrams indicate. **a:** In the conduction layer, water molecules (assumed to have the same 1.4-Å radius as oxygen ions) stay near single and paired lithium ions. **b:** protons jump from a water molecule in an interstitial position. Resulting oxygen ion (O^{18} in this case) moves into bridging position as the bridging oxygen ion moves into a new interstitial position, where it combines with the protons. Figure 8

concentration of defects—and the long-range Coulomb interaction among them—present especially challenging problems in adapting many-body models and techniques to the study of ion transport in solid electrolytes. Models restricted to nearest-neighbor interactions are clearly inadequate in dealing with solid electrolytes. It remains for future work to modify methods such as path probability² to include long-range Coulomb interactions. Computer simulation^{5,7} has had some success with simple systems such as AgI and CaF_2 , but it will take a considerable amount of effort to apply these calculations to complex systems such as beta-alumina.

The ever increasing need to conserve oil is a strong incentive for developing devices for electrochemical energy conversion and storage. A practical high-energy-density rechargeable battery, suitable for powering electric vehicles, would allow coal or nuclear fuel to replace much of the oil consumed in transportation. The demands such devices place on the performance of electrolytes and electrodes assure the need for continued research on solid electrolytes in the years ahead.

* * *

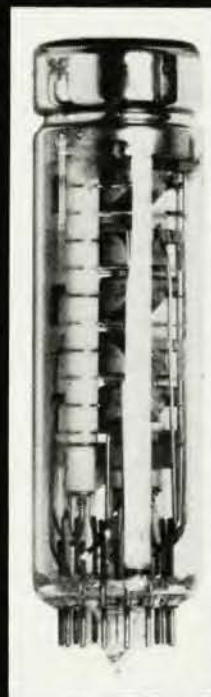
Our research on solid electrolytes is sponsored by the United States Department of Energy, Division of Materials Science, under

contract W-7405-eng-26 with Union Carbide Corporation.

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