Solid Electrolytes: 
Alkali-Ion Transport in 
Skeleton Structures

Massachusetts Inst of Tech Lexington Lincoln Lab

30 Jun 76
A new three-dimensional $K^+$-ion conductor, $K_1.9M_{98}S_{11.05}O_{4}$, has been identified. Its resistivity at 300°C is 28 $\Omega$-cm, less than one-fourth the value for the best potassium $\alpha$-alumina. More definitive measurements have been made of the $Na^+$-ion transport in $Na_3Zr_2Si_2P_2O_{12}$ (NASICON). Its resistivity at 300°C is 3 $\Omega$-cm, compared with 4 $\Omega$-cm for $\beta^+$-alumina. Moisture tests have shown that NASICON is insensitive to water vapor. Static tests in molten $Na_2S_4$ for 10 days at 400°C indicate chemical stability; similar tests in molten Na and dynamic tests in a Na-Na cell are in progress. Conclusive evaluation of stability awaits the preparation of additional test specimens.
SOLID ELECTROLYTES: ALKALI-ION TRANSPORT IN SKELETON STRUCTURES

SEMIANNUAL TECHNICAL SUMMARY REPORT
TO THE
NATIONAL SCIENCE FOUNDATION
AND TO THE
DEFENSE ADVANCED RESEARCH PROJECTS AGENCY

1 JANUARY - 30 JUNE 1976

ISSUED 23 SEPTEMBER 1976

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We have identified a new three-dimensional K$^+$-ion conductor, K$_{1.9}$Mg$_{0.95}$Si$_{1.05}$O$_4$ (KSICON). Its resistivity at 300°C is 28 Ω-cm, which is less than one-fourth the value for the best potassium β-alumina. We have also performed more definitive measurements of the fast, three-dimensional Na$^+$-ion transport in the compound Na$_3$Zr$_2$Si$_2$PO$_4$ (NASICON). After correcting for contact resistance, the resistivity measured at 300°C is 3 Ω-cm, compared with a value of 4 Ω-cm for a sample of β"-alumina supplied by the Ford Motor Company. Moisture tests show that NASICON is insensitive to water vapor, a definite improvement on β"-alumina. Static tests in molten Na$_2$S$_4$ for 10 days at 400°C indicated chemical stability, similar testing in molten sodium was initiated, and it has been established that substitution of Hf for Zr represents no chemical problem. Dynamic tests in a Na-Na cell are in progress, but conclusive evaluation for chemical stability awaits the preparation of additional test specimens of nearly theoretical density.
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1. SUMMARY

Since our discovery of fast Na⁺-ion transport in Na₃Zr₂Si₂PO₁₂ (which we have designated NASICON, for Na superionic conductor), our work has been more sharply divided into two separate tasks: a continuing search for new solid electrolytes, and ceramic development/testing of NASICON.

New Solid Electrolytes: In previous reports, we have mentioned the Carnegieite structure of high-temperature NaAlSiO₄, which is built up of corner-shared tetrahedra. The interstitial space of the cubic (AlSiO₄)³⁺ network, or skeleton, is identical to the skeleton itself, but displaced by half a lattice parameter. In this structure, half the interstitial cation sites are occupied by Na⁺ ions, and the "bottleneck" through which a Na⁺ ion must jump to get from one site to another is a hexagon outlined by tetrahedral-site edges. With a cell size of a = 7.38 Å, water is not a contaminant of NaAlSiO₄. Unfortunately, the cubic structure is not stable at room temperature. However, Na₂CaSiO₄ and Na₂MgSiO₄ are reported to form stable structures with (M²⁺SiO₄)²⁻ networks related to that of Carnegieite, except that the networks are distorted so as to allow for shorter Na-O bonding. These distorted structures have bottlenecks with a smallest diameter less than 4.31 Å, significantly smaller than twice the sum of Na⁺ and O²⁻ ionic radii (4.8 Å). Presumably this is why compounds in the system Na₂₋ₓCaₓSiₓ₋ₓPₓO₄ have observed to have poor ionic conductivity. The Carnegieite (AlSiO₄)³⁺ network has been stabilized at room temperature by the addition of extra Na₂O molecules in the interstitial space, but these extra molecules block Na⁺-ion transport. For example, cubic NaAlSiO₄·(Na₂O)ₓ, where x = 0.25 and 0.5, has Na⁺-ion conductivities at 300°C more than two orders of magnitude lower than that of γ-alumina.

Since the Na⁺ ion is apparently too small to support the (AlSiO₄)³⁺ network of Carnegieite, we undertook a study of K⁺-ion analogs. The system K₂₋ₓMgₓSiₓO₄ has the cubic network with no distortion at room temperature. Single-crystal structure determination for K₂MgSiO₄ gave space group Im3 m. The K⁺ ions are surrounded by twelve O²⁻ ions at a K-O distance of 3.2 Å, which is much too large for accommodation of a small Na⁺ ion. The diameter of the regular-hexagon bottleneck is 5.48 Å, just larger than twice the sum of the K⁺ and O²⁻ ionic radii, 5.46 Å. Since no additional molecules have been introduced to stabilize the structure, good K⁺-ion transport was anticipated.

Ceramic disks of K₁₋₀.9Mg₀.₉₅Si₁₋₀.₅₅O₄ (KSICON) with 94-percent theoretical density were prepared by hot pressing, and the K⁺-ion conductivity was determined with pseudoreversible graphite electrodes at 1000 kHz. The results, summarized in Fig. 1-1, gave a resistivity at 300°C of 28 Ω·cm and an activation energy of 0.35 eV. This is the best solid electrolyte for K⁺-ion transport that is yet known.

Testing of Na₃Zr₂Si₂PO₁₂ (NASICON): The resistivity of NASICON reported in our preceding Semimannual Technical Summary (31 December 1975, DDC AD-A022199/4) was determined with pseudoreversible graphite electrodes and included an impedance at the electrodes due to polarization. In order to eliminate the electrode contribution, a rod of the compound was fabricated and the resistances of various lengths of this rod were determined. The results, plotted...
Fig. 1-1. Conductivity-temperature product vs $1/T$ for $K_{1.05}Mg_{0.95}Si_{1.05}O_4$ (KSiCON).
Fig. 1-2. Determination of resistivity via a resistance-vs-length plot.

In Fig. 1-2, give the expected straight-line relationship between resistance $R$ and specimen length $x$:

$$R = A + Bx$$

where $A$ is the electrode contribution to the resistance. Subtraction of this contribution yields a value of 3 $\Omega$-cm for the resistivity of ceramic NASICON at 300°C.

For comparison, the resistivity of a sample of $\beta^n$-$\text{Al}_2\text{O}_3$ supplied by the Ford Motor Company was determined as a function of temperature by the same measurement technique. These measurements gave a resistivity of 4 $\Omega$-cm at 300°C and an activation energy of 0.1 eV, in excellent agreement with values reported in the literature.

It is well known that $\beta^n$-alumina is sensitive to water. In order to test the sensitivity of NASICON to humidity, we placed three ceramic disks above water in a sealed container, i.e., in an environment of 100-percent humidity. One disk was removed after 4 days, the second after 7 days, and the third after 28 days. None of these samples showed any dimensional change or mechanical degradation. We dried them, applied colloidal graphite for electrodes, and determined their resistivities at 300°C. The measured values ranged from 5 to 6 $\Omega$-cm, with the lowest value for the sample subjected longest to 100-percent humidity. We also made several independent measurements of the resistivity of a companion sample that had been set aside for use as a control, removing the graphite and recoating between each determination. These values also ranged between 5 and 6 $\Omega$-cm. (Apparently colloidal graphite is not an ideal pseudoreversible electrode for NASICON, since its effectiveness varies from application-to-application. A search for a more reproducible electrode has been initiated.) We conclude that NASICON is resistant to water damage and is not affected by humid environments.
For use in Na-S cells, NASICON must be stable in the presence of molten Na and Na$_2$S. A static test for chemical stability in molten polysulfide was made by immersing a 94-percent-dense specimen in molten Na$_2$S$_4$ for 10 days at 400°C. The recovered specimen was cleaned and examined. No measurable weight, dimensional, or resistance changes were found. We conclude that NASICON is quite stable in molten polysulfides. However, longer tests under dynamic conditions are necessary before long-term stability of the material can be established.

Tests for stability in molten sodium have been initiated. Preliminary static tests reveal a need for more pure ZrO$_2$ in synthesizing the compound, but substitution of Hf for Zr presents no problem. For dynamic testing, the following apparatus was constructed for U-tube sodium-sodium cells. Two half-inch vacuum quick-connects are mounted in a water-cooled brass plate designed to rest on a wide-mouthed dewar. The clamped "O" rings at the bottom of these quick-connects seal the glass U-tube and hold it in place inside the dewar; those at the top hold dispensing funnels that are replaced by electrodes after a sodium fill is completed. A valved vacuum connection is made to the sides of the quick-connects, and supports are provided to keep the glass tube from moving when its internal pressure charges. A jig for proper spacing of the U-tube arms was also constructed.

A NASICON disk 0.424 x 0.093 in. was sealed across the center of a length of Corning Code 7280 glass tubing, and another two lengths of tubing were sealed to the ends at right angles to form a U-tube. Three feet of nichrome wire were wound around the middle section of this U-tube and were held in place with Kaptan tape. A thermocouple was taped to the glass immediately over the sample. Then the U-tube was mounted in the quick-connects and vacuum baked at 300°C overnight before filling with sodium.

In order to avoid contamination of the sodium, the central portion of the stopcock in each dispensing funnel has to remain ungreased, and hence did not form a gas-tight seal between the body of the funnel and its tip. This circumstance made necessary a very elaborate filling procedure in which both dispensing funnels had to be in position, connected to the U-tube, while they themselves were charged from a primary funnel, with many cycles of evacuate, heat, cool, and backfill with argon. Finally, the electrodes had to be substituted for the funnels without letting the liquid sodium freeze or oxidize.

As expected, the sodium-ceramic contacts showed no frequency dependence and no asymmetry in the U-tube configuration; the sample resistance remained the same for both directions of current flow. We measured resistivities of $\rho = 31 \ \Omega \cdot \text{cm}$ at 155°C and $\rho = 14.7 \ \Omega \cdot \text{cm}$ at 200°C at a current level of 125 mA. Sometime during the night, at least 5 hr later, the sample developed a short and cracked (or vice versa), cracking the glass and aborting the run. From these measurements, it became clear that more dense samples are required. We believe that electron tunneling between pores in the ceramic causes a buildup of sodium metal in the pores, starting from the surface. In time, filling of the voids with metallic sodium causes the circuit to be shorted.

Subsequent attempts have been plagued with nonessential problems. Our latest run suffered from an overfill in one arm of the U-tube, which became blocked by a plug of solidified sodium. Consequently, expansion of the liquid sodium caused the glass to crack shortly after the sample reached 300°C, where we obtained a DC resistivity of $\rho_{300°C} = 5.0 \ \Omega \cdot \text{cm}$ at a current density of $1/C = 1.1 \text{A/cm}^2$. 
We are still developing techniques for the fabrication of dense ceramic membranes. So far, methods other than hot-pressing have yielded specimens as dense as 95 percent of theoretical. While hot-pressing has given close to theoretical density, such specimens will be used only for preliminary testing. Inexpensive fabrication requires finding other methods to achieve comparable densities, and these are being sought.
NEW SOLID ELECTROLYTES

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ABSTRACT

Fast alkali-ion conductors consist of a rigid, three-dimensional network stabilized by electrons from the mobile ions, which partially occupy a two- or three-dimensionally linked interstitial space. The networks thus far identified may be classified into three groups, depending on whether the three-dimensional, rigid skeleton is built from tetrahedra, octahedra, or a combination of the two. Each group is then divided into subgroups, depending on whether the anions are bonded to two, three, or four network cations. The system $K_{2-x}Mg_{1-x}Si_{1+y}O_4$ represents the first group, where $MgO_4$ and $SiO_4$ tetrahedra are shared by corners in such a way that each oxygen is bonded by two skeleton cations to form a three-dimensional network. Systems $Na_{1-x}Ta_2O_6F \cdot xO$ and $NaSbO_3 \cdot 1/6NaF$ represent the second group, where the three-dimensional networks are formed by sharing corners and/or edges of $TaO_5F$ and $SbO_6$ octahedra. The system $Na_{1-x}Zr_2Si_2P_3O_{12}$ represents the third group, where the three-dimensional skeleton is made from corner-shared $SiO_4$ (or $PO_4$) tetrahedra and $ZrO_6$ octahedra. Relations between activation energy, bottleneck size and chemical bonding are discussed. The ionic conductivity of $Na_3Zr_2Si_2P_3O_{12}$ is $0.3 \text{ S} \cdot \text{cm}^{-1}$ at $300 \text{ °C}$, which is competitive with the best $\beta^*$-alumina.

INTRODUCTION

Solid electrolytes that transport alkali ions are being developed for use in high-specific-energy secondary batteries, thermoelectric generators, and electrolytic cells for extracting metals from molten salts. This paper restricts itself to a general consideration of the crystallographic features to be looked for in such an electrolyte.

The essential structural feature is the existence of a rigid, three-dimensional network having an interstitial lattice partially occupied by alkali ions $A^+$ that is connected in at least one dimension. The mobility of the $A^+$ ions is governed by the transition probability for an ion transfer from one site to a neighbor of the interstitial lattice. In the electrolytes discussed in this talk, the rigid network consists of metal atoms $M = Al$, $M_2$, $M_3$, $M_4$, and oxygen atoms $O$. If only alkali ions occupy the interstitial space, the general chemical formula may be represented by $Al_\ell(M_\ell O_{\ell -})^{\ell+}$, where the rigid network $(M_\ell O_{\ell -})^{\ell+}$ is stabilized by accepting $\ell$ electrons from the mobile $A^+$ ions. However, it is not uncommon for additional molecules such as $H_2O$, $A_2O_3$, or $Al$ to also enter interstitial space. Because these additional molecules

This work was sponsored by the Defense Advanced Research Projects Agency and NSF RANN.
### Table I. Classification of Solid Electrolytes, $A_xM_yO_z$

<table>
<thead>
<tr>
<th>3D Network System</th>
<th>$A^+$-ion transport</th>
<th>$A^+$ ion: per cc</th>
<th>Shortest $A^+\cdot A^+$, Å</th>
<th>Bottleneck $A^+\cdot O$, Å</th>
<th>$\Delta E$, eV</th>
<th>$\rho_{300^\circ C}$, $\Omega$·cm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LINKED TETRAHEDRA</strong></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>A. $O^{2-}$ bonded to 2 cations</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1. $K_{2-2x}Mg_{1-x}Si_{1+x}O_4$, $x=0.05$</td>
<td>3D</td>
<td>$16.4 \times 10^{21}$</td>
<td>3.35</td>
<td>Hexagon</td>
<td>2.74</td>
<td>(0.35)</td>
</tr>
<tr>
<td><strong>LINKED OCTAHEDRA</strong></td>
<td></td>
<td></td>
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<tr>
<td>A. $O^{2-}$ bonded to 2 cations</td>
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<td></td>
</tr>
<tr>
<td>1. $NaSbO_3\cdot 1/6NaF$</td>
<td>3D</td>
<td>$17.4 \times 10^{21}$</td>
<td>2.87</td>
<td>Triangle</td>
<td>2.38</td>
<td>0.35</td>
</tr>
<tr>
<td>2. $Na_{1+2x}Ta_2O_5\cdot O_x$, $x=0.28$</td>
<td>3D</td>
<td>$10.9 \times 10^{21}$</td>
<td>3.70</td>
<td>Hexagon</td>
<td>2.67</td>
<td>0.40</td>
</tr>
<tr>
<td>B. $O^{2-}$ bonded to 3 cations</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1. $K_xMg_{y/2}Ti_{1-x}2O_{16}$, $x=0.8$</td>
<td>1D</td>
<td>$5.4 \times 10^{21}$</td>
<td>2.94</td>
<td>Square</td>
<td>2.34</td>
<td>-</td>
</tr>
<tr>
<td>C. $O^{2-}$ bonded to 2, 3 cations</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. $K_2Sb_4O_{11}$</td>
<td>3D</td>
<td>$7.6 \times 10^{21}$</td>
<td>3.50</td>
<td>Rectangle</td>
<td>2.52</td>
<td>0.40</td>
</tr>
<tr>
<td><strong>LINKED TETRAHEDRA AND OCTAHEDRA</strong></td>
<td></td>
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<tr>
<td>A. $O^{2-}$ bonded to 2 cations</td>
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</tr>
<tr>
<td>1. $Na_{1+x}Zr_2Si_3P_3-xO_{12}$, $x=2$</td>
<td>3D</td>
<td>$11.1 \times 10^{21}$</td>
<td>3.52</td>
<td>Hexagon</td>
<td>2.49</td>
<td>0.29</td>
</tr>
<tr>
<td>B. $O^{2-}$ bonded to 2, 3 and 4 cations</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1. $p^+$ - alumina</td>
<td>2D</td>
<td>$5.6 \times 10^{21}$</td>
<td>3.23</td>
<td>Rectangle</td>
<td>2.71</td>
<td>0.16</td>
</tr>
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</table>
tend to act as contaminants, they are initially ignored in the general discussion of crystallographic principles to be considered in the search for new solid electrolytes that transport alkali ions.

As indicated in Table I, this talk is restricted further to a consideration of rigid network built from $\text{MO}_4$ tetrahedra, $\text{MO}_6$ octahedra, or a combination of the two. These polyhedra may be connected in a variety of ways, and the anion can bond to two or more network cations.

For fast $\text{A}^+$-ion transport, the A sublattice is connected, the A-site polyhedra sharing common faces. A common face - or "bottleneck" - should have a smallest diameter greater than twice the sum of the anion and alkali-ion radii. For fast $\text{Na}^+$-ion transport in an oxide, for example, the smallest diameter should exceed 4.8 Å.

In addition to these geometrical constraints, chemical bonding also plays a role. Ideally, the potential energy of the $\text{Na}^+$ ion at a bottleneck position should be similar to that at an A-sublattice site. This can be accomplished by having an increase in Madelung energy cancelled by a decrease of elastic and/or covalent-bond energy. Intuitively, a balancing of these energies is more probable in structures where the covalent contribution to the A-O bonds is minimized by a polarization of the anion electron cloud away from the $\text{A}^+$ ion. This polarization can be accomplished in two ways: (1) the anions can bond with more than two cations of the network and (2) the anions can form strongly covalent M-O bonds within the rigid network. The first approach limits the dimensionality of the $\text{A}^+$-ion transport. For example, where the anions bond to four or more network cations, the anion array is close-packed and there is no connected interstitial sublattice for $\text{A}^+$-ion transport. If anions bond to three network cations, either one-dimensional or two-dimensional transport can occur: $\text{H}^+$ or $\text{Li}^+$ ions transport in one dimension in the tetragonal rutile structure, two-dimensional transport occurs in layered compounds.

Three-dimensional $\text{A}^+$-ion transport requires the presence of anions bonding to only two network cations. In this case, polarization of the $\text{O}^{2-}$-ion charge density away from the $\text{A}^+$ ion requires strongly covalent π and σ M-O bonds within the rigid network.

One-dimensional transport in tunnel structures is readily blocked by stacking faults and impurities. Two-dimensional transport in polycrystalline ceramics suffers a loss in mobile-ion density and grain-boundary conductance if the transporting layers are widely separated, as in β-alumina. Moreover, anisotropic thermal expansion reduces the mechanical strength and life of thermally cycled membranes. Three-dimensional transport is therefore preferable, and this restricts to two the number of M-O bonds per anion. Minimization of the covalent contribution to the A-O bonds appears to recommend, in this case, the selection of such strongly covalent complexes as $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{IO}_3^{3-}$, $\text{CO}_3^{2-}$, $\text{PO}_4^{3-}$, or $\text{SiO}_4^{4-}$ together with a transition-metal cation having an empty d shell for strong π bonding. In view of the requirement that the compound not be reduced by the molten alkali metal, the transition-metal cations are essentially reduced to two alternatives: $\text{Zr}^{4+}$ and $\text{Ta}^{5+}$.

It follows from these arguments that the solid electrolytes under consideration may be classified into three groups, depending upon whether the rigid network is built from $\text{MO}_4$ tetrahedra, $\text{MO}_6$ octahedra, or a combination of the two. Moreover, as indicated in Table I, each of these groups may be subdivided in accordance with the number of M-O bonds per $\text{O}^{2-}$ ion. Some significant structural properties of the illustrative examples cited in Table I are discussed below.
A rigid network $M_yO_z$ built of linked tetrahedra must have a ratio $z/y = 2$, since no other ratio can allow a three-dimensional network. All zeolites, for example, have $z/y = 2$, corresponding to two $M$-$O$ bonds per network anion. However, most of these aluminosilicates have too large an interstitial space; if their cell size exceeds 10 Å, they are generally stabilized by water or some other molecule that fills the interstitial space and blocks $A^+$-ion diffusion.

Carnegieite, the high-temperature form of NaAlSiO$_4$, has a cubic ($AlSiO_4^-$) network with cell size $a = 7.38$ Å, which is small enough that water is not a contaminant. Unfortunately the structure is not stable at room temperature. At this temperature, only Na$_2$CaSiO$_4$ and Na$_2$MgSiO$_4$ are reported to form stable structures with $(M^{2+}SiO_4)^{2-}$ networks related to that of Carnegieite; and these networks are distorted by bonding with the Na$^+$ ions. These distorted networks have distorted-hexagonal bottlenecks with a smallest diameter less than 4.31 Å, significantly smaller than the sum of Na$^+$ and O$^{2-}$ ionic radii (4.8 Å). Presumably this is why compounds in the system Na$_2$CaSi$_{1-x}$P$_x$O$_4$ were observed to have poor ionic conductivity.

The Carnegieite $(AlSiO_4^-$) network has been stabilized to room temperature by the addition of extra molecules in the interstitial space: cubic Na$_2$Al$_2$Si$_2$O$_8$ $(Na_2O)_x$, where $x = 0.5$ and 1. At 300°C, the Na$^+$-ion conductivity of these compounds is three orders of magnitude poorer than that of $Al_2$-alumina.

Since the Na$^+$ ion is apparently too small to support the $(AlSiO_4^-)$ network of Carnegieite, $K^+$-ion analogs were prepared. The system $K_{2-2x}Mg_xSi_{4-x}O_4$ has the cubic network with no distortion at room temperature. Single-crystal structure determination gave space group Fd3m. The $K^+$ ions are surrounded by twelve O$^{2-}$ ions at a K-O distance of 3.2 Å, which is much too large for accommodation of a small Na$^+$ ion. The bottleneck is a regular hexagon formed by MO$_4^-$tetrahedra edges; the diameter of 5.46 Å (see Fig. 1) is large enough for fast $K^+$-ion transport. (Twice the sum of $K^+$ and O$^{2-}$ ionic radii is 5.46 Å.) Since no "additional molecules" are introduced to stabilize this structure, good $K^+$-ion transport was anticipated and found.

**NETWORK FORMED BY LINKED OCTAHEDRA**

If the cations $M$ in $A_xM_yO_z$ are coordinated octahedrally by the anions, formation of a three-dimensional network requires a ratio $z/y < 3$. These networks may be subdivided into three groups: (1) $z/y = 3$ corresponding to two $M$-$O$ bonds per network anion, (2) $z/y = 2$ corresponding to three $M$-$O$ bonds per network anion, and (3) $2 < z/y < 3$, corresponding to some cations with two, others with three, M-$O$ bonds per network anion.

### A. Two M-O Bonds per Network Anion

1. **Na$_2$SbO$_3$·1/6 NaF.** The $(SbO_3^-)$ network of this cubic structure contains pairs of edge-shared octahedra that are corner-shared to form the three-dimensional array illustrated in Fig. 2. Each O-atom is bonded to two Sb atoms. This network contains tunnels along the $<111>$ axes that intersect at the origin and body-center positions. The tunnel-intersection sites of the interstitial space are occupied by F$^-$ ions. The tunnel segments between intersection sites, which consist of three face-shared octahedra squashed along the tunnel axis, are partially occupied by Na$^+$ ions. The central octahedron, site 8c of the structure, is bounded by two triangular bottlenecks of O$_2$ atoms; its face-shared octahedra, sites 16f, have a triangular face of O$_4$ atoms in common with the F$^-$ polyhedron. The Na$^+$ ions are distributed between 8c and
16f sites, but electrostatic forces correlate vacancies at the 16f sites bordering an occupied 8c site. The Debye-Waller factor indicates anomalously large thermal motion of the Na$^+$ ions in 16f sites along $\langle100\rangle$ directions, indicating excellent ion transport between 16f sites of neighboring tunnel segments around the $\Gamma$ ions. The existence of large numbers of Na$^+$ ions at 8c positions indicates that the potential energy for a Na$^+$ ion at this site does not differ too much from that at the crystallographically inequivalent 16f sites. The principal bottleneck to Na$^+$-ion motion is, therefore, the O$_2$ triangle, which has a distance from its center to an O$_2$ position of 2.38 Å. This distance is just large enough for fast Na$^+$-ion transport. This relatively tight bottleneck and the absence of $\pi$-bonding orbitals at the Sh$^{5+}$ ions may account for the relatively large activation energy (0.35 eV) observed in this compound. Nevertheless, a relatively large pre-exponential factor in the conductivity expression due to a high Na$^+$-ion concentration of $17.4 \times 10^{21}$ ions/cm$^3$—lowers the resistivity at 300°C to 13 Ωcm (or less, since no correction was made for contact resistance).

2. The defect pyrochlore NaTa$_2$O$_4$F$^-$ · $\times$Na$_2$O. The cubic pyrochlore structure with chemical formula $A_2B_2X_6X'$ has a rigid $B_2X_6$ network of corner-sharing octahedra. With space group Fd$ar{3}$m, assignment of B cations to positions 16c places the interstitial, larger A cations at 16d and the interstitial X$'$ anions at 8b. The interstitial $A_2X'$ array consists of a three-dimensional network of corner-shared X$A_4^-$ tetrahedra.

Two types of defect pyrochlores have been identified. One has vacancies at the 8b positions, the other has vacancies at the 16d positions and a large A$^+$ cation substituting for the X$'$ anion at 8b. The first type is illustrated by Ag$_2$Sb$_2$O$_6^-$, the second by RbTa$_2$O$_4$F$^-$. In the latter compound, the F$^-$ ions are randomly substituted for O$^{2-}$ ions of the ($B_2X_6$)$^+$ network. In both cases, the interstitial array is partially occupied by cations; however, the 16d and 8b sites are not crystallographically equivalent, so fast ion transport requires the introduction of vacancies among the occupied 16d or 8b sites or an adjustment of the cell size that makes nearly equivalent the potential energy for A$^+$ ions on 16d and 8b sites. The Madelung energy stabilizes A$^+$ ions on 16d sites, elastic forces stabilize large A$^+$ ions on 8b sites, where the A-O distances exceed 3.2 Å. The A$^+$($B_2X_6$)$^+$ defect pyrochlores are stabilized by the large Rb$^+$ and Cs$^+$ ions; if the size of the $B_2X_6$ array is small enough, a K$^+$ ion may also be used, as in K[AgAlF$_6$]. In the case of RbTa$_2$O$_4$F$^-$, which can be synthesized directly, the potassium analog can only be made by ion exchange; and the ion-exchanged product is hygroscopic. Water enters the 8b sites, displacing the K$^+$ ions to the 16d sites in K[AgAlF$_6$] · xH$_2$O, x = 1. In the case of ion exchange with sodium, additional Na$_2$O molecules are introduced, the O$'$ atoms occupying 8b positions in NaTa$_2$O$_4$F$^-$ · xNa$_2$O', x = 0.28. In K[AgAlF$_6$], the cell size is small enough to exclude water, but it also inhibits K$^+$ ion occupancy of the 16d sites. Since the K$^+$ ions must traverse a 16d site to jump between 8b positions in K$_{1-x}$Na$_{x}$Al$_{1-x}$F$_6$, this size inhibition makes the 16d position at the center of a puckered hexagon a constrictive bottleneck. In NaTa$_2$O$_4$F$^-$ · xNa$_2$O', this bottleneck, shown in Fig. 3, is large enough to accommodate the Na$^+$ ions; the equivalent Na-O distance is 2.58 Å. However, transport of Na$^+$ ions from 16d to 16d site is partially blocked by the O$'$ ions, and the short 16d-8b distance of 2.27 Å indicates strong Na-O$'$ bonding, which probably accounts for the high activation energy, 0.4 eV, observed for ion transport. Nevertheless, at 300°C the resistivity is only 150 Ωcm for NaTa$_2$O$_4$F$^-$ · 0.28 Na$_2$O.
B. Three M-O Bonds per Network Anion

The hollandite structure of $K_{x}M_{1-2x}Ti_{8-x/2}O_{16}$, $x = 0.8$, has an $M_{6}O_{16}$ network formed by $M_{6}O_{16}$ octahedra sharing corners and edges as shown in Fig. 4. In this structure, each anion is bonded to three $M$ atoms, and the interstitial space partially occupied by $K^+$ ions consists of one-dimensional tunnels that are isolated from one another. The $A^+$ ions occupy a large site bounded by twelve anions. In $K_{0.8}M_{0.4}Ti_{7.6}O_{16}$, the K-O distance is 3.3 Å, but in the square bottleneck between sites along a tunnel—see Fig. 4—the K-O distance would be only 2.3 Å, too small for $K^+$-ion transport with an activation energy of only 0.2 eV. The absence of any detectable d.c. transport is consistent with this observation; the low activation energy (0.2 eV) for high-frequency a.c. conductivity is apparently for $K^+$-ion displacements within the large $K^+$-ion sites.

C. Two and Three M-O Bonds per Network Anion

The compound $K_{2}Sb_{4}O_{14}$ has a rigid network of $Sb_{6}$ octahedra sharing corners and edges in such a way that some oxygen atoms share two $Sb$ atoms, others three. One-dimensional tunnels run parallel to the $b$ and $c$ axes. The bottleneck of a $b$-tunnel is illustrated in Fig. 5; it has a shortest O-O diameter of 5.16 Å. The $c$-tunnel and cross-tunnel bottlenecks are rectangular with shortest O-O diameters of 5.04 and 5.38 Å, respectively. These diameters are too short for fast $K^+$-ion transport, and a resistivity at 300°C was observed to be $4 \times 10^5 \Omega$cm.

NETWORK FORMED BY LINKED OCTAHEDRA AND TETRAHEDRA

A. Two M-O Bonds per Network Anion

The system $Na_{1+x}Zr_{2}Si_{2}P_{3-x}O_{12}$ has a three-dimensional network of $P_{4}$ and $Si_{4}$ tetrahedra corner-shared with $ZrO_{6}$ octahedra. Every O atom bonds with one $Zr$ atom and one $P$ or $Si$ atom. As shown in Fig. 6, the network is built up of $Zr_{2}(P_{1-y}Si_{y}O_{4})_{3}$ units, and the $(1 + x)$ Na$^+$ ions $(x = 3y)$ occupy a three-dimensionally linked interstitial space. The end members of this system have hexagonal symmetry; in a compositional range about $Na_{3}Zr_{2}Si_{2}PO_{12}$ the structure is distorted to monoclinic symmetry. The interstitial space contains two distinguishable crystallographic sites in the hexagonal phase, three in the monoclinic phase: per formula unit $4Na = Na(1) + 3Na(2)$ or $Na(1) + Na(2) + 2Na(3)$ sites. In the hexagonal phase, Na(2) sites form close-packed layers, and the Na(1) are octahedrally coordinated with the Na(2) layers. Each Na(2) atom has two Na(1) neighbors. In the monoclinic symmetry, the 3Na(2) layers become Na(2) + 2Na(3) layers, and each Na(1) site is octahedrally coordinated by 2Na(2) and 4Na(3) sites, as shown in Fig. 7. The bottlenecks between Na(1) and Na(2) or Na(3) sites are puckered hexagons formed by three $ZrO_{6}$ octahedral edges alternating with three tetrahedral edges, as illustrated in Fig. 8. The shortest diameter across this hexagon is 4.95 Å, which is larger than twice the sum of the Na$^+$ and $O^{2-}$ ionic radii (4.8 Å). Thus the geometrical condition for fast Na$^+$-ion transport is satisfied provided the preference energies for the Na$^+$ ions at different interstitial sites are not too dissimilar. Moreover, each O atom forms a strong, covalent $\sigma$ bond with $P$ or $Si$ atoms; it is able to form strong $\pi$ bonds with the $Zr 3d$ orbitals. Therefore, the anion charge should be well polarized into the network, away from the Na sites.

The end member Na$Zr_{2}Si_{2}PO_{12}$ has all the Na$^+$ ions at Na(1) positions and a poor ionic conductivity. Na$Zr_{2}(SiO_{4})_{3}$ has all the Na sites occupied, so this compound is also a poor Na$^+$-ion conductor. $Na_{3}Zr_{2}Si_{2}PO_{12}$, on the other hand, has a resistivity at 300°C of only 3 $\Omega$cm with an
activation energy of about 0.24 eV. Although the difference in preference energies for Na(1) and Na(2) sites prevents fast ion transport in NaZr₂(PO₄)₃, it does not in Na₃Zr₂Si₂PO₁₂. This suggests that a correlated double-jump diffusion takes place, the Na⁺ ions moving out of Na(1) sites on one side as they move in on the other.

B. Two, Three, and Four M-O Bonds per Network Anion

The structure of β-alumina, (Na₂O)₁₋ₓAl₂O₃, consists of blocks of Al₂O₃ with spinel structure separated by layers of Na₂O. Within the spinel block, close-packed oxygen atoms bond to four Al atoms, and no position is available to Na⁺ ions. Therefore β-alumina conducts Na⁺ ions only in the separated Na₂O layers. The Na₂O layers contain two types of O atoms: those bounding a layer have three Al neighbors to one side, those within a layer have two Al neighbors on opposite sides, as indicated in Fig. 9. Two types of Na⁺-ion sites exist in the layers, the Beevers-Ross and anti-Beevers-Ross sites, but the preference energies are apparently comparable. In β⁺-alumina, a symmetry change makes them equivalent. The excess xNa₂O, which forces occupancy of a fraction of the anti-Beevers-Ross site in β-alumina, may induce correlated Na⁺-ion transport of the type suggested for Na₃Zr₂Si₂PO₁₂. The rectangular bottleneck between these sites has a shortest O-O diameter of 5.42 Å, which is much larger than twice the sum of the ionic radii: 4.8 Å. A remarkably low activation energy of 0.17 eV for the Na⁺-ion resistivity is consistent with the large-area bottleneck and a polarization of the electronic charge at the boundary O²⁻ ions away from the Na⁺ ions towards the spinel blocks.

CONCLUSION

Several solid electrolytes capable of fast alkali-ion transport have been identified. They may be described as consisting of a rigid, three-dimensional network containing mobile A⁺ ions in an interstitial space connected in two or three dimensions. Structures containing one-dimensional tunnels exhibit poor conductivity, especially as polycrystalline ceramics. Structures having a three-dimensionally linked interstitial space have the highest density of alkali-ion sites, and hence a potentially large pre-exponential factor in the resistivity expression: \[ \rho = \rho_0 \left( \frac{T_0}{T} \right) \exp\left(-\frac{\epsilon}{kT}\right). \]

A small activation energy \( \epsilon \) appears to require that the following constraints be met:

1. The A⁺ ions should move on energetically equivalent sites. If two crystallographically distinguishable sites are used for transport, a small difference in site energy is tolerable provided the number of A⁺ ions exceeds the number of more stable sites, thus allowing correlated ion transfer to take place. (2) The bottleneck interface between A⁺-ion sites should have a large enough area that, when an A⁺ ion is in the interface, the shortest A-O bond is greater than the sum of the ionic radii. (3) The anion electronic-charge density should be polarized away from the A⁺ ions so as to minimize the covalent contribution to the A-O bonds. This can be accomplished (a) by bonding to three network cations on one side of the anion, as occurs in β-alumina for the anions bordering the Na₂O layers, or (b) by strong π and σ covalent bonding within a network if the anions bond to only two network cations, as occurs in Na₃Zr₂Si₂PO₁₂.

Finally, the existence of fast-ion transport in three dimensions has been demonstrated for Na⁺ ions in Na₃Zr₂Si₂PO₁₂ and for K⁺ ions in K₁.₅Mg₁.₅Si₁.₅O₄. These two compounds may have important practical applications.
Acknowledgements

The author wishes to thank J. B. Goodenough for fruitful discussions, J. A. Kafkas for ceramic processing as well as conductivity measurements, and C. H. Anderson, Jr. for technical assistance.

Fig. 1. Bottleneck (outlined by heavy lines) in cubic $\kappa_{2-2x}Mg_{1-x}Si_{1+x}O_4$.

Fig. 2. Cubic structure of $NaSbO_3$. Dark balls represent $Sb^{5+}$ ions, light balls $Na^+$ ions. The $O^{2-}$ ions are at corners of octahedron.
Fig. 3. A (110) projection of cubic pyrochlore $A_2B_2X_6X'$. The linked octahedra represent the $DX_6$ network, the shaded small circles the interstitial $A$ cations in positions 16c, and the large open circles projected onto the shaded circles represent the two near-neighbor $X'$ ions in 8b sites on either side of an $A$ cation.

Fig. 4. Bottleneck (outlined by dashed lines) in the one-dimensional tunnels of Hollandite, $K_xMg_{x/2}Ti_{8-x/2}O_{16}$. 
Fig. 5. Bottlenecks (diameters indicated by hatched bars) in $K_2Sb_4O_{11}$.

Fig. 6. $Zr_2(PO_4)_3$ unit (shaded) of hexagonal Na$Zr_2P_3O_{12}$. 
Fig. 7. Monoclinic structure of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$. 

Fig. 8. Bottleneck in $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$. 

Fig. 9. Schematization of $\beta$-alumina layer structure.