

SOLID ELECTROLYTES CONTAINING BOTH MOBILE AND IMMOBILE ALKALI IONS

H. Y.-P. HONG

Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173 (U.S.A.)

Summary

The basic structural feature of oxides with high alkali-ion conductivity is a rigid, three-dimensional network consisting of immobile cations and O^{2-} anions, with the mobile alkali ions partially occupying an interstitial space that is interconnected in at least one dimension. In the best-known oxide solid electrolytes, all the alkali ions are mobile. Recently, however, high alkali-ion conductivity has been observed in materials having structures in which some of the alkali ions are incorporated into the rigid network. In this paper we will discuss why structures containing both mobile and immobile alkali ions are advantageous for solid electrolytes and review the properties of the new materials, one of which — $Li_{14}ZnGe_4O_{16}$ — has the highest Li^+ -ion conductivity so far reported.

Introduction

Solid electrolytes containing mobile cations can be classified into two categories based on structural features. In materials of the first type, the non-mobile units are bonded together to form a rigid, three-dimensional network having interstitial spaces partially occupied by the mobile ions. Examples are β -alumina [1], $Na_3Zr_2Si_2PO_{12}$ [2], $Na_5YSi_4O_{12}$ [3, 4], and $Li_{14}ZnGe_4O_{16}$ [5]. In materials of the second type, the non-mobile units are linked to each other by bonding to the mobile ions. Examples are AgI [6], Rb_4AgI_5 [6, 7], LiI [8], and Li_3N [9]. Because of the strong covalency of the O^{2-} anion, oxide solid electrolytes have structures of the first type. The remainder of this paper will be restricted to the oxides, so that only this type of structure will be discussed.

In the best-known oxide solid electrolytes, including Na- β -alumina and $Na_3Zr_2Si_2PO_{12}$ (NASICON), all the alkali ions are mobile. Recently, however, high alkali-ion conductivity has been observed in materials with the compositions $Li_{14}DT_4O_{16}$, where D is a divalent cation and T is a tetravalent cation, and $Na_5RSi_4O_{12}$, where R is a trivalent cation. These materials

TABLE 1
Network properties of oxide solid electrolytes

Bonding	Examples
Linked tetrahedra	
O^{2-} bonded to 2 cations	$K_{2-2x}Mg_{1-x}Si_{1+x}O_4$
O^{2-} bonded to 4 cations	$Li_{14}ZnGe_4O_{16}$
Linked octahedra	
O^{2-} bonded to 2 cations	$NaSbO_3 \cdot 1/6 NaF, Na_{1+2x}Ta_2O_5F \cdot O_x$
O^{2-} bonded to 3 cations	$K_xMg_x/2Ti_{8-x}/2O_{16}$
O^{2-} bonded to 2 or 3 cations	$K_2Sb_4O_{11}$
Linked tetrahedra and octahedra	
O^{2-} bonded to 2 cations	$Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$
O^{2-} bonded to 2, 3, or 4 cations	β -alumina, β -gallia
O^{2-} bonded to 2, 3, or 5 cations	$Na_5YSi_4O_{12}$

have structures in which some of the alkali ions are incorporated into the rigid network. The next Section of this paper discusses why structures containing both mobile and immobile alkali ions are advantageous for solid electrolytes and the last Section reviews the properties of the new materials.

Structural principles

In an oxide with high alkali-ion conductivity, the three-dimensional network consists of immobile cations and O^{2-} anions, with the mobile alkali ions partially occupying the interstitial space, which is interconnected in at least one dimension. The type formula for such a material may be written as $A_x^+(M_yO_z)^{x-}$, where A^+ represents the mobile alkali ions and M the immobile network cations. The network is formed by the linkage of $M-O$ polyhedra, either MO_4 tetrahedra, MO_6 octahedra, or both. Depending on the structure, each O^{2-} ion may be bonded to two, three, or four M ions, leaving two, one or zero sp^3 orbitals available for bonding to the mobile ions. Therefore, we may classify solid electrolytes on the basis of their constituent polyhedra and the number of network cations per O^{2-} ion, as summarized in Table 1.

The transport of mobile alkali ions in an oxide solid electrolyte takes place by the jump of these ions from occupied to unoccupied positions in the interstitial space, through bottlenecks formed by the O^{2-} ions. For any appreciable ionic conductivity the interstitial positions must be only partly occupied, and for high conductivity the activation energy for a jump between these positions must be small. Therefore, the distance between adjacent positions should not be too great, and the bottlenecks must be large enough to permit easy ion passage. The bottleneck size increases with the number of O^{2-} ions involved. For fast ion transport a rectangular bottleneck

TABLE 2
M-O ratios in three-dimensional networks

Network units	Oxygen bonded to	
	3 cations	4 cations
MO ₄ tetrahedra	M ₃ O ₄	MO
MO ₄ octahedra	MO ₂	M ₂ O ₃

is large enough in the case of Li⁺, but a pentagon or distorted hexagon is required for Na⁺ and a regular hexagon for K⁺.

The ionic mobility is determined not only by the geometrical factors mentioned but also by the strength of the interaction between the mobile ions and the O²⁻ ions forming the bottlenecks. For the highest mobility this interaction should be made as weak as possible by reducing the covalent contribution to the A-O bonds. This can be accomplished by increasing the degree of covalent interaction between the O²⁻ ions and the network cations. Such an increase can be achieved by increasing the number of M ions to which each O²⁻ ion is bonded, thus reducing the number of sp³ orbitals available for interaction with the A⁺ ions. As a rule of thumb, for fast Na⁺- and K⁺-ion transport there should be at least two M-O bonds per O²⁻ ion; because of the greater intrinsic strength of the Li-O bond, for fast Li⁺-ion transport the number of these bonds per O²⁻ ion should be at least three and preferably four.

The incorporation of alkali ions into the rigid network of a solid electrolyte is advantageous because it permits an increase in the number of M-O bonds per O²⁻ ion. This number determines the ratio of M ions to O²⁻ ions, which is equal to the ratio of the average number of M-O bonds per O²⁻ ion to the average number of these bonds per M ion. For example, as summarized in Table 2, in a network formed by the linkage of MO₄ tetrahedra, to have four M-O bonds per O²⁻ ion there must be equal numbers of M and O²⁻ ions. Since the net charge on the (MO)^{x-} network must be negative in order to balance the positive charge on the mobile A⁺ ions, in this structure the average valence of the M ions must be less than two. Therefore such a structure can exist only if some of the M ions are monovalent — a condition that can be satisfied by incorporating alkali ions into the network. More generally, for a material represented by A_x⁺(M_yO_z)^{x-}, $x = 2z - vy$, where v is the average valence of the M ions: Since $v = 2z/y$ for $x = 0$, a material with mobile A⁺ ions cannot exist unless $v < 2z/y$. For a given network structure, this condition can be satisfied more easily by incorporating monovalent alkali ions into the network to reduce v . Several recently synthesized compounds illustrating these principles are discussed in the following Section.

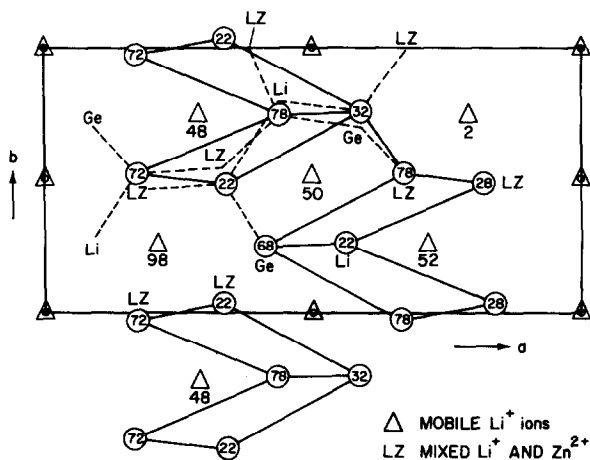
$\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$: FRAMEWORK- $\text{Li}_{11}\text{Zn}(\text{GeO}_4)_4$; MOBILE ION- Li_3


Fig. 1. Projection of the LISICON structure on the a - b plane.

Examples

Figure 1 shows the structure of the $\text{Li}_{14}\text{DT}_4\text{O}_{16}$ compounds, as exemplified by $\text{Li}_{14}\text{ZnGe}_4\text{O}_{16}$. In this structure the rigid network is formed by the linkage of MO_4 tetrahedra, and each O^{2-} ion is bonded to four M ions. The requirement that the average valence of the M ions must be less than two is satisfied because 11 of the 14 Li^+ ions per formula unit are members of the network, so that the compound can be represented by $\text{Li}_3^+(\text{Li}_{11}\text{DT}_4\text{O}_{16})^{3-}$, for an average M valence of 1.8. We have prepared the four compounds with $\text{D} = \text{Zn}$ or Mg , and $\text{T} = \text{Si}$ or Ge . Of these, $\text{Li}_{14}\text{ZnGe}_4\text{O}_{16}$ (LISICON) has the highest conductivity and lowest activation energy. We attribute these properties, which make this compound the best Li^+ -ion conductor known, to the high number of M-O bonds per O^{2-} ion, coupled with a favorable bottleneck size.

In the $\text{Na}_5\text{RSi}_4\text{O}_{12}$ compounds, as exemplified by $\text{Na}_5\text{YSi}_4\text{O}_{12}$, the rigid network is composed of both MO_4 tetrahedra and MO_6 octahedra. Of the 5 Na^+ ions per formula unit, $2\frac{1}{3}$ are mobile, 2 occupy tetrahedral network sites (along with the Si ions), and the remaining $\frac{2}{3}$ occupy octahedral sites (along with the Y ions). The average valence of the M ions is 2.8. The average number of M-O bonds per O^{2-} ion is 2.8, and on the average each of the O^{2-} ions forming the bottlenecks to Na^+ ion transport is bonded to 2.4 M ions.

It has recently been reported [10] that Na- β -gallate and Na- β'' -gallate are also examples of solid electrolytes containing some immobile alkali ions, since Na-K ion-exchange experiments indicate that 10 - 15% of the Na^+ ions

TABLE 3

Properties of oxide solid electrolytes

Solid electrolyte	Percentage of mobile alkali ion	M-O bond ratio*	Activation energy (eV)	Resistivity at 300 °C (Ω cm)
Na- β -alumina	100	2.86	0.14	3
Na ₅ YSi ₄ O ₁₂	47	2.40	0.15	6
Na ₃ Zr ₂ Si ₂ PO ₁₂	100	2.00	0.20	3
Li ₁₄ ZnGe ₄ O ₁₆	21	4.00	0.24	8
Li- β -alumina	100	2.86	0.31	144
Li ₃ Zr ₂ Si ₂ PO ₁₂	100	2.00	0.50	1 500

*Average number of M cations to which each bottleneck O²⁻ ion is bonded.

in these compounds are immobile. Thus these materials are intermediate between Na- β -alumina and Na- β '-alumina, their Al analogs, in which all of the Na⁺ ions are mobile, and Na₅YSi₄O₁₂, in which 53% of these ions are immobile.

In Table 3, the activation energies and resistivities at 300 °C for Na₅YSi₄O₁₂ and Li₁₄ZnGe₄O₁₆ are compared with the values of these parameters for other Na⁺ and Li⁺-ion conductors. For Na₅YSi₄O₁₂, the activation energy is 0.15 eV for the temperature range between 175 and 300 °C and the resistivity at 300 °C is 6 Ω cm. This activation energy is essentially the same as that of Na- β -alumina, in which most of the bottleneck O²⁻ ions are bonded to three M ions, and significantly less than the value of 0.20 eV observed for NASICON, in which each O²⁻ ion is bonded to only two M ions. For LISICON, the activation energy is 0.24 eV and the resistivity at 300 °C is 8 Ω cm; this material is the best Li⁺-ion conductor known. Comparison of the data for LISICON with those for Li- β -alumina and for the Li analog of NASICON shows a strong increase in both activation energy and resistivity, with a decrease in the number of network cations to which the bottleneck O²⁻ ions are bonded. Thus the incorporation of Li⁺ ions into the three-dimensional network, which permits each O²⁻ ion to be bonded to four M cations, makes an important contribution to the excellent conducting properties of LISICON.

Acknowledgments

This work was sponsored by the Department of Energy and the Defense Advanced Research Projects Agency.

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