

The products of this decomposition process can be correlated with the poor physical and corrosion-resistant properties.

An examination of Nasicon ceramics prepared at different compositions using several processing methods demonstrates that these materials undergo decomposition into their component oxides during sintering. Many, if not all, of the poor physical properties of these materials can be attributed to this decomposition phenomenon. Poor mechanical properties resulting from nonuniform particle shrinkage, microcracking, second-phase constituents, and coarse spherical voids are a direct result of the decomposition of this material. Furthermore, many of the negative results obtained during electrolytic testing of these ceramics may be attributed to the decomposition of this material during densification. Significant new developments in either the areas of processing or composition are needed before contiguous, corrosion-resistant Nasicon electrolytes can be consistently produced.

PRINCIPLES OF SUPERIONIC CONDUCTION

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The objective of this program is to provide insight into the mechanisms of fast ion conduction in alkali ion conductors of potential relevance to battery systems. This will be done by (1) performing measurements of ionic conductivity of potential fast-ion conductors with synthesis of new structure types as well as crystal-chemical modifications of structures with demonstrated fast-ion conduction and (2) specifying probability distribution and thermal motion of the mobile ions through precise neutron scattering techniques in materials in which conduction varies markedly with composition.

Synthesis and properties of Nasicon-related solid solution systems

A large number of phases $Al_n^+X_2^{k+}(T^1+O_4)_3$ where $0 < n < 4$ and $n + 2k + 3 = 24$, assume the Nasicon structure type. In solid solutions in which substitution is made for either the octahedral framework cation, X , or the tetrahedral cation, T , the C -axis of this rhombohedral structure and the unit cell volume typically rise through an anomalous maximum for intermediate compositions. The ionic conductivity of the mobile alkali ion, usually low or moderate for the end members, rises to a maximum at or near the same composition. It is not clear whether the change in cell volume, the concentration of mobile ions, a change in the 'window' between alkali-ion sites, or a combination of these influences is responsible for the enhanced conduction.

A very large number of potential solid solution systems are possible between end members with the Nasicon structure type. In spite of this, synthesis and conductivity measurements had been performed for only one system, Nasicon *per se*, $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, when this project was begun. Studies of five other systems were subsequently reported by other workers as our studies were in progress. All were Na phosphate systems and involved replacement of the octahedral Zr cation (with Nb, Y, Cr, In, and Yb, respectively). In the initial phases of this program, solid solutions were synthesized across 10 different solid solution systems and their conductivities measured. Particular attention was paid to substitutions for the tetrahedral framework cation, and the relative conductivity for different alkali ions. Among the more interesting results was the finding that solid solutions $\text{Na}_4\text{Zr}_2\text{Ge}_x\text{Si}_{3-x}\text{O}_{12}$ and $\text{Na}_4\text{Zr}_2\text{PGe}_x\text{Si}_{2-x}\text{O}_{12}$ formed Nasicon-like structures with crystallographic anomalies similar to Nasicon *per se*. However, as the alkali content is constant and fixed at a value for complete filling of the alkali sites, the changes cannot be attributed to different site occupancies or changed Na-Na interactions. Reasoning that a framework of smaller cations might provide enhanced Li^+ conductivity, it was shown that $\text{LiTi}_2(\text{PO}_4)_3$ displayed a conductivity that was not only larger than its Na and K analogues, but quite respectable in magnitude ($\sigma_{300} = 10^{-2}$ reciprocal ohm-cm, 50 percent larger than Li- β alumina and an order or magnitude larger than Li Nasicon).

To interpret the mechanism of these changes in conductivity and to provide further increases in conductivity, the synthesis and conductivity measurement of solid solutions based on $\text{LiTi}_2(\text{PO}_4)_3$ has begun. These systems are of crystal chemical interest in that both larger and smaller cations exist for which substitution in either the tetrahedral and octahedral framework sites seems possible. Moreover, some of the substitutions leave the alkali ion content fixed, while others will either increase or decrease the concentration. The effects of changed mobile ion concentration and change in framework geometry may thus be separated. Synthesis of solid solutions in the system $\text{Li}_{1+x}\text{Ti}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ has been completed. Solution of Si is limited, extending not greater than $x = 0.15$. Materials were synthesized in two ways (solid-state reaction and decomposition of coprecipitated gels) to ensure that the polyphase products indeed represented a limit to solid solubility and not incomplete reaction of the precursors. The conductivity of the solid solutions and the synthesis of solid solutions involving the octahedral framework site will be the subject of work in the immediate future.

It should be noted that our studies of Nasicon-related solid solution systems, designed initially to provide insight into the relation between crystal-chemistry and conductivity, have assumed a more practical significance. It has recently been discovered that Nasicon *per se*, $\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{12}$, may not be stable in the presence of molten sodium, due to instability of the P-O bond. Development of a solid solution of comparable conductivity that contained little or no P would therefore be of technological importance.

Synthesis and properties of new alkali ion conductors

Recent Russian literature contains reports of several silicate crystal structures with characteristics (frameworks of tetrahedral and octahedral cations, interconnected channels, and alkali ions with anomalously high thermal motion) that suggest a strong possibility for fast ion conduction. No conductivity measurements, however, have been reported. These phases, including $\text{NaNdSi}_6\text{O}_{14}$, $\text{K}_2\text{TiSi}_6\text{O}_{15}$, and $\text{K}_3\text{NdSi}_6\text{O}_{15}$, have related structures and the possibility — analogous to Nasicon — for solid solutions in which framework dimensions and mobile ion concentration might be varied.

Initial attempts to synthesize these phases through solid-state reaction were made, but were unsuccessful: the high silica content caused glass formation at temperatures sufficiently high to produce reaction. Hydrothermal techniques using a simple reaction cell capable of only limited temperatures and pressures were used. These runs, necessarily of long duration, produced only fine-grained, poorly crystallized products. A more elaborate apparatus for synthesis at higher temperatures and pressures was then assembled and fully tested. The device contains two-zone furnaces and a pair of stellite reaction bombs in which temperatures to 1000 °C and pressures to 50 kpsi (3.4 kbar) may be achieved. This operating range should be more than adequate for silicate synthesis. Initial syntheses are currently in progress.

Structural analysis of the Nasicon solid solution system

Conductivity in the Nasicon system $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ rises to a broad maximum near $x = 2.3$, a composition at which crystallographic anomalies occur, as noted above. The reason for the enhancement is not clearly understood and may involve changes in framework geometry and/or change in concentration of the mobile ions. The structure distorts from rhombohedral to an unknown monoclinic structure for a range of intermediate X , which includes the composition of optimum conductivity. It is worth noting that

- No structure has been determined for a solid solution. All structural information has been obtained from end members.
- The monoclinic structure of the highly conducting Nasicon solid solutions has not been established.
- Nothing is known about Si/P ordering or the distribution of Na among available sites in monoclinic Nasicon.
- The origin of the anomalous maximum in cell volume and its relation to conductivity is not understood.

To answer these questions, we have undertaken and completed structure determinations of four solid solutions in the Nasicon system.

Two series of compositions $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, with $x = 0, 1.6, 2.0, 2.4, 2.5,$ and 3.0 , were synthesized by solid-state reactions. As commonly noted by other workers, a small volume fraction of monoclinic ZrO_2 was present in the reaction product. Processing conditions were adjusted to reduce this to a minimum: no detectable ZrO_2 at low x (less than 0.5 wt.%) and only one weak maximum, that corresponding to the most intense peak in the ZrO_2 spectrum, at large x .

Four compositions, $x = 1.0, 1.6, 2.0$ (Nasicon), and 2.5 , were selected for structure determination. Conductivity in the system rises through a broad maximum between $x = 1.8$ and 2.5 . The selected compositions thus allow structure determinations at a composition at which conductivity sharply increases with composition, at Nasicon *per se*, and at the onset and conclusion of the broad maximum. The structures of the end members $x = 0$ and $x = 3$ are available from previously reported single-crystal analyses.

Neutron powder diffraction intensities were recorded at the National Bureau of Standards research reactor. Intensities were recorded at intervals of 0.05° over a range $10^\circ > 2\theta < 100^\circ$ using monochromated neutrons of 1.5423 angstroms wavelength.

The structures of the solid solutions were established and refined using Rietveld powder profile analysis. Least squares adjustment of atomic positions, anisotropic temperature factors, and Na site occupancies proceeded satisfactorily to agreement levels of 5.4, 5.0, 4.9, and 6.6 percent respectively, values within 1 percent of that estimated on the basis of standard deviations in counting rates. The agreement is regarded as excellent in view of the complexity of the structures (9 positional parameters and 24 thermal parameters, and 29 coordinates and 68 independent thermal parameters are required to describe the rhombohedral and monoclinic phases, respectively).

The important features obtained from the structural analyses may be summarized as follows:

- Monoclinic Nasicon is isostructural with $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ as previously suspected.
- The Na(1) site of $\text{NaZr}_2(\text{PO}_4)_3$ remains fully occupied at all compositions. Additional Na progressively fills the Na(2) site which in $\text{Na}_4\text{Zr}_2(\text{SiO}_4)_3$ is fully occupied.
- In monoclinic phases, there is strong (but not complete) ordering of Si and P. Moreover, and somewhat surprisingly, the tetrahedra are significantly distorted.
- In the monoclinic phases, the Na(2) site splits into two symmetry-independent positions. These sites are not equally populated by Na.
- The anomalous maximum in the C-axis arises from rotation and distortion of the tetrahedra. The ZrO_6 octahedron remains relatively unchanged.

- The size of 'windows' between neighboring Na sites increases to a maximum at the Nasicon composition as a result of distortion of the tetrahedra. Change in framework geometry as well as variation in concentration of the mobile ions thus seems responsible for the enhanced composition.

The objectives of this project remain unchanged for 1983, and research will continue in an effort to clarify the principles of superionic conduction as a basis for the design of electrolytes with improved properties.

Recent publications

- 1 I. Kohatsu, A. K. Ekholm and B. J. Wuensch, Electrical conductivity of some Nasicon-related solid solution systems, 84th Annual Meeting, American Ceramic Society, *Bull. Am. Ceram. Soc.*, 61 (3) (1982) 419.
- 2 I. Kohatsu, A. K. Ekholm and B. J. Wuensch, Synthesis and characterization of Nasicon-like fast-ion conductors, 83rd Annual Meeting, American Ceramic Society, *Bull. Am. Ceram. Soc.*, 60 (3) (1981) 360.
- 3 L. J. Schioler, B. J. Wuensch and E. Prince, Structural changes in the Nasicon solid solution system, Fall Meeting, Basic Science and Electronic Divisions of American Ceramic Society, *Bull. Am. Ceram. Soc.*, 61 (8) (1982) 805.

POLYMERIC ELECTRODES FOR AMBIENT TEMPERATURE LITHIUM BATTERIES

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This research program is directed at exploring the electrochemical behavior and stability of various polymeric electrodes and electrolytes for use in ambient temperature lithium batteries. The current focus of the program is on studying the properties of polyacetylene as a potential cathode and anode material for nonaqueous lithium batteries.

Investigations of the electrochemical reactions and chemical stability of oxidized and reduced polyacetylene films were carried out using cyclic voltammetry, controlled potential electrolysis, chronopotentiometry, resistivity measurements, thermogravimetric analysis, and differential scanning calorimetry. Electrochemical reactions were performed with propylene carbonate electrolytes containing LiClO_4 and LiAsF_6 . Stability measurements used samples of unreacted polyacetylene as well as material that had been oxidized chemically with bromine and iodine and electrochemically with AsF_6^- as the anion.

Both fresh polyacetylene and samples that have been oxidized to the conducting state react readily with oxygen and moisture. At room temper-