

Results of preliminary electrical conductivity measurements show that with increasing Li content (a) the ionic conductivity increases rapidly reaching $10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 350°C for a composition of $\text{Li}_2\text{O}/\text{B}_2\text{O}_3 \approx 0.5$, and (b) decreasing activation energies fall to $\sim 0.5 \text{ eV}$ at high lithium contents. Studies are proceeding to test the effects of additives, morphology, and moisture on the electrical transport properties of these glasses.

Corrosion resistance studies of these glasses in molten lithium and lithium salts are now being initiated.

Recent publications

- 1 H. L. Tuller and D. R. Uhlmann, Electrical conduction and corrosion processes in fast lithium ion conducting glasses, *Prog. Rep. Contract EX-76-A-01-2295*, April 1979.
- 2 D. P. Button, H. L. Tuller and D. R. Uhlmann, Fast ion transport in oxide glasses, *5th Univ. Conf. Glass Science, R.P.I., Tory, NY, August 1979*.

FABRICATION AND CHARACTERIZATION OF NASICON CERAMIC ELECTROLYTES

Ceramtec, Inc., 580 Arapeen Drive, Salt Lake City, UT 84108 (U.S.A.)

The objective of this project is to fabricate thirty-six unsealed NASICON electrolyte tubes which are prepared from mechanically mixed powder mixtures using state-of-the-art procedures in processing. Homogeneous powder preparation methods and the sintering of electrolytes prepared from these powders will be studied on a best efforts basis consistent with available funds. Hot-pressing techniques are being used to prepare dense, conductive, and mechanically strong ceramic bodies which can serve as the standard to be achieved by conventional ceramic processing. NASICON electrolytes are being evaluated in electrically dynamic sodium-sodium test cells prior to evaluation in sodium-sulfur cells by battery developers.

During the current period, Ceramtec has developed scaled-up fabrication procedures, similar to those developed at the Lincoln Laboratory, using mechanical powder mixtures of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, SiO_2 and unstabilized monoclinic ZrO_2 for the fabrication of polycrystalline NASICON ($\text{Na}_{1+x} \cdot \text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$; $x = 2$) electrolyte tubes (16 mm o.d. \times 200 mm long) with acceptable dimensional tolerances, mass densities over 3.20 g/cm^3 , sodium ion resistivities under 5 ohm cm at 300°C . However, these tubes all contain a small residual amount (up to about 5%) of free ZrO_2 in the sintered body. The tubes containing residual ZrO_2 have shown very poor resistance to mechanical degradation in molten sodium ($300 - 400^\circ \text{C}$) both in static and electrically dynamic conditions. The tubes are also mechanically weak.

Whether or not the presence of free ZrO_2 is responsible for the low mechanical strengths and poor resistance to degradation in liquid sodium remains to be determined. However, the presence of residual zirconia is undesirable possibly for two reasons.

(1) Zirconia undergoes a phase transformation with a significant volume change (tetragonal to monoclinic) between ~ 1000 and ~ 1100 °C. NASICON is typically sintered at temperatures over 1200 °C. Consequently, the phase transformation in zirconia which occurs upon cooling from the sintering temperature might introduce microcracks in the ceramic leading to a reduction in mechanical strength.

(2) The presence of zirconia as a second phase may also indicate the presence of other phases containing, perhaps, SiO_2 , which might be readily attacked by liquid sodium.

The fundamental reason for the occurrence of residual zirconia after sintering NASICON ceramics is not completely understood at this time. Several factors may be important. First, since no reliable phase equilibrium data exist, it is not entirely clear whether or not single phase NASICON at any given composition is even stable at the sintering temperature. We do know that NASICON at $x = 2$ melts incongruently at about 1275 °C with the expulsion of free zirconia. Second, inadequate mixing and sluggish solid state diffusion may lead to unreacted or residual zirconia after sintering. Finally, milling with zirconia media could lead to small amounts of residual zirconia which could remain after firing or even act as a catalyst for additional zirconia formation. Additional work is needed to resolve this issue.

A sol-gel process involving the gelation of a colloidal suspension of silica in a solution containing dissolved phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) and zirconium ($(\text{NH}_4)_2\text{Zr}(\text{OH})_2(\text{CO}_3)_2$) compounds has been developed in the current program for the preparation of a powder containing single phase NASICON. Decomposition of the gelled material into NASICON ($x = 2.0 - 2.3$) occurs at temperatures ≤ 1150 °C. Whether or not this powder can be prepared in a state suitable for sintering to acceptable densities remains to be determined. Preliminary results are encouraging.

Another approach to the formation of NASICON is the mechanical mixing and subsequent firing of zircon (ZrSiO_4) and Na_3PO_4 powder mixtures. This method, reported originally by Pober at MIT, is currently under study. This procedure has the potential of making reasonably strong, sintered NASICON ceramic bodies which are free of residual zirconia. Small amounts of residual zircon may be present, however.

Finally, preliminary hot-pressing experiments in graphite dies with mechanical powder mixtures have been conducted at temperatures between 1160 and 1240 °C at pressures around 34 MPa. The physical properties of this material are the best achieved to date with densities of 3.34 g/cm^3 , sodium ion resistivities of 3.1 - 3.4 ohm cm at 300 °C and strengths of 212 ± 19 MPa. These properties have been achieved in spite of the fact that some residual zirconia is present.

Clearly, extensive work remains on the preparation of NASICON cera-

mics over a range of compositions using (1) gellation, (2) improved powder mixing and milling techniques, (3) hot-pressing, and (4) other procedures for the preparation of NASICON ceramic electrolytes which can be tested successfully in Na-Na cells.

At this stage of development it is apparent that the phase composition of sintered NASICON is critical to its mechanical strength and stability in molten sodium under both static and electrically dynamic conditions. We are confident and fully expect this material to be a strong and economically viable candidate for use as the electrolyte in sodium-sulfur cells.

In future work powder preparation techniques and sintering (hot-pressing) procedures which lead to the fabrication of strong, conductive, and dense material will be given high priority. Our current approach is to prepare nearly single phase NASICON electrolyte tubes with high mechanical strengths. If these tubes withstand both static and electrically dynamic corrosion in liquid sodium at temperatures between 300 and 400 °C, thirty-six electrolyte tubes (16 mm o.d. × 200 mm length) will be delivered for evaluation in prototype sodium-sulfur cells.

The major technical problem requiring resolution is the identification of residual secondary phases (*e.g.*, ZrO_2 , $ZrSiO_4$, SiO_2 , etc.) in polycrystalline NASICON which may be detrimental to mechanical strength and/or resistance to electro-mechanical degradation in sodium-sodium and sodium-sulfur cells. This problem is well within the scope of the current program. Its solution, however, may be rate limiting in the fabrication of electrolytes with satisfactory in-cell performance characteristics.

Recent publications

- 1 G. R. Miller, B. J. McEntire, T. D. Hadnagy, R. S. Gordon and A. V. Virkar, Processing and properties of sodium- β'' -alumina and NASICON ceramic electrolytes, in P. Vashishta, J. N. Mundy and G. K. Shenoy (eds.), *Fast Ion Transport in Solids, Electrodes and Electrolytes*, North Holland, Amsterdam and New York, 1979.
- 2 B. J. McEntire, G. R. Miller and R. S. Gordon, Sintering of polycrystalline ionic conductors: β'' - Al_2O_3 and NASICON, to be published in *Proc. Fifth Int. Conf. Sintering and Related Phenomena, Notre Dame, Indiana, June 18 - 20, 1979*.

RESEARCH AND DEVELOPMENT

Massachusetts Institute of Technology, Cambridge, MA 20139 (U.S.A.)

The objective of this program, which was recently completed, has been to discover and develop new alkali-ion solid electrolytes for batteries having both high energy density and high specific power, as well as for thermo-