

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- $\beta''$ -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:  $\beta''$ - $Al_2O_3$  and NASICON, to be published in *Proc. Fifth Int. Conf. Sintering and Related Phenomena, Notre Dame, Indiana, June 18 - 20, 1979*.

### RESEARCH AND DEVELOPMENT

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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-

electric generators and alkali-metal processing systems. The program included both a systematic search for new superionic conductors and an evaluation of promising materials to determine their suitability for practical use. The evaluation consisted of characterization of the electrical properties, development of ceramic fabrication procedures, and laboratory testing of ceramic specimens under projected battery operating conditions.

Previous exploratory research at Lincoln Laboratory led to the discovery of two new superionic conductors, NASICON ( $\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{12}$ ) and LISICON ( $\text{Li}_{14}\text{ZnGe}_4\text{O}_{16}$ ). During the present contract period, procedures were developed for the fabrication of very high quality, closed-end NASICON ceramic tubes with densities exceeding 98% of theoretical and conductivity as high as  $0.4 \Omega^{-1} \text{cm}^{-1}$  at  $300^\circ\text{C}$ . This procedure involved a final sintering at  $1230^\circ\text{C}$ . The stability of these tubes was examined in stainless-steel-bodied Na/S test cells. In the longest test a NASICON tube at  $300^\circ\text{C}$  survived 4000 30-minute charge-discharge cycles at  $100 \text{ mA/cm}^2$  of electrolyte.

Single crystals of  $\text{Na}_3\text{Sc}_2\text{P}_5\text{O}_{12}$ , a structural analog of NASICON, were prepared and a conductivity of  $0.2 \Omega^{-1} \text{cm}^{-1}$  was determined. Similar conductivities were observed for the compound  $\text{Na}_5\text{YSi}_4\text{O}_{12}$ , but Na/S test-cell results showed that this material did not have adequate stability for high-temperature Na battery applications. Initial stability tests indicated that LISICON reacted readily with lithium at  $200^\circ\text{C}$ , and no further tests were performed.

The initial goal of the Lincoln Laboratory effort on solid electrolytes, to find a promising fast  $\text{Na}^+$ -ion conductor for use in high temperature Na batteries, has been realized. We have shown the following: NASICON has a conductivity at  $300^\circ\text{C}$  as high as that of the best specimens of Na- $\beta$ " alumina, can be prepared from cheap, readily available starting materials, and sintered at a very reasonable temperature ( $1230^\circ\text{C}$ ), is insensitive at room temperature to water vapor or even liquid water, has adequate mechanical strength, and exhibits high chemical stability. At this point procedures should be developed for fabrication of large tubes so that NASICON may be evaluated in prototype practical battery systems.

## Recent publications

- 1 H. Y-P. Hong, Crystal structure and ionic conductivity of  $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ , *Mater. Res. Bull.*, 13 (1978) 117.
- 2 H. Y-P. Hong, J. A. Kafalas and M. Bayard, High  $\text{Na}^+$ -ion conductivity in  $\text{Na}_5\text{YSi}_4\text{O}_{12}$ , *Mater. Res. Bull.*, 13 (1978) 757.
- 3 H. Y-P. Hong, Crystal structure and ionic conductivity of a new superionic conductor,  $\text{Na}_3\text{Sc}_2\text{P}_5\text{O}_{12}$ , 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.
- 4 M. Bayard, Analysis of the alternating current properties of LISICON ceramics, 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.

- 5 J. A. Kafalas and H. Y-P. Hong, NASICON, a new solid electrolyte for Na/S batteries, *Proc. 28th Power Sources Symp.*, Electrochemical Society, Princeton, New Jersey, 1979, p. 2.
- 6 J. A. Kafalas and R. J. Cava, Effect of pressure and composition on fast Na<sup>+</sup>-ion transport in the system Na<sub>1+x</sub>Zr<sub>2</sub>Si<sub>x</sub>P<sub>3-x</sub>O<sub>12</sub>, 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.
- 7 H. Y-P. Hong, Solid electrolytes containing both mobile and immobile alkali ions, *J. Power Sources*, 5 (1980) 137.

## PHYSICAL CHEMISTRY OF MOLTEN SALT BATTERIES

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The objective of this project, new in 1979, is to provide studies of polarization phenomena in molten salt batteries related to current-induced composition gradients in mixed molten salt electrolytes. The kinds of battery systems considered include those consisting of: a lithium alloy negative electrode and an iron sulfide positive electrode with LiCl-KCl as the electrolyte; other active alloy (*e.g.*, calcium) negative electrodes with more complex electrolytes; Na/ $\beta$ "Al<sub>2</sub>O<sub>3</sub> negative electrode with SCl<sub>3</sub>AlCl<sub>4</sub> positive electrode and NaCl-AlCl<sub>3</sub> electrolyte.

A previously described model (J. Braunstein and C. E. Vallet, *Migrational polarization in high-current density molten salt battery and fuel cell analogs*, *J. Electrochem. Soc.*, 126 (1979) 960) of ion flows in molten salt mixtures has now been extended to incorporate composition changes and gradients in an alloy electrode, and the way in which these gradients interact with the composition gradients in the electrolyte. Results of these computations, using available thermodynamic and transport data for LiAl alloys and for molten LiCl-KCl mixtures, can indicate conditions of current density and electrode thickness at which the composition changes at different depths in the LiAl electrode may be expected to cause phase changes in the alloy. These computations are being used also to design experiments for measuring the extent of electrolyte component separation in LiAl/LiCl-KCl/FeS<sub>x</sub> batteries. (Such separation has been observed by Giner *et al.* during discharge of an Al/Cl<sub>2</sub> battery with NaCl-KCl-AlCl<sub>3</sub> electrolyte where AlCl<sub>3</sub> precipitated at the anode (J. Giner and G. L. Holleck, Report, NASA CR-1541 (March 1970), *J. Electrochem. Soc.* 119).)

Equipment has been assembled and measurements initiated of concentration polarization at LiAl electrodes in molten LiCl-KCl as a function of current, potential, time, and initial electrolyte composition. The measurements consist of electrolysis-e.m.f. relaxation measurements such as those