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ELECTRICAL CONDUCTION AND CORROSION IN LITHIUM CONDUCTING GLASSES

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139 (U.S.A.)

The objective of this project is to investigate and characterize the electrical and corrosion-resistant properties of fast lithium ion conducting glasses which appear to be highly promising candidates for use as solid electrolytes in high energy density batteries.

This program consists of three major efforts related to the development of a glassy solid electrolyte: glass formability and processing studies, charge transport studies, and corrosion resistance investigations. At this preliminary stage, emphasis has been directed towards identifying compositions in the lithium borate system which are reasonably good glass formers as well as fast ion conductors. Glass processing steps including (a) powder preparation, (b) melting procedures, (c) chill techniques, and (d) post fabrication annealing treatments, were correlated with the final morphology of the glasses produced. These included degree of crystallization, phase separation, and cracking. Compositions with $\text{Li}_2\text{O}/\text{B}_2\text{O}_3$ ratios of 0.1 - 0.7 were investigated. Glasses with up to $\text{Li}_2\text{O}/\text{B}_2\text{O}_3 = 0.5$ were readily formed, while glasses with even higher lithium contents could be produced by adding salts such as LiCl .

The above studies demonstrated that it is possible to obtain glasses in the lithium borate system over a wide range of Li/B ratios. Effects of widely varying alkali contents on both the transport and corrosion resistant properties of such glasses are now being investigated.

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.
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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.