

- 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-

ature, oxygen and moisture irreversibly degrade the polymer, presumably by oxidizing and interrupting the conjugated double bond network essential for its properties as an electronic conductor.

Polyacetylene can be electrochemically oxidized to a level of $m = 0.07$ in the formula, $(\text{CHX}_m)_n$, and subsequently reduced with an overall coulombic efficiency of 85 to 90 percent, if the electrolyte is present in minimal quantities and if it is extremely clean. At an oxidation level corresponding to $m = 0.07$, the potential of a polyacetylene electrode is about 3.9 V versus a Li electrode in propylene carbonate containing LiClO_4 . Further oxidation is increasingly inefficient because of electrolyte breakdown. At an oxidation level of $m = 0.07$, a Li/ CH_x nonaqueous cell has a projected specific energy approximately equivalent to that of a commercially available lead-acid battery. It appears that attaining higher energy densities will require electrolytes that are stable in the voltage range above 3.9 V versus Li.

This year's investigations clearly show that polyacetylene is a fascinating but unforgiving electrode material. It is extremely sensitive to reaction with oxygen and moisture. But, it is a remarkable compound that can function either as an anode or a cathode in a nonaqueous electrochemical cell. Whether it will find a niche in technology will be determined by the results of future research.

Investigations proposed for 1983 are directed toward understanding the electrochemistry and stability of polyacetylene anodes, determining whether the energy density of a polyacetylene anode can be increased by using electrolytes other than propylene carbonate, and exploring the mechanisms of electrochemical and chemical oxidation and reduction of polyacetylene, which determine its potential power density and usefulness in solid-state cells.

Recent publications

- 1 D. Frydrych and G. C. Farrington, Electrochemical oxidation of polyacetylene in electrolytes containing AsF_6^- and ClO_4^- , submitted to *J. Electrochem. Soc.*
- 2 R. Huq and G. C. Farrington, Stability of fresh and oxidized polyacetylene, submitted to *J. Electrochem. Soc.*
- 3 F. L. Tanzella, W. Bailey, D. Frydrych *et al.*, Ion transport in PEO-alkali salt complex polymeric electrolytes, *Solid State Ionics*, 5 (1981) 681.