

IMPROVED BETA"-ALUMINUM OXIDE ELECTROLYTES THROUGH TRANSFORMATION TOUGHENING

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The purpose of this research program is to improve the fracture toughness and strength of the sodium electrolyte, beta"-alumina, by incorporating zirconia as a second phase and to optimize these mechanical properties with the properties required for use of the electrolyte in advanced storage batteries.

The use of the zirconia phase transformation to toughen ceramics has been established in the last several years. To use this technique, the zirconia must be retained in its high-temperature, tetragonal phase. This is accomplished by producing microstructures in which the zirconia is well dispersed and has a grain size $\geq 1 \mu\text{m}$. The initial phase of this work has therefore emphasized the fabrication of such microstructures. The route chosen is based on dispersing ultrafine powders of beta"-alumina and zirconia in alcohols, such as 1-butanol.

These dispersions are stable and electrophoretic measurements have shown that both powders are positively charged, with zeta potentials in the range 30 to 60 mV. Green ceramic bodies are then produced by filtration of the suspensions using a powder mold. Thus, presence of agglomerates that occur in dry consolidation routes is avoided, and moreover, the second phase is expected to be well dispersed. After careful drying, the composite materials are densified by normal techniques. Beta"-alumina/zirconia composites containing up to 20 vol.% zirconia have been fabricated using commercial powders. The starting powders were found to contain agglomerates $> 2 \mu\text{m}$. Milling of the dispersions can be used to break up the agglomerates, but this was found to lead to contamination and microstructural defects. An improved technique using an ultrasonic probe and sedimentation, if necessary, was therefore introduced.

Observation of the fired microstructure showed that the zirconia was well dispersed with an average grain size of $\sim 1 \mu\text{m}$. X-ray diffraction confirmed that the zirconia was retained in its tetragonal state and that beta"-alumina was the only other detectable phase. It was established that the presence of the zirconia second phase eliminated the tendency for exaggerated grain growth that occurs in the single-phase materials. This is expected to be beneficial in the use of these materials as electrolytes.

Measurement of the mechanical properties of the composite materials has shown that the strength and fracture toughness can be increased by a factor of two compared with the single-phase material. The influence of the zirconia on the ionic conductivity is currently underway so that the strength/resistivity ratio of these materials can be optimized. It is also worth noting

that surface grinding of these materials usually leads to substantial surface compressive stresses, which should also be useful in increasing the reliability of these materials.

Plans and technical objectives for 1983

Fabrication

-Choose fabrication route and composition that maximizes strength/resistivity ratio of these composites;

-Explore use of centrifugal casting as a technique for consolidating green ceramic bodies;

-Study techniques for producing agglomerate-free, ceramic powders containing both the zirconia and the beta"-alumina phases.

Performance

-Study behavior of material in presence of liquid sodium;

-Determine whether the composite materials are more resistant to the electrolytic degradation that occurs during the use of these materials in advanced battery systems (in conjunction with L. DeJonghe, LBL).

FABRICATION AND CHARACTERIZATION OF NASICON SOLID ELECTROLYTES

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The objectives of this project are to fabricate Nasicon ($\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$) tubes and their quality control evaluation so as to evaluate Nasicon as an alternative to $\beta''\text{-Al}_2\text{O}_3$ electrolyte for use in Na/S batteries.

Processing and characterization of Nasicon ceramic electrolytes have been conducted using a number of different techniques. Sintering of these materials was accomplished at temperatures between 1100 and 1375 °C. Results of this work have shown that Nasicon ceramics with compositions around $x = 2$ (i.e., $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$), are not monophase, possess poor mechanical strength and an anomalous thermal expansion behavior, and are subject to chemical instability in the presence of liquid sodium (at 300 °C). Using wet-chemical techniques, X-ray diffraction analysis, and scanning electron microscope (SEM) observations, it was found that Nasicon apparently exhibits phase and chemical decomposition at densification temperatures.