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Effects of fabrication conditions on mechanical properties and microstructure of duplex β″-Al_2O_3 solid electrolyte

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ABSTRACT

Na-beta batteries are an attractive technology as a large-scale electrical energy storage for grid applications. However, additional improvements in performance and cost are needed for wide market penetration. To improve cell performance by minimizing polarizations, reduction of electrolyte thickness was attempted using a duplex structure consisting of a thin dense electrolyte layer and a porous support layer. In this paper, the effects of sintering conditions, dense electrolyte thickness, and cell orientation on the flexural strength of duplex BASEs fabricated using a vapor phase approach were investigated. It is shown that sintering at temperatures between 1500 and 1550 °C results in fine grained microstructures and the highest flexural strength after conversion. Increasing thickness of the dense electrolyte has a small impact on flexural strength, while the orientation of load such that the dense electrolyte is in tension instead of compression has major effects on strength for samples with a well-sintered dense electrolyte.
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1. Introduction

Electrical energy storage (EES) technologies have been demanded to improve reliability and efficiency of future grids [1]. Among various EES technologies, high-temperature Na-beta batteries (NBBs) such as Na–S and Na-metal halide (ZEBRA) batteries (typically operated at 250–350 °C), which use β or β″ alumina as electrolyte and molten sodium as anode, have received great attention due to the high round-trip efficiency, high energy density and capability of energy storage [2,3].

One of the key components which determine cell polarizations and electrochemical performance of NBBs is β″-alumina solid electrolyte (BASE). BASE is conventionally fabricated by sintering β″-Al_2O_3 powders. β″-Al_2O_3 powders have been synthesized by conventional solid-state reaction [4], sol–gel process [5], co-precipitation technique [6], spray-freeze/freeze-drying method [7], etc. The as-synthesized powders are sintered into required shapes (such as a disc or one-end closed tube) by isostatic pressing, electrophoretic deposition, slip casting or extrusion techniques [8]. The main drawback of conventional fabrication processes is sodium evaporation at high processing temperatures [9,10]. An alternative method to overcome this issue is a vapor phase approach [11–13]. In the vapor phase process, the starting materials such as α-Al_2O_3 and yttria-stabilized zirconia (YSZ) are first sintered at 1600 °C in air followed by conversion of α-Al_2O_3 to β″-Al_2O_3 at around 1450 °C in β″-Al_2O_3 packing powders. The conversion occurs by coupled transport of sodium and oxygen ions with YSZ acting as a fast oxygen conduction path to accelerate the conversion reactions. Advantages of the method include: (i) full conversion of α-Al_2O_3 to β″-Al_2O_3; (ii) elimination of the need for encapsulation, as the conversion temperature is lower than that in the conventional process; (iii) grain size is maintained similar to that prior to conversion; (iv) resistance to moisture attack, and (v) higher strength due to the YSZ addition [14].

Even though significant progress has been achieved in the NBB technologies during the past few decades, the batteries are still facing challenges in performance and cost for broad market penetration. To improve the performance of NBB's further, especially at lower temperatures, it is necessary to decrease resistance of the BASE while maintaining good strength. This requires that the BASE becomes more conductive for the same thickness, or that the thickness of the BASE decreases to reduce the area-specific resistance (ASR). Increasing the conductivity of the material is extremely difficult for mass production, since it requires that the BASE needs to

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be nearly single crystal or the anisotropy between grains should be minimized [15].

Decreasing the thickness of the BASE is easy to a point. However, there is a critical thickness below which the material no longer has the strength to function. This problem related to the mechanical strength of thin BASE can be overcome by creating a dual-layered (duplex) structure, where a thin dense BASE layer is integrated with a thick porous support layer that adds strength to the BASE, yet does not substantially increase the resistivity.

This paper focuses on planar duplex BASEs with thin dense electrolyte layers (50 μm and 100 μm thick) and thick porous support layers (1 mm thick). Effects of sintering conditions, thickness of dense electrolyte, and cell orientation on the flexural strength of duplex BASEs were investigated. The relationship between flexural strength and microstructure was studied in order to further understand the sintering temperature/flexural strength correlation.

2. Experimental

2.1. Duplex BASE fabrication

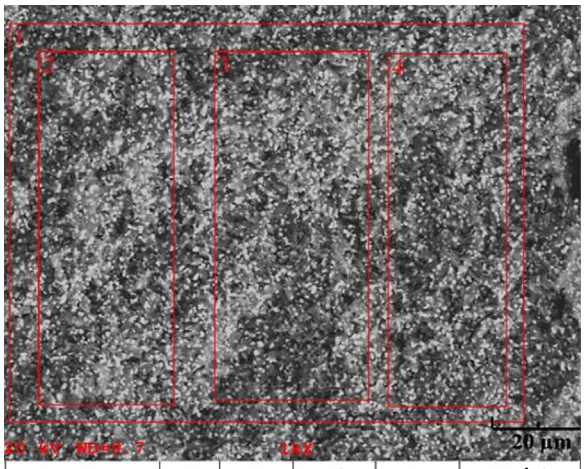
Powders of α-alumina (α-Al_2O_3, Almatis Premium Alumina, 99.8 wt%) and 5 mol% yttria stabilized zirconia (5YSZ, Imerys Fused Minerals, 5.4 wt% Y_2O_3) were first mixed to desired volume ratios followed by attrition milling in iso-propanol to achieve a median particle size (d_{50}) less than 0.5 μm. This not only ensures nearly uniform particle size, but also eliminates regions of compositional non-uniformity. Slurries for dense and porous support layers were prepared by mixing milled powders with solvents (methyl ethyl ketone, ethanol, emphos PS-136), a binder (polyvinylbutyral, B-79), and a plasticizer (benzyl butyl phathalate) and then tape cast to desired thicknesses. For porous support tapes, a sacrificial pore former (Superior Graphite, SLC1512P) was added to the slurry to create the voids in the structure during sintering.

Tapes were cast using a doctor blade placed on silicone coated Mylar. Thickness is controlled by adjusting the blade height with two micrometers. This allows for fine-tuning of thickness across the width of the blade by careful zeroing of the blade on a milled-flat surface. Slurry is poured into the blade reservoir and the Mylar film is pulled under the stationary doctor blade at a constant rate to evenly coat the slurry onto the Mylar. The slurry is dried to remove the solvents and form a stable tape before moving. Once dry, the tape can be easily peeled from the Mylar film for use. For the current work, slurry compositions and casting rates for the dense and porous tapes were held constant. The doctor blade settings were maintained constant for the porous layer tapes used in all trials, while the doctor blade settings were maintained the same for all 50 μm dense tapes, and at a second setting for all 100 μm tapes. Tape thicknesses were measured after drying to ensure that proper thicknesses were maintained for all layers prior to use to ensure sample-to-sample variation was not a factor in the results.

A single layer of dense electrolyte tape was placed on top of multiple layers of porous support tapes, vacuum bagged, and run through a hot roll laminator (ChemInstruments HL-100 Custom) at 135 °C to create a monolithic laminate which was large enough to cut out a number of pieces for sintering. Laminated pieces were sintered for 2 h at temperatures between 1500 °C and 1600 °C, with multiple holds to allow the binder and pore formers to burn out.

Bulk density of the dense layer after sintering at 1600 °C was 4.64 g/cc with 3.75% open porosity. The porous layer, sintered under the same conditions had a bulk density of 3.80 g/cc with 21% open porosity.

After sintering, the parts were converted from α-Al_2O_3 to β″-Al_2O_3 by covering them in "packing powder" comprised of β″-Al_2O_3 powder with 10 wt% $NaAlO_2$ added. The packing powder acts as the sources of β″-Al_2O_3 stabilizers such as Na and Li to convert the sintered α-Al_2O_3 in the parts to β″-Al_2O_3. Conversion was done in a dedicated furnace at 1400 °C for 10 h. Fig. 1 shows multi-location EDS results of a representative fracture surface of the dense Electrolyte. It can be seen that the Na to Al ratio of the entire thickness (Area 1) is the same as for the regions at the outer edge, center, and edge that is facing the porous support (areas 2, 3 and 4, respectively). This indicates that the conversion conditions are sufficient to completely convert α-Al_2O_3 to β″-Al_2O_3.



Location	O	Na	Al	Zr	Na/Al
1 (Overall of Dense)	59.12	3.15	27.11	10.61	0.12
2 (Outside Edge of Dense)	58.21	3.14	27.68	10.97	0.11
3 (Center of Dense)	59.20	3.38	26.91	10.51	0.13
4 (Porous Layer Edge of Dense)	59.05	3.16	27.41	10.38	0.12

Fig. 1. EDS analysis conducted on a representative converted dense layer.

Fig. 2 shows phase analysis of XRD patterns of the as-sintered parts as well as after conversion. Fig. 2a shows that the as-sintered part is Corundum (α-Al_2O_3) with two YSZ phases. Fig. 2b shows that the two YSZ phases are unaffected; however, the corundum phase is completely converted to Sodium Lithium Aluminum Oxide. This confirms that the α-Al_2O_3 has been completely converted to β″-Al_2O_3. If parts were not to be tested within 24 h of conversion, they were placed into vacuum bags for storage to minimize moisture contact.

2.2. Strength testing

Flexural strength was measured using the ball-on-ring (BOR) technique [16]. Ball-on-ring tests were performed by placing a circular sample onto a support ring of known size and applying load at the center of the support ring by a single ball from the opposite surface. The thickness and diameter of each sample tested must be measured prior to testing. If possible, Poisson's ratio should be determined for the sample. Since this is not possible when using a porous support layer, an assumed Poisson's ratio of 0.25 is used, as measured Poisson's for the fully dense versions of materials used in this work have been measured at 0.288–0.312. The use of lower Poisson's ratio value may underestimate strength, but should