



# Synthesis of iron-doped Na-β"-alumina + yttria-stabilized zirconia composite electrolytes by a vapor phase process



Leila Ghadbeigi<sup>a</sup>, Alex Szendrei<sup>a</sup>, Pablo Moreno<sup>b</sup>, Taylor D. Sparks<sup>a</sup>, Anil V. Virkar<sup>a,\*</sup>

<sup>a</sup> Department of Materials Science and Engineering, University of Utah, 122 S. Central Campus Drive, Salt Lake City, UT 84112, USA

<sup>b</sup> BCME Department, San Jose State University, San Jose, CA 95912, USA

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## ABSTRACT

Two phase samples containing ~30 vol.% of 3 mol% Y<sub>2</sub>O<sub>3</sub>-stabilized zirconia (TZ-3Y) and ~70 vol.% of α-Al<sub>2</sub>O<sub>3</sub> doped with 5 mol% Fe<sub>2</sub>O<sub>3</sub> were fabricated by sintering powder compacts in air at 1450 °C. The added Fe<sub>2</sub>O<sub>3</sub> was fully dissolved in Al<sub>2</sub>O<sub>3</sub> as determined by X-ray diffraction. The two phase samples were packed in Na-β"-alumina powder of nominal composition 8.85 wt.% Na<sub>2</sub>O, 0.75 wt.% Li<sub>2</sub>O and balance Al<sub>2</sub>O<sub>3</sub> and heat treated in air at 1250 °C for 20 h. The samples were sectioned, polished and examined by X-ray diffraction, optical microscopy and scanning electron microscopy. The as-sintered samples were ~97% of theoretical density with an approximate grain size of ~0.8 μm. In the samples packed in Na-β"-alumina powder and heat treated in air, Fe-doped α-Al<sub>2</sub>O<sub>3</sub> converted into Fe-doped Na-β"-alumina. A sample of 2.35 mm in thickness could be fully converted into iron-doped Na-β"-alumina in 17 h at 1450 °C. Ionic conductivity was measured by electrochemical impedance spectroscopy (EIS) over a temperature range from 197 °C to 485 °C. The bulk conductivity of the converted sample exhibited Arrhenius behavior with an activation energy of 0.20 eV and a pre-exponential factor of 421 Ω<sup>-1</sup>cm<sup>-1</sup> K.

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## 1. Introduction

Na-β"-alumina has a nominal composition of Na<sub>2</sub>O·6Al<sub>2</sub>O<sub>3</sub> (with a small amount of Li<sub>2</sub>O or MgO added in the conventional sintering process) and a rhombohedral structure which can be indexed as a hexagonal unit cell with  $a = 6.06 \text{ \AA}$  and  $c = 33.74 \text{ \AA}$  [1,2]. Three Al–O spinel blocks are stacked one on top of the other rotated through 120°. The spinel blocks are joined by bridging oxygen ions [2]. Sodium ions reside in the c-planes separating the spinel blocks and are highly mobile in the conduction plane. Thus, Na-β"-alumina is a highly anisotropic ionic conductor with virtually no ionic conductivity perpendicular to the c-direction. In most applications, therefore, Na-β"-alumina is used in a polycrystalline form. Polycrystalline samples with random orientation of grains exhibit isotropic conductivity which is typically about half that of single crystals in the conduction planes. In addition, there is usually some resistance to the transport of sodium ions across grain boundaries, which decreases with increasing temperature. Thus, the ionic conductivity of Na-β"-alumina is an inverse function of its grain size. For a sample of about 4 to 5 μm in grain size, the ionic resistivity of Na-β"-alumina at 300 °C is about 3 to 5 Ωcm making it one of most highly conducting solid electrolytes. Its high ionic conductivity, excellent chemical stability and highly refractory nature makes it an ideal candidate for high temperature electrochemical devices based on

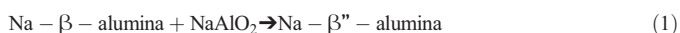
sodium ion conduction. The largest application of Na-β"-alumina as a solid electrolyte is in sodium–sulfur batteries and sodium-metal chloride batteries [3,4]. NGK in Japan is the largest manufacturer of Na-S batteries which markets them under the name NAS batteries. In the NAS battery Na-β"-alumina is used as a one end closed tube of about 50 mm diameter, 2 mm thickness and about 50 cm length. The actual battery module is rated at 50 kW with a discharge time of 8 h corresponding to a storage capacity of 400 kWh. This forms the basic building block of modular batteries. Batteries as large as 64 MWh have been demonstrated. Currently, some units have been in operation for over 10 years and are used for load-leveling applications. Sodium-metal chloride (typically nickel chloride) batteries are called ZEBRA batteries [4]. These are also fabricated in several kWh sizes and are being explored for stationary as well as transportation (locomotive) applications.

The conventional process for the fabrication of Na-β"-alumina involves the following steps [5]: Powders of Na<sub>2</sub>CO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> are mixed in an appropriate ratio to form a mixture corresponding to ~8–9 wt.% Na<sub>2</sub>O and balance Al<sub>2</sub>O<sub>3</sub>. Studies have shown that if such a binary mixture is heated to a high temperature (>1250 °C), it leads to the formation of Na<sub>2</sub>O·11Al<sub>2</sub>O<sub>3</sub> and NaAlO<sub>2</sub>. The former structure is called Na-β'-alumina. It is also a sodium ion conductor but with ionic conductivity one fifth that of Na-β"-alumina. It has been long known that a small amount of Li<sub>2</sub>O or MgO must be added to form Na-β"-alumina by conventional sintering in air. The added lithium or magnesium enters the spinel blocks and partially substitutes for aluminum. Al is

\* Corresponding author.

E-mail address: [anil.virkar@utah.edu](mailto:anil.virkar@utah.edu) (A.V. Virkar).

3+ while Li is 1+ and Mg is 2+. Thus, for charge compensation an additional amount of sodium is introduced into the conduction plane. With lithium as the stabilizer the typical composition is 8.85 wt.% Na<sub>2</sub>O, 0.75 wt.% Li<sub>2</sub>O and 90.4 wt.% Al<sub>2</sub>O<sub>3</sub> [5]. Densification in the conventional process involves a transient liquid phase mechanism. There is a eutectic in the Na<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub> system between NaAlO<sub>2</sub> and Na<sub>2</sub>O.11Al<sub>2</sub>O<sub>3</sub> which occurs at ~1580 °C. For densification to occur the sample is heated to a temperature slightly above the eutectic temperature. Densification occurs rapidly (within seconds or minutes). This is also accompanied by the reaction of NaAlO<sub>2</sub> and Na<sub>2</sub>O.11Al<sub>2</sub>O<sub>3</sub> (and also with added Li<sub>2</sub>O or MgO) to form the desired Na-β"-alumina phase. This is accompanied by exaggerated grain growth causing a duplex microstructure which is deleterious to its strength. Also the vapor pressure of Na<sub>2</sub>O is relatively high and considerable loss of Na<sub>2</sub>O can occur through the vapor phase. Thus sintering of Na-β"-alumina is achieved by encapsulating the samples in platinum or MgO containers. Significant cost is associated with the use of either type of container. In order to minimize the grain growth and also allow for full conversion to Na-β"-alumina to occur by the reaction



the furnace temperature is rapidly lowered to about 1450 °C after sintering for a few minutes above 1580 °C. The samples are heat treated at 1450 °C, while still under encapsulation, for 1 to 2 h before slow cooling to room temperature. Using such a process it is possible to obtain nearly ~100% Na-β"-alumina. However, a thin film of NaAlO<sub>2</sub> usually remains trapped along the grain boundaries. As a result Na-β"-alumina made by the conventional process is attacked by atmospheric moisture and carbon dioxide. Reaction of grain boundary NaAlO<sub>2</sub> with moisture involves its dissolution. Reaction with CO<sub>2</sub> involves the formation of Na<sub>2</sub>CO<sub>3</sub>. In either case cracks and delaminations occur along the grain boundaries. Thus, Na-β"-alumina made by the conventional process is stored in desiccators and heated to about ~600 °C before use in electrochemical devices.

A novel vapor phase process was developed in which a two phase composite of α-Al<sub>2</sub>O<sub>3</sub> and an oxygen ion conductor, such as yttria-stabilized zirconia (YSZ), is made by conventional sintering powder compacts such that both phases are contiguous [6]. In the subsequent step the sintered samples are packed in Na-β"-alumina powder and heat treated at a temperature between about 1150 °C and 1450 °C for several hours. Na<sub>2</sub>O from the packing powder is incorporated into α-Al<sub>2</sub>O<sub>3</sub> by the reaction



The incorporation of Na<sub>2</sub>O occurs by coupled diffusion of 2Na<sup>+</sup> through the formed Na-β"-alumina and of O<sup>2-</sup> through the YSZ. Since the diffusion of O<sup>2-</sup> is rapid through YSZ and the diffusion of 2Na<sup>+</sup> is rapid through Na-β"-alumina, rapid conversion of α-Al<sub>2</sub>O<sub>3</sub> into Na-β"-alumina occurs. The resulting material is a two phase mixture of Na-β"-alumina and YSZ, both forming contiguous phases. The overall kinetics of conversion involves one diffusional step (coupled diffusion of 2Na<sup>+</sup> through Na-β"-alumina and of O<sup>2-</sup> through YSZ) and two interface steps. One of the interface steps is at the gas/solid interface where Na<sub>2</sub>O from the gas phase is incorporated at the Na-β"-alumina/YSZ/gas phase three phase boundaries (TPBs) with 2Na<sup>+</sup> entering Na-β"-alumina and O<sup>2-</sup> entering YSZ. The second interface step occurs at the reaction front, the Na-β"-alumina + YSZ/α-Al<sub>2</sub>O<sub>3</sub> + YSZ interface, where reaction (2) occurs. Fig. 1 shows a schematic of the transport processes and reaction occurring during vapor phase conversion [7].

There are many ions which in principle can partially substitute for Al<sup>3+</sup> in the spinel structure. The valence of the substituting ion and its size relative to the size of Al<sup>3+</sup> are expected to be the primary factors which determine if a substitution is possible. The phase diagram between Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> shows that the solubility of Fe<sub>2</sub>O<sub>3</sub> in Al<sub>2</sub>O<sub>3</sub> is ~13.5 mol% at 1400 °C [8]. In the system Na<sub>2</sub>O–Fe<sub>2</sub>O<sub>3</sub>, a Na-β-Fe<sub>2</sub>O<sub>3</sub>

(analogous to Na-β-alumina) is known to be stable above 680 °C, but no β"-phase has been reported [8]. However, as Fe<sub>2</sub>O<sub>3</sub> exhibits some solubility in Al<sub>2</sub>O<sub>3</sub>, it may be possible to form iron-doped Na-β"-alumina. The objective of this work was to determine if iron-doped Na-β"-alumina can be formed by the vapor phase process by exposing a composite of YSZ and Fe-doped Al<sub>2</sub>O<sub>3</sub> to Na<sub>2</sub>O vapor.

## 2. Experimental procedure

A powder mixture containing 95 mol% α-Al<sub>2</sub>O<sub>3</sub> (CR-30 Baikowski) + 5 mol% Fe<sub>2</sub>O<sub>3</sub> and 3 mol% Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> (TZ-3Y, Tosoh) was made with 70 vol.% α-Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub> and 30 vol.% TZ-3Y. According to the Al<sub>2</sub>O<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub> phase diagram, the maximum solubility of Fe<sub>2</sub>O<sub>3</sub> in Al<sub>2</sub>O<sub>3</sub> is ~13.5 mol% at 1400 °C [9]. Thus, 5 mol% Fe<sub>2</sub>O<sub>3</sub>, if completely dissolved in α-Al<sub>2</sub>O<sub>3</sub>, is expected to be well within the solubility range. The powder mixture was ball milled in Fritsch Pulversette planetary mill at 300 rpm for 3 h. Several discs were prepared by die-pressing using a uniaxial press under a pressure of 97 MPa. The discs were then sintered in air at 1450 °C for 3 h in a Lindberg Blue CC5926PCOMC-1 furnace. The typical thickness of the discs was between 2 and 3 mm. Densities of the sintered discs were measured by the fluid immersion method using water. The discs were then placed in an alumina crucible, loosely packed in Na-β"-alumina powder containing ~8.85 wt.% Na<sub>2</sub>O, ~0.75 wt.% Li<sub>2</sub>O and balance Al<sub>2</sub>O<sub>3</sub>, covered with a lid and then heat-treated at 1250 °C in air for 20 h. The expectation was that this treatment would convert Fe-doped Al<sub>2</sub>O<sub>3</sub> + TZ-3Y two phase material into Fe-doped Na-β"-alumina + TZ-3Y two phase material by the vapor phase process involving coupled diffusion of Na<sup>+</sup> through Fe-doped Na-β"-alumina and of O<sup>2-</sup> through TZ-3Y. Baseline samples containing ~70 vol.% Al<sub>2</sub>O<sub>3</sub> and ~30 vol.% TZ-3Y were also fabricated and subjected to the conversion treatment by packing in Na-β"-alumina powder.

After conversion the samples were cross-sectioned, coarsely polished and thermally etched in air at 1250 °C for 15 min. A NOVA NANOSEM 600 scanning electron microscope was used to measure the grain size. An Olympus BH2-UMA Nomarsky interference microscope was used to measure the conversion thickness. X-ray diffraction patterns were obtained using CuKα radiation on a Phillips X'Pert X-ray diffractometer to determine the phases present in the as-sintered and converted samples. Lattice parameters were obtained using GSAS software with Rietveld refinement. The composition of the Al<sub>2</sub>O<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub> solid solution was estimated from a linear fit to the lattice parameters assuming Vegard's law. One sample was heat treated at 1450 °C packed in Na-β"-alumina powder for 17 h. The objective was to fully convert the sample for the measurement of conductivity by EIS.

Platinum paste (Heraeus) electrodes were applied symmetrically on both surfaces of the disc and fired at 800 °C for 0.5 h. The electrode area was 1.27 cm<sup>2</sup> and the sample thickness was 2.35 mm. EIS was performed with a Solartron electrochemical interface (SI 1287) and impedance/gain-phase analyzer (SI 1260) using a 4-probe method. The range of frequencies tested was 100 Hz to 1 MHz, with a 4 mV amplitude. The temperature of the sample was varied from 197 °C to 485 °C using a Barnstead Thermolyne 2100 tube furnace. The temperature of the sample was monitored with a Omega K-type thermocouple read from a Keithley 2000 meter. The high frequency intercept was obtained from the Nyquist plots, which was attributed to the bulk resistance of the sample.

## 3. Results and discussion

X-ray diffraction patterns were refined by the Rietveld refinement method using XPGUI GSAS software. Fig. 2(a), (b), (c) and (d) are respectively XRD patterns of sintered α-Al<sub>2</sub>O<sub>3</sub> + TZ-3Y, converted Na-β"-alumina + TZ-3Y, sintered Fe-doped α-Al<sub>2</sub>O<sub>3</sub> + TZ-3Y and converted Fe-doped Na-β"-alumina + TZ-3Y. Lattice parameters determined by refining XRD patterns are listed in Table 1. As seen in the table, the Fe-doped α-Al<sub>2</sub>O<sub>3</sub> has slightly larger lattice parameters than the undoped

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