Performance analysis of Na- β'' -Al₂O₃/YSZ solid electrolytes produced by conventional sintering and by vapor conversion of α -Al₂O₃/YSZ

Samuel Clark Ligon^{1*}, Gurdial Blugan¹, Marie-Claude Bay², Corsin Battaglia², Meike V. F. Heinz², Thomas Graule¹

¹ Laboratory for High Performance Ceramics, Empa, Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, 8600 Duebendorf, Switzerland

² Materials for Energy Conversion, Empa, Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, 8600 Duebendorf, Switzerland

* Correspondence: clark.ligon@empa.ch

Abstract:

High temperature Na₂O vapor conversion of α -Al₂O₃ with different concentrations of YSZ was used to produce Na- β'' -Al₂O₃ solid electrolyte (BASE) materials. The influence of different ratios of yttria (YSZ-3 and YSZ-8) on conversion and material properties (ionic conductivity and flexural strength) was also investigated. Extent of conversion to Na- β'' -Al₂O₃ was calculated by semi-quantitative XRD phase analysis. Al₂O₃ composites with 20% or less YSZ were incompletely converted to Na- β'' -Al₂O₃ after two hours at 1450 °C. Al₂O₃ composites with 30-40% YSZ-3 appear fully converted by XRD but have lower conductivity and higher strength compared to conventionally sintered Na- β'' -Al₂O₃ composites with the same concentration of YSZ-3. SEM of the materials indicated differences in morphology and grain size. XRD of Al₂O₃ composites with YSZ-8 showed significantly lower conversion than those with YSZ-3. This is attributed to the larger grain size of YSZ-8, which limits the homogeneity of composites with Al₂O₃ and thus does not assist in oxygen diffusion as well as YSZ-3. Although the vapor converted BASE materials tended to have lower conductivities at 300 °C, they have lower activation energies (0.20 eV) compared

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to conventionally sintered Na- β'' -Al₂O₃ composites (0.30 eV) and higher conductivity at ambient temperature. Vapor converted BASE materials also have better mechanical properties, which should allow fabrication of thinner electrodes.

Keywords: beta-alumina; sodium batteries; zirconium toughened alumina; vapor phase conversion

Introduction

Sodium batteries are receiving increasing attention as stationary power sources to improve integration between renewable energy sources (hydroelectric and solar power plants) and the electric grid.[1-3] Sodium- β'' -alumina (Na- β'' -Al₂O₃) has high sodium-ion conductivity at elevated temperature (300 °C) and is commercially employed as a solid-state electrolyte in sodium-nickel-chloride (NaNiCl) and sodium-sulfur (NaS) batteries.[4-6] Na- β'' -Al₂O₃ is conventionally produced by calcining mixtures of Na₂CO₃ and Al₂O₃ powders.[7] The resultant alumina material should ideally have 8–9 wt.% Na₂O.[8] At temperatures above 1250 °C, a thermodynamically more stable but less conductive phase (Na- β -Al₂O₃) forms preferentially instead of Na- β'' -Al₂O₃. [9] To prevent this, small quantities of Li₂O and MgO are added to stabilize the desired Na- β'' -Al₂O₃ phase.[10] The calcined powder inevitably contains a mixture of Na- β -Al₂O₃, Na- β'' -Al₂O₃ and Na-AlO₂. [11] This powder is then further processed by milling and spray drying before pressing into the desired shape for the battery cell. A cloverleaf-shaped open tubular design is typically used for commercial BASE membranes although planar cell designs have received increased interest.[12] The pressed powder tube is then sintered at a temperature of approximately 1600 °C to form the final ceramic piece. To prevent evaporation of Na₂O, sintering must be performed within platinum bags or MgO spinel crucibles.[12, 13] To prevent rapid and inhomogeneous grain growth of Na- β'' -Al₂O₃, sintering is typically performed rather quickly. For these and other reasons, alternative routes to produce BASE materials are explored.[14]

A promising alternative route to BASE membranes was introduced in the 1990s by Virkar, who converted composites of pre-sintered α -Al₂O₃ with yttria stabilized zirconia (YSZ) to Na- β'' -Al₂O₃/YSZ by vapor

phase conversion.[15] The principal role of YSZ is to allow oxygen ion transport since its diffusion rate within Na- β'' -Al₂O₃ alone is very low. Virkar's group saw 100% conversion for 70/30 Al₂O₃/YSZ-3 after two hours at 1450 °C and noted that higher ratios of Al₂O₃ required much longer dwell times.[16] Parthasarathy derived a theoretical model for the vapor phase conversion process based on coupled transport of Na₂O along gas/Na- β'' -Al₂O₃/YSZ three phase boundaries and also clearly delineated the role of grain size on conversion kinetics. Composites with average grain size below 1 μ m underwent vapor conversion more quickly than composites with larger YSZ grains.[11] An additional advantage in using YSZ with Al₂O₃ is an increase in strength and fracture toughness, which could allow for the fabrication of thinner BASE membranes.[13] Indeed other researchers have investigated composites of Na- β'' -Al₂O₃/YSZ formed by traditional sintering to improve mechanical properties.[17] The disadvantage in using YSZ is a loss of ionic conductivity, and thus a compromise between conductivity and mechanical properties is typically made.[18, 19] We have chosen to investigate the mechanical and electrical properties of different compositions of Na- β'' -Al₂O₃/YSZ BASE membranes synthesized by traditional sintering of Na- β'' -Al₂O₃/YSZ powders and by vapor phase conversion from α -Al₂O₃/YSZ (Figure 1). Since YSZ-3 tends to improve mechanical properties better and YSZ-8 has higher oxygen ion conductivity,[20] both YSZ materials have been considered. Semi-quantitative XRD was performed on all BASE materials to determine the extent of conversion to Na- β'' -Al₂O₃. SEM was used to determine any changes in morphology after vapor conversion and to compare with traditionally sintered Na- β'' -Al₂O₃/YSZ composites.

Figure 1. Flow diagrams for producing Na-β'' Al₂O₃/YSZ composite ceramics via (a) the traditional sintering route and (b) via vapor conversion of α-Al₂O₃/YSZ.

Materials and Methods

Sample preparation

Different compositions (100/0, 90/10, 80/20, 70/30, and 60/40 by volume ratio) of Al₂O₃ (either α- or Na-β''-) and yttria-stabilized zirconia (either YSZ-3 or YSZ-8) were weighed and mixed with 2 wt.% Mowital PVB in a 100 mL polypropylene container (see supplementary information for details). To this was added equal volumes of 5 mm diameter zirconia milling balls and ethanol. The mixture was ball milled with a speed of approximately 200 rpm for 24 hours. Afterwards the mixture was filtered to remove the balls, dried in an oven at 80 °C, manually ground with a mortar and pestle, and sieved (180 μm). Discs for mechanical testing were formed by pressing approximately 3 grams of powder with a 32 mm diameter dye using 100 MPa. Rectangular samples for conductivity measurements were pressed using approximately 0.90 grams with a dye (26 mm x 7 mm) and 180 MPa.

Sintering and conversion to Na-β''-Al₂O₃/YSZ

Na- β'' -Al₂O₃/YSZ discs and rectangles were sintered in air at 1600 °C for 5 minutes in a Nabertherm HT 40/17 oven (Lilienthal, Germany). Samples were placed atop 45 mm Na- β'' -Al₂O₃ diameter support discs within spinel crucibles. A rate of 3 °C min⁻¹ was used for both heating and cooling.

Disc and rectangular α -Al₂O₃/YSZ samples were sintered in air at 1600 °C for 2 hours in a Carbolite HTF 1800 furnace. A rate of 3 °C min⁻¹ was used for both heating and cooling. Vapor phase conversion to Na- β'' -Al₂O₃/YSZ was attempted using slightly modified conditions based on those suggested by Virkar.[21] Individual α -Al₂O₃/YSZ ceramic pieces were placed atop 45 mm diameter pressed Na- β'' -Al₂O₃ support discs and buried with an additional 4 grams of Na- β'' -Al₂O₃ loose powder. The powder buried pieces were encapsulated within magnesium spinel crucibles with an internal volume of approximately 95 mL and then placed within a Nabertherm HT 40/17 oven (Lilienthal, Germany). Vapor phase conversion was performed for two hours at 1450 °C using heating and cooling rates of 3 °C min⁻¹. Discs and rectangular samples were manually polished lightly with SiC paper to remove residual Na- β'' -Al₂O₃ powder before further analysis.

Na⁺ conductivity measurement

Temperature-dependent ionic conductivity was measured by electrochemical impedance spectroscopy with a Zahner IM6ex instrument (Kronach, Germany). A 4-point-probe configuration with four isolated Pt wires linearly aligned with fixed separations (5 mm; 6 mm; 5 mm) was used. Prior to measurement, a colloidal graphite suspension (Aquadag) mixed with NaNO₃ and NaNO₂ was applied to the rectangular samples at the points of contact. The samples were heated within a tube furnace (Carbolite HST/200) to 350 °C before slowly cooling to room temperature. Impedance was measured every five minutes from 1 Hz to 1 MHz with an amplitude of 20 mV. Temperature was tracked with a data logger (EL-USB-TC) and a digital thermometer (TM-947SD from Lutron). The impedance of both pure Na- β'' -Al₂O₃ samples and Na- β'' -Al₂O₃/YSZ composites feature rather constant values at phase angles close to 0 ° for frequencies

below 10 kHz, which is ascribed to the total resistance R of the electrolyte (see Bode diagrams in supplementary material). From this, the sample conductivity $\sigma = (1/R) \cdot (L/A)$ was calculated using the cross-sectional area of the sample (A) and the distance between the two inner electrodes (L).

Results & Discussion

Sample preparation and density

α - Al_2O_3 /YSZ and Na- β'' - Al_2O_3 /YSZ composite ceramic discs of different compositions (100/0, 90/10, 80/20, 70/30 with both YSZ-3 and YSZ-8) were prepared by similar pathways. In all cases, the raw powders were milled for 24 hours, then ground and sieved to ensure homogeneity. The powders were pressed into discs and then sintered at 1600 °C. In the case of α - Al_2O_3 /YSZ composites, a dwell time of two hours was used while Na- β'' - Al_2O_3 /YSZ composites were held at this temperature for only 5 minutes. While such high temperatures are needed to properly sinter both α - Al_2O_3 and Na- β'' - Al_2O_3 powders to form ceramics, Na- β'' - Al_2O_3 tends to degrade to Na- β - Al_2O_3 at 1600 °C and thus conductivity will decrease if sintering is performed too long.[11] By comparison, vapor phase conversion was conducted at a lower temperature (1450 °C) where Na- β'' - Al_2O_3 is stable.

α - Al_2O_3 and Na- β'' - Al_2O_3 have different densities (3.95 g cm⁻³ vs. 3.27 g cm⁻³) as do YSZ-3 and YSZ-8 (6.05 g cm⁻³ vs. 5.9 g cm⁻³). Density measurements of all the different ceramic composites provides insight both into relative density in comparison with these theoretical values and provides a first approximation for the extent of vapor conversion. Note, however, that a decrease in density may be related either to a transition from α - Al_2O_3 to β'' - Al_2O_3 or to an increase in porosity. As Figure 2 and Figure 3 indicate, the densities of vapor converted α - Al_2O_3 /YSZ with low YSZ concentration (0 vol.% and 10 vol.%) are only slightly lower than that of the starting α - Al_2O_3 /YSZ ceramic. This indicates that these composites are still mainly α - Al_2O_3 and that conversion is low. The densities of vapor converted Al_2O_3 with 20% or more YSZ are more similar to the values measured for Na- β'' - Al_2O_3 /YSZ ceramics with the same composition. This holds true both for the composites with YSZ-3 and with YSZ-8, although the densities of vapor converted composites with YSZ-3 are comparatively closer to the densities of Na- β'' - Al_2O_3 /YSZ

ceramics of the same composition. For the composite with 40% YSZ-3, the density of the vapor converted ceramic and the traditionally sintered Na- β'' -Al₂O₃/YSZ ceramic are almost the same (4.33 g cm⁻³ vs. 4.31 g cm⁻³). By comparison, the vapor converted composite with 40% YSZ-8 is significantly denser than the Na- β'' -Al₂O₃ with 40% YSZ-8 (4.33 g cm⁻³ vs. 4.26 g cm⁻³).

Figure 2. Comparison of measured density for composites of α -Al₂O₃/YSZ-3 (Alpha exp.), Na- β'' -Al₂O₃/YSZ-3 (Beta exp.) and vapor converted Al₂O₃/YSZ-3 (A/B exp.). Lines for the calculated fully dense α -Al₂O₃/YSZ-3 (Alpha theory) and Na- β'' -Al₂O₃/YSZ-3 (Beta theory) composites are provided for reference.

Figure 3. Comparison of measured density for composites of α -Al₂O₃/YSZ-8 (Alpha exp.), Na- β'' -Al₂O₃/YSZ-8 (Beta exp.) and vapor converted Al₂O₃/YSZ-8 (A/B exp.). Lines for the calculated fully dense α -Al₂O₃/YSZ-8 (Alpha theory) and Na- β'' -Al₂O₃/YSZ-8 (Beta theory) composites are provided for reference.

SEM

SEM was used to examine morphology of all of the synthesized ceramic composites. With a magnification of 10 kx, granularity can be seen on the surface of all the samples. SEM images of Al₂O₃/YSZ composites with 20% YSZ and 40% YSZ (below and above the expected YSZ percolation threshold of 30%) are shown below (those with YSZ-3 in Figure 4 and those with YSZ-8 in Figure 5). Images of composites with 10% and 30% YSZ are provided within the supplemental section. For comparison purposes, all of the composites are presented before and after vapor conversion along with images of Na- β'' -Al₂O₃ composites with the same concentration of YSZ. In most of the images, white zirconia grains (YSZ-3 or YSZ-8) can be distinguished from dark grey alumina grains (α -Al₂O₃ or Na- β'' -Al₂O₃). Generally, all of the α -Al₂O₃ composites have similar fused tile morphology with tight grain boundaries and this is different from the morphology of the vapor converted composites, which is also different from the Na- β'' -Al₂O₃/YSZ composites. It is worth mentioning that α -Al₂O₃ grain size seems to get smaller with increasing YSZ-3 concentration (about 3 μ m with 10% YSZ-3 vs. 1 μ m with 40% YSZ-3) but remains about the same

size ($\approx 3 \mu\text{m}$) for all of the composites with YSZ-8. This may be because YSZ-8 is mainly cubic while YSZ-3 is tetragonal and better disperses within the Al_2O_3 matrix during sintering.[22, 23] The vapor converted composites and traditionally sintered $\text{Na-}\beta''\text{-Al}_2\text{O}_3/\text{YSZ}$ composites all have more porosity than the $\alpha\text{-Al}_2\text{O}_3/\text{YSZ}$ composites. $\text{Na-}\beta''\text{-Al}_2\text{O}_3$ platelets are randomly oriented in the composites, and grain size seems to be larger for the $\text{Na-}\beta''\text{-Al}_2\text{O}_3$ composites with YSZ-8 compared to the composites with YSZ-3. This should help conductivity but also decreases strength. The vapor converted composites with 10% YSZ-3 look pretty similar to those with 10% YSZ-8 (Figure S 3 and Figure S 4). In both cases, the zirconia grains are smaller and well dispersed within a matrix of Al_2O_3 with poorly defined grains. With higher YSZ concentrations, the vapor converted composites with YSZ-3 look progressively less like those with YSZ-8. For the vapor converted composite with 40% YSZ-3 (Figure 4d), grains of both alumina and zirconia are significantly smaller and appear more homogenous compared to those with 40% YSZ-8 (Figure 5d). While XRD suggests full conversion to $\text{Na-}\beta''\text{-Al}_2\text{O}_3$ for the composite with 40% YSZ-3 (Figure 7), the vapor converted material displays a very different morphology compared to the traditionally sintered $\text{Na-}\beta''\text{-Al}_2\text{O}_3$ composite with 40% YSZ-3 (Figure 4d vs. Figure 4f). This is because vapor conversion is performed well below the melting eutectic of $\text{Na-}\beta''\text{-Al}_2\text{O}_3$ at 1580°C , and thus resultant average grain size is smaller.

SEM was also performed on cross sections of vapor converted $\text{Al}_2\text{O}_3/\text{YSZ}$ composites above and below the expected percolation threshold of 30% YSZ (Figure S 5 and Figure S 6). As was expected, the YSZ phase is discontinuous in the composites with 20% YSZ and continuous in those with 40% YSZ, which helps explain better bulk conversion in the latter. All of the images appear homogenous and a visible partition from surface converted $\text{Na-}\beta''\text{-Al}_2\text{O}_3/\text{YSZ}$ to mainly $\alpha\text{-Al}_2\text{O}_3/\text{YSZ}$ in the bulk was not seen.

Figure 4. SEM images of α - Al_2O_3 composites with 20% YSZ-3 (a) and with 40% YSZ-3 (b). The same composites following 2 hours at 1450 °C in Na_2O vapor (c and d). Images of conventionally sintered $\text{Na-}\beta''$ - Al_2O_3 with 20% YSZ-3 (e) and 40% YSZ-3 (f) are provided for comparison. All images taken on non-polished surfaces with a magnification of 10 k $\times$.

Figure 5. SEM images of α - Al_2O_3 composites with 20% YSZ-8 (a) and with 40% YSZ-8 (b). The same composites following 2 hours at 1450 °C in Na_2O vapor (c and d). Images of conventionally sintered $\text{Na-}\beta''$ - Al_2O_3 with 20% YSZ-8 (e) and 40% YSZ-8 (f) are provided for comparison. All images taken on non-polished surfaces with a magnification of 10 kx.

XRD

It is not easy to reliably and quantitatively determine the extent of conversion from α - Al_2O_3 to $\text{Na-}\beta''$ - Al_2O_3 . One method is to perform semi-quantitative phase analysis on X-ray diffraction patterns. Since vapor phase conversion has been shown previously to proceed from the sample surface,[11] XRD was performed both on the surface of samples and on bulk ground powders. In the first case, a 1 cm wide fragment of the ceramic disc (obtained after mechanical testing) was mounted directly within the XRD

sample holder. To analyze the bulk, the sample was ground with an agate mortar and pestle and deposited atop a silicon plate within the sample holder. Figure 6 displays XRD for surface and bulk samples of vapor converted $\text{Al}_2\text{O}_3/\text{YSZ-3}$ composites along with the starting $\alpha\text{-Al}_2\text{O}_3/\text{YSZ-3}$ composite. Significant peaks from the three phases ($\alpha\text{-Al}_2\text{O}_3$, $\text{Na-}\beta''\text{-Al}_2\text{O}_3$ and YSZ-3) are marked. Using these patterns, HighScore software (from Malvern Panalytical) was employed to match peaks with those from literature diffractograms of $\alpha\text{-Al}_2\text{O}_3$, $\text{Na-}\beta''\text{-Al}_2\text{O}_3$, YSZ-3, or YSZ-8 and then calculate composition by integration. Extent of conversion (ξ) was calculated according to the following equation.

$$\xi = \frac{\% \beta'' \text{Al}_2\text{O}_3}{\% \beta'' \text{Al}_2\text{O}_3 + \% \alpha \text{Al}_2\text{O}_3} \quad (1)$$

Two literature diffractograms for lithium stabilized $\text{Na-}\beta''\text{-Al}_2\text{O}_3$ with slightly different stoichiometry ($\text{Na}_{1.67}\text{Li}_{0.33}\text{Al}_{10.67}\text{O}_{17}$ by Jorgensen et al.[24] and $\text{Na}_{1.77}\text{Li}_{0.385}\text{Al}_{10.23}\text{O}_{17}$ by Pearson et al.[25]) were recognized by the software and treated equally in calculations. Although $\text{Na-}\beta\text{-Al}_2\text{O}_3$ was not recognized in the samples by the software most likely due to overlap with $\text{Na-}\beta''\text{-Al}_2\text{O}_3$ peaks, the partially converted composites more than likely contain a mixture of $\text{Na-}\beta\text{-Al}_2\text{O}_3$ and $\text{Na-}\beta''\text{-Al}_2\text{O}_3$. [26] This helps explain the small peaks at 44.2° and 33.6° in the diffractogram of the vapor converted 80/20 $\text{Al}_2\text{O}_3/\text{YSZ-3}$ composite seen in the bulk but not on the surface, which is already fully converted to $\text{Na-}\beta''\text{-Al}_2\text{O}_3$.

Figure 6. XRD of $\text{Al}_2\text{O}_3/\text{YSZ-3}$ composites before and after vapour conversion. a) with 10% YSZ-3; b) with 20% YSZ-3; c) with 30% YSZ-3; d) with 40% YSZ-3. In each image, the top blue curve (A/B bulk) is from the bulk powder after vapour conversion, the middle red curve (A/B surface) is from the surface after vapour conversion, and the bottom black curve ($\alpha\text{-Al}_2\text{O}_3/\text{YSZ-3}$) is the composite before vapour conversion. Significant peaks from $\alpha\text{-Al}_2\text{O}_3$, $\beta''\text{-Al}_2\text{O}_3$ and YSZ-3 are marked.

As Figure 7 presents, extent of conversion is highly dependent on composition and is in all cases higher on the surface than within the bulk. For all the YSZ ratios tested, composites with YSZ-3 had higher surface and bulk conversion compared to composites with YSZ-8. It had been hypothesized that YSZ-8 might allow better conversion than YSZ-3 due to its higher oxygen diffusion value. The benefits of higher oxygen diffusion were never realized, though, since the composites with YSZ-8 were less homogenous with much larger grains compared to the composites with YSZ-3 (Figure 4 and Figure 5).

Figure 7. Conversion of α -Al₂O₃/YSZ to Na- β'' -Al₂O₃/YSZ as determined by semi-quantitative XRD.

To better understand conversion efficiency, we calculated theoretical densities for all the different composites by assuming they consisted of α -Al₂O₃, Na- β'' -Al₂O₃ and YSZ alone. The concentration of the two alumina phases in each composite was defined by the extent of conversion values (ξ). We then calculated a relative density value (ρ_{rel}) as the ratio of the density measured by the Archimedes method (ρ_{exp}) (Figure 2 and Figure 3) to the theoretical density consisting of β'' -Al₂O₃/YSZ and α -Al₂O₃/YSZ.

$$\rho_{rel} = \frac{\rho_{exp}}{\rho_{\beta/YSZ} \cdot \xi + \rho_{\alpha/YSZ}(1 - \xi)} \quad (3)$$

The calculated relative densities are provided as graphs in the supplemental section (Figure S 1 and Figure S 2). Generally, all of the composites with YSZ-3 had relative densities between 96 and 99%. The vapor converted composites with YSZ-8 had comparatively lower relative densities, particularly above 20% YSZ-8 (92 – 94%). These values correlate well with SEM images, where the vapor converted composites with YSZ-8 all seem to have higher porosity than the composites with YSZ-3. This is particularly true for the composites with 20% YSZ (Figure 5c vs. Figure 4c) and those with 30% YSZ (Figure S 4d vs. Figure S 3d). Cubic YSZ-8 crystals have much less surface area/volume compared to tetragonal YSZ-3, which limits the rate of vapor conversion. Moreover, the packing efficiency in composites with cubic YSZ-8 seems to be worse.

Na⁺ conductivity

Total conductivity of vapor phase converted α -Al₂O₃/YSZ-3 ceramics and traditionally sintered Na- β'' -Al₂O₃/YSZ-3 was determined from impedance measurements taken at different temperatures. Figure 8 displays the Arrhenius plots for traditionally sintered Na- β'' -Al₂O₃/YSZ-3 and vapor converted Al₂O₃/YSZ-3 with four different concentrations of YSZ (10%, 20%, 30% and 40%). While the Na- β'' -Al₂O₃/YSZ-3 composite with 10% YSZ-3 has a much higher conductivity at all temperatures, the plots at all other concentrations have intersection points. With 20% YSZ-3, the Na- β'' -Al₂O₃/YSZ-3 composite remains more conductive above 77 °C, but below this temperature the vapor converted material is more conductive. For the composites with 30% YSZ-3, this intersection occurs at 133 °C and for the composites with 40% YSZ-3 the vapor converted material is more conductive already at 151 °C. According to XRD, the vapor converted Al₂O₃/YSZ-3 composite with 40% YSZ-3 has the same composition as the Na- β'' -Al₂O₃/YSZ-3 composite. A comparatively better Na⁺ conductivity in vapor converted Al₂O₃/YSZ-3 at lower temperatures thus indicates additional influences, e.g. grain size effects.[27]

Figure 8. Arrhenius plots for different compositions of vapor phase converted $\text{Al}_2\text{O}_3/\text{YSZ-3}$ (A/B) and $\text{Na-}\beta''\text{-Al}_2\text{O}_3/\text{YSZ-3}$ (Beta). a) Composites with 10% YSZ-3; b) Composites with 20% YSZ-3; c) Composites with 30% YSZ-3; d) Composites with 40% YSZ-3. For all plots, blue dots are used as markers for vapor converted $\text{Al}_2\text{O}_3/\text{YSZ-3}$ (A/B) while orange diamonds are used as markers for conventionally sintered $\text{Na-}\beta''\text{-Al}_2\text{O}_3/\text{YSZ-3}$. The grey curve for conventionally sintered 100% $\text{Na-}\beta''\text{-Al}_2\text{O}_3$ (100% Beta) is provided for reference.

Apparent activation energies (E_a) were determined by linear interpolation of all curves in Figure 8 according to

$$\sigma T = \sigma_0 \exp\left(-\frac{E_a}{k_b T}\right), \quad (3)$$

where σ_0 is a pre-exponential factor and k_b is Boltzmann's constant. Apparent activation energies (E_a) for all of the different tested composites are provided in Table 1. The apparent activation energy is very similar for the conventionally sintered $\text{Na-}\beta''\text{-Al}_2\text{O}_3$ composites regardless of YSZ-3 concentration. The average value of 0.30 eV corresponds well with that measured by Zhu et al. for $\text{Na-}\beta''\text{-Al}_2\text{O}_3$ with 10.8% Na_2O . [7] This value is also somewhere between those given by Virkar et al. when comparing fine grained lithium stabilized $\text{Na-}\beta''\text{-Al}_2\text{O}_3$ (0.221 eV) with polycrystalline samples (0.332 eV). [28] By comparison, the vapor converted BASE composites have lower and more varied activation energies between 0.19 eV and 0.25 eV. The vapor converted composite with 10% YSZ-3 has a conductivity at 300 °C of 0.016 S cm^{-1}

and an apparent activation energy of 0.25 eV in spite of low Na- β'' -Al₂O₃ content (less than 20% according to Figure 7). For the samples with 20-40% YSZ-3, the extent of conversion is higher and the activation energies are more similar. The average value of 0.20 eV for these samples matches well with values from Sparks and Ghadbeigi for vapor converted Al₂O₃ with 30 vol.% YSZ-3 (0.17 – 0.23 eV).[13] In that paper, a correlation between activation energy and grain size was also noted. This helps to clarify why the conventionally prepared Na- β'' -Al₂O₃/YSZ composites in our studies exhibit larger activation energies than the vapor converted composites since the former all have significantly larger average grain size than the latter (Figure 4c and d vs. Figure 4e and f).

Figure 9. Na⁺ conductivity at 300 °C for vapor converted Al₂O₃/YSZ-3 (blue squares) compared to conventionally sintered Na- β'' -Al₂O₃/YSZ-3 (orange dots).

Figure 9 displays the conductivity at 300 °C of all of the composites as it relates to concentration of YSZ-3. This is a typical operating temperature for sodium-nickel chloride batteries, and thus provides a good reference for comparing performance. In the case of traditionally sintered Na- β'' -Al₂O₃/YSZ conductivity decreases with increasing percentage of YSZ. For vapor converted composites, conductivity increases and appears to reach a maximum with 30% YSZ before decreasing slightly. Table 1 provides this data

along with calculated activation energies and pre-exponential factors for all of the composites. The measured conductivity for the traditionally sintered 100% Na- β'' -Al₂O₃ (0.18 S cm⁻¹) sample is less than that measured for commercial Na- β'' -Al₂O₃ membranes (0.25 – 0.3 S cm⁻¹). With increasing concentration of YSZ-3, the conductivity at 300 °C continues to decrease, reaching a value of 0.027 S cm⁻¹ for the 40% composite. By comparison, the vapor converted membranes have lower conductivities for all of the tested compositions. The measured conductivity at 300 °C appears to reach a maximum of 0.023 S cm⁻¹ for the composite with 30% YSZ-3. This value is similar to that given by Sparks for Al₂O₃ with 30% YSZ-3 sintered at 1500 °C and vapor converted at 1450 °C for 10 hours (0.026 S cm⁻¹).^[13] The conductivity at 300 °C of the vapor converted composite with 40% YSZ-3 is lower but also not much less than that of the traditionally sintered Na- β'' -Al₂O₃ with 40% YSZ-3. Additional data and interpretation of low and high temperature impedance spectroscopy is provided in the supplemental section.

Table 1. Comparison of apparent activation energy (E_a) and conductivity for all of the synthesized BASE composites.

BASE composite	E_a (eV)	σ_0 (S cm ⁻¹ K)	Na ⁺ conductivity at 300 °C (S cm ⁻¹)
direct sintered Na- β'' -Al ₂ O ₃	0.29	36200	0.18
with 10% YSZ-3	0.30	35600	0.12
with 20% YSZ-3	0.31	22800	0.072
with 30% YSZ-3	0.30	14700	0.053
with 40% YSZ-3	0.30	8250	0.027
vapor converted Al ₂ O ₃	-	-	-
with 10% YSZ-3	0.25	1430	0.016
with 20% YSZ-3	0.21	861	0.022
with 30% YSZ-3	0.19	656	0.023
with 40% YSZ-3	0.20	545	0.017

Mechanical testing

Zirconia is often used both as a reinforcing aid for sintering and to enhance the mechanical properties of α - and Na- β'' -Al₂O₃. [29] For the composites sintered with Na- β'' -Al₂O₃, an almost linear increase in flexural strength is observed with increasing concentration of YSZ-3. The strength of the vapor phase converted composites are more than 100 MPa higher than the directly sintered Na- β'' -Al₂O₃ ceramics with the same YSZ-3 concentration (Figure 10). The vapor phase converted ceramic with 20% YSZ-3 has a strength of more than 350 MPa, which is more than twice that measured for the Na- β'' -Al₂O₃ ceramic with 20% YSZ-3. However, the relation between strength and YSZ-3 concentration is not linear for the vapor converted materials. This is because with increasing YSZ-3 concentration, the extent of conversion to mechanically weaker Na- β'' -Al₂O₃ is higher. This provides some clarification to the decrease in strength for the composite with 30% YSZ-3. Even though XRD indicates complete conversion, the vapor converted composite with 40% YSZ-3 is more than 100 MPa stronger than the β'' composite with 40% YSZ-3. This is clarified by SEM images, which present a significant difference in average grain size of the two composites (Figure 4). Indeed the lower temperature (1450 °C vs. 1600 °C) used for vapor conversion produces composites with smaller grains, which lowers conductivity slightly but also significantly improves mechanical properties. Flexural strength of BASE composites with YSZ-8 (both conventionally sintered and by vapor phase conversion) was tested as well, and in all cases the values were below 100 MPa. These results can also be clarified by SEM (Figure 5) and support the case for using YSZ-3.

Figure 10. Flexural strength of traditionally sintered Na-β"-Al₂O₃/YSZ-3 composites (orange dots) compared to vapor converted α/β-Al₂O₃/YSZ-3 composites (blue squares). Results are depicted as the average of at least three samples with error bars indicating the standard deviation.

Conclusions

The vapor phase conversion of α-Al₂O₃/YSZ composites at 1450 °C is a viable alternative route for fabricating BASE membranes. The electrical and mechanical properties of the resultant materials are dependent on YSZ concentration and tend not to be the same as traditionally sintered Na-β"-Al₂O₃ composites with the same YSZ concentration. Lower conductivity is principally due to incomplete conversion. Based on semi-quantitative XRD, conversion to Na-β"-Al₂O₃ is higher on the surface of samples than within the bulk and tends to increase with increasing YSZ concentration. Conversion to Na-β"-Al₂O₃ was higher for composites with YSZ-3 versus those with YSZ-8, which was unexpected since the latter has higher bulk oxygen conductivity. Based on SEM, grains of both zirconia and alumina appear smaller and better dispersed in the composites with YSZ-3 compared to those with YSZ-8. This improves interfacial contact between phases and thus improves conversion to Na-β"-Al₂O₃. The vapor converted composites with YSZ-3 tend to have smaller grains than the traditionally sintered Na-β"-Al₂O₃ with YSZ-3, which helps explain better strength for the former and better Na⁺ conductivity for the latter. Nevertheless, the vapor converted composites had lower Na⁺ conductivity apparent activation energies and comparatively

higher conductivities at lower temperatures. In future work, it may be worthwhile to investigate additives such as lithium or titanium dioxide[30] to stabilize the Na- β'' -Al₂O₃ phase in vapor converted composites and to use longer reaction times to increase bulk conversion.

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Supplementary material

Additional experimental information regarding materials and instrumentation is provided. A plot of relative density calculated as the ratio of the experimental and theoretical values at different YSZ concentrations is provided. SEM images from the surfaces of Al₂O₃ composites with 10% YSZ and 30% YSZ along with cross sectional images of composites with 20% YSZ and with 40 YSZ are also provided. In addition, Nyquist and Bode plots at 50 °C and at 300 °C for conventionally sintered and vapor converted composites are available.

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