Enhanced Sintering of β'' -Al₂O₃/YSZ with the Sintering Aids of TiO₂ and MnO₂

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ABSTRACT

β'' -Al₂O₃ has been the dominated choice for the electrolyte materials of sodium batteries because of its high ionic conductivity, excellent stability with the electrode materials, satisfactory mechanical strength, and low material cost. To achieve adequate electrical and mechanical performance, sintering of β'' -Al₂O₃ is typically carried out at temperatures above 1600°C with deliberate efforts on controlling the phase, composition, and microstructure. Here, we reported a simple method to fabricate β'' -Al₂O₃/YSZ electrolyte at relatively lower temperatures. With the starting material of boehmite, single phase of β'' -Al₂O₃ can be achieved at as low as 1200°C. It was found that TiO₂ was extremely effective as a sintering aid for the densification of β'' -Al₂O₃ and similar behavior was observed with MnO₂ for YSZ. With the addition of 2 mol% TiO₂ and 5 mol% MnO₂, the β'' -Al₂O₃/YSZ composite was able to be densified at as low as 1400°C with a fine microstructure and good electrical/mechanical performance. This study demonstrated a new approach of synthesis and sintering of β'' -Al₂O₃/YSZ composite, which represented a simple and low-cost method for fabrication of high-performance β'' -Al₂O₃/YSZ electrolyte.

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Key words: β'' -Al₂O₃ solid electrolyte, boehmite, sintering aid, titanium oxide, manganese oxide.

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1. Introduction

Electrochemical energy storage systems or batteries have gained great attentions recently for both grid and transportation applications [1,2]. Among various types of storage technologies, Na-beta alumina batteries (NBBs), based on a β'' - Al_2O_3 solid electrolyte (BASE) and a molten sodium [1,3,4], have been widely studied. There are mainly two types of NBBs, based on the particular cathode materials. One is sodium-sulfur (Na-S) battery which uses molten sulfur as the cathode [3,4]. The other one is ZEBRA battery, in which solid transition metal halide, such as NiCl_2 or FeCl_2 , is typically used as the cathode materials [3, 5-8].

Since the invention of NBBs in the late 1960s, β'' - Al_2O_3 has been the dominated choice for the battery electrolyte materials, primarily due to the high ionic conductivity (typically 0.2-0.4 S/cm at 300°C), excellent compatibility/chemical stability with the electrode materials, satisfactory mechanical strength and low material cost [3].

β'' - Al_2O_3 powders can be synthesized by conventional solid-state reaction [9-12], sol-gel process [13-18], co-precipitation technique [15,19], spray-freeze/freeze-drying method [20,21], etc. The solid-state reaction processes are typically carried out with the starting materials of α - Al_2O_3 , Na_2CO_3 or NaNO_3 , a small amount of MgO or $\text{Mg}(\text{NO}_3)_2$ and/or Li_2CO_3 or LiNO_3 . The procedures involve multiple ball-milling and calcination steps, followed by final sintering treatment above 1600°C. The disadvantages of the process include sodium loss during the high-temperature sintering, formation of secondary phases such as NaAlO_2 , low yield rate of β'' - Al_2O_3 [3]. In order to maximize the amount of β'' - Al_2O_3 , a number of techniques can be employed, including post-sinter annealing [22], two-peak firing schedule [23], Zeta process [24] and seeding of reaction mixture with

pre-reacted β'' - Al_2O_3 [22]. However, all the processes require high purity α - Al_2O_3 precursors and a long period of time at high temperatures.

As an alternative to the high purity α - Al_2O_3 precursors, cheap abundant material of boehmite (AlOOH) can be used to synthesis β'' - Al_2O_3 [25]. It was found that pure β'' - Al_2O_3 can be obtained at as low as 1200°C without the formation of side products such as α - Al_2O_3 , NaAlO_2 , or β - Al_2O_3 . According to Poulieff et al. [26] and Vanzyl et al. [25], the oxygen stacking sequence of the Al_2O_3 precursor is inherited by the final product. With boehmite as the precursor, a transition γ - Al_2O_3 structure is formed after dehydration at around 540°C , which is characterized with a regular cubic closely-packed oxygen array. At the temperatures of 1000°C or above, the transition phase reacts with Na_2O and Li_2O to form single-phase β'' - Al_2O_3 with a similar oxygen sub-lattice as that of γ - Al_2O_3 [3,25].

In addition to the powder synthesis, sintering of green body to achieve a high density and adequate electrical/mechanical properties is also challenging [3]. The sintering temperature typically needs to be above 1600°C to achieve a full density. However, the major issue during such high-temperature sintering is the formation of duplex microstructure with large grains ($50\text{-}500\mu\text{m}$) randomly distributed in a fine-grained matrix (grain size $\leq 10\mu\text{m}$) [9,23,27], which significantly reduces the mechanical strength of β'' - Al_2O_3 . Grain growth is extremely sensitive to the maximum temperature and the hold time [3,4]. There are several techniques can be employed to suppress the exaggerated grain growth during sintering such as a short hold time at the high temperatures, a two-peak firing schedule, hot pressing at lower temperatures, zone sintering with a reduced time in the high-temperature zone , etc [4].

Another approach to fabricate β'' - Al_2O_3 is vapor phase process [3,28]. In this process,

α -Al₂O₃ or α -Al₂O₃/YSZ (yttria-stabilized zirconia) sample is fired at 1600°C in air to achieve a full density (>99%). The sintered sample is then buried in packing powders (β "-Al₂O₃, prepared separately) and heat-treated at high temperatures (e.g., 1450°C) in air for a period of time. The conversion of α -Al₂O₃ to β "-Al₂O₃ occurs by coupled transport of sodium and oxygen ions from the packing powders into the α -Al₂O₃ or α -Al₂O₃/YSZ sample. Advantages of this method include: (i) full conversion of α -Al₂O₃ to β "-Al₂O₃, (ii) (iii) grain size in the same level as that prior to conversion, and (iv) the converted sample resistant to moisture attack. The major disadvantage of the process is that a large quantity of packing powders is needed to assist the conversion.

In this paper, we explored the possibility of sintering and densifying β "-Al₂O₃ and /YSZ at lower temperatures with the help of sintering aids. The boehmite was selected as the starting precursor, considering that pure β "-Al₂O₃ can easily be achieved by using boehmite. Small amounts of TiO₂ and MnO₂ were added into boehmite or boehmite plus YSZ. The effort of the additives on the phase, composition, sintering behavior, microstructure, mechanical and electrochemical properties has been investigated.

2. Experimental

2.1. Sample preparation

β "-Al₂O₃ or β "-Al₂O₃/YSZ was prepared via a solid-state reaction. Boehmite (AlOOH), NaNO₃ (Sigma-Aldrich, 99.9%), LiNO₃ (Sigma-Aldrich, 99.99%), Ti{OCH(CH₃)₂}₄ (Alfa Aesar, 97%), YSZ (5YSZ, UCM Advanced Ceramics), and Mn(NO₃)₂·xH₂O (Alfa Aesar, 99.98%) were used as starting materials. The precursor powders of boehmite, NaNO₃ and LiNO₃ were weighted according to the formula Na_{1.67}Al_{10.67}Li_{0.33}O₁₇ and 2 mol% Ti{OCH(CH₃)₂}₄ with respect to boehmite was added

into the powders. The precursors were then thoroughly mixed in isopropyl alcohol using zirconia media for 12 h, dried and fired at 900°C for 10 h in air. The powders were attrition-milled, isostatic-pressed and finally fired at 1400 or 1500°C in air for 5 h to achieve dense discs of β'' -Al₂O₃. To synthesis β'' -Al₂O₃/YSZ, YSZ powders were added into the raw powder mixture with a final volume ratio between Al₂O₃ and YSZ of 7:3. And 5 mol% Mn(NO₃)·xH₂O with respect to YSZ also may be added into the powder mixture. After thoroughly mixed, the powders were treated in a similar procedure with a few of ball-milling and calcination steps to achieve dense β'' -Al₂O₃/YSZ samples.

2.2. Sample characterization

The phase structures of the sintered β'' -Al₂O₃ or β'' -Al₂O₃/YSZ samples were determined by powder XRD. The pellets were crushed and ground in an agate mortar to obtain fine-grained powders for XRD analysis. The measurement was carried out at room temperature in the 2 θ range of 10-70° with Cu K α radiation. The backscattered electron images were observed using scanning electron microscopy (SEM, Model JSM-5900LV, JEOL Company, Japan) equipped with an energy-dispersive X-ray spectroscope (EDS).

The sintering curves of green samples (diameter: 6.3 mm, length: 10 mm) were recorded using a push-rod dilatometer (UnithermTM, Model 1161, Anter Corporation, USA). Sintering of the pellets was performed in air at temperatures up to 1550°C for 5 h with a heating rate of 3°C/min. The dilatometer was calibrated with an Al₂O₃ standard bar of the same length.

The sintered samples (discs with a diameter approximately 26 mm and a thickness of 1.0 mm) were mechanically tested by the ball-on-ring test using a universal testing machine (Model 4204, Instron Corporation, USA).

2.3 Cell construction and testing

The schematic of a single cell was shown in our previous report [29,30]. An electrolyte disc with the diameter of 26 mm was glass-sealed to an α -Al₂O₃ ring. To measure the ionic conductivity of the electrolyte, a symmetric electrochemical cell was employed and both of electrodes of the cell were Na-Cs alloy (molar ratio of 1:4). The Na-Cs alloy shows excellent wetting performance on the surface of β "-Al₂O₃, which, therefore, can ensure an intimate contact between the electrode/electrolyte interface [31]. The impedance spectra of the symmetric cell were collected with an electrochemical interface (Solartron 1287, Solartron Analytical) and a frequency response analyzer (Solartron 1260, Solartron Analytical) under open-circuit voltage (OCV). The frequency range was from 2 MHz to 0.01 Hz and the ac amplitude was 10 mV. During regular cell testing, the cell cathode was granules consisting of Ni, NaCl and small amounts of additives. After a final drying treatment to get rid of all traces of moisture under vacuum at 270°C, molten NaAlCl₄ secondary electrolyte was infiltrated into the granules. The weight of cathode granules used in a cell was 1g. A foil and a spring made of Mo were placed on the top of the cathode as current collector. At the anode side, a spring-loaded metal shim was inserted into the anode compartment to serve as a sodium reservoir. Anode and cathode end plates were then compressed to the α -Al₂O₃ ring with gold o-rings. Nickel leads were welded to the electrode end plates as current collectors. The active cell area was $\sim 3\text{ cm}^2$.

The assembled cell was heated in air to 190°C at which it was initially charged up to 2.8 V with a constant current of 10 mA. The cells were then discharged back to 80% of the initial maiden charge capacity using the same current. After the initial cycle, the cell was

cycled between the cut-off voltages of 1.8 to 2.8 V. The charge was under the constant current of 20 mA, which corresponded to a $\sim C/6$ rate for the cycled capacity of 130 mAh. The discharge was under a constant power of 225 mW (an average current of 110 mA and a rate of $\sim 1C$).

3. Results and discussion

3.1 Phase composition

Fig. 1 shows the XRD patterns of the mixture of boehmite, NaNO_3 , and LiNO_3 after firing at various temperatures. It can be seen that a poor crystalline phase was formed at 900°C . The increasing crystallinity of a single phase $\beta''\text{-Al}_2\text{O}_3$ was observed with the firing temperatures from 1100, 1200 to 1600°C . And there were no side products such as $\alpha\text{-Al}_2\text{O}_3$, NaAlO_2 , or $\beta\text{-Al}_2\text{O}_3$ formed during the heat-treatments. These results are generally in agreement with our previous results [3] and other literature [25] that pure $\beta''\text{-Al}_2\text{O}_3$ can be synthesized directly from boehmite precursor at temperatures as low as 1200°C .

In order to study the effort of sintering aid on the stability of $\beta''\text{-Al}_2\text{O}_3$ phase, 2 mol% TiO_2 and 5 mol% MnO_2 were added into the mixture of boehmite, NaNO_3 , and LiNO_3 . The mixture was fired at the temperatures from 1200 to 1600°C . The XRD results were shown in Fig. 2a and b. It can be seen that there was no secondary phase formed at temperatures of 1400°C or below with the addition of either TiO_2 or MnO_2 . Furthermore, no impurity was detected for the mixture containing MnO_2 even at 1600°C (see Fig. 2b), indicating that there was no observable reaction between $\beta''\text{-Al}_2\text{O}_3$ and MnO_2 . For the addition of TiO_2 , however, a secondary phase of $\beta\text{-Al}_2\text{O}_3$ was detected at 1600°C . It could be related to the side reactions between TiO_2 with Al_2O_3 or Na_2O during the heat-treatment, which changed the stoichiometry between the components and led to the formation of secondary phase.

For example, the reactions between Na_2O and TiO_2 may form various compounds, which will be discussed later. These reactions may consume Na_2O in the $\beta''\text{-Al}_2\text{O}_3$, and the decrease of sodium content leads to phase transit from $\beta''\text{-Al}_2\text{O}_3$ phase to the lower sodium-concentration secondary phase of $\beta\text{-Al}_2\text{O}_3$.

It has been well-known that the strength and fracture toughness of $\beta''\text{-Al}_2\text{O}_3$ can be enhanced by the incorporation of ZrO_2 or YSZ [3]. In current study, YSZ powders were added into the starting materials of boehmite, NaNO_3 , and LiNO_3 , which would form a $\beta''\text{-Al}_2\text{O}_3$ /YSZ composite during high-temperature treatment. According to our previously study [29], there was no chemical reactions between YSZ and these constituents during the treatment. The XRD results with the addition of TiO_2 and/or MnO_2 to the boehmite/YSZ mixture were shown in Fig. 3a and b. It can be seen that addition of TiO_2 to the boehmite/YSZ composite was quite similar as that to boehmite (see Fig. 2a). Pure $\beta''\text{-Al}_2\text{O}_3$ phase can be achieved at 1400°C and secondary phase of $\beta\text{-Al}_2\text{O}_3$ were gradually formed at higher temperatures (e.g., 1500 and 1600°C). Fig. 3b shows the results with the addition of both TiO_2 and MnO_2 to the mixture of boehmite/YSZ. It was generally in agreement with the results of adding TiO_2 and MnO_2 separately to the mixture of boehmite in Fig. 2. In a summary, adding MnO_2 to boehmite or boehmite/YSZ did not change the phase composition or cause phase transition up to the sintering temperature of 1600°C ; however, the addition of TiO_2 led to the formation of secondary phase of $\beta\text{-Al}_2\text{O}_3$ in additional to the main phase of $\beta''\text{-Al}_2\text{O}_3$ at temperatures of 1500°C or above.

3.2 Sintering behavior and microstructure

Fig. 4 shows the sintering curves of boehmite and boehmite/YSZ pellets with and without the addition of sintering aids. A typical sintering profile, including two or more

segments with one segment of expansion and another one of shrinkage, was observed in the curves. As seen in Fig. 4, at temperatures below 900°C, all of the samples showed a positive thermal expansion with the increase of temperature. The shrinkage of the samples was initiated at 900°C and accelerated at around 1200°C. The total shrinkage for various samples was listed in Table 1. According to Fig. 4 and Table 1, it can be seen that, after heated to 1550°C, the total shrinkage for boehmite without the addition of sintering aid was only around 2%. With the addition of 5 mol% MnO₂ into boehmite, the shrinkage rate was slightly improved to 2.4%. While, when 2 mol% TiO₂ was added, the shrinkage rate was as high as 7.5%, which was more than three time of that without the addition of sintering aid. As seen in Fig. 4, obvious differences were observed in the sintering curves after 1200 °C for these three samples. Since boehmite or the transition γ -Al₂O₃ phase was transformed to β'' -Al₂O₃ phase at 1200°C or above (see Fig. 1), it can be concluded that TiO₂ was a much better sintering aid for β'' -Al₂O₃ compared to MnO₂, which was significantly helpful for the densification of β'' -Al₂O₃ above 1200°C.

The densification of β'' -Al₂O₃ could be related to the reactions between Na₂O and TiO₂, which may form compounds such as Na₈Ti₅O₁₄, Na₂Ti₃O₇, and Na₂Ti₆O₁₃ [32,33]. According to the binary phase diagram between Na₂O and TiO₂, the melting point of these phases is generally between 1000 and 1300°C. During sintering of β'' -Al₂O₃ above 1000°C, these phases start to become a liquid state and the existence of liquid phases may assist the sinter of β'' -Al₂O₃ of densification. Since only a small amount of TiO₂ was added into the mixture of boehmite, NaNO₃, and LiNO₃, the reaction products between Na₂O and TiO₂ were not observed from the XRD patterns in Fig. 2a and 3. However, as an evidence, the formation of β -Al₂O₃ from β'' -Al₂O₃ was observed in Fig. 2a and 3 after heat-treatments at

1500 and 1600°C. TiO_2 might consume the Na_2O from $\beta''\text{-Al}_2\text{O}_3$ to form the above-mentioned compounds. And the decrease of sodium content in $\beta''\text{-Al}_2\text{O}_3$ led to phase transit from $\beta''\text{-Al}_2\text{O}_3$ phase to the lower sodium-concentration phase of $\beta\text{-Al}_2\text{O}_3$. As a comparison, no liquid phases were formed between Na_2O and MnO_2 in this temperature range. And no secondary phases such as $\beta\text{-Al}_2\text{O}_3$ or $\alpha\text{-Al}_2\text{O}_3$ were detected even after sintering boehmite containing 5mol% MnO_2 to 1600°C (see Fig. 2b). It indicated that MnO_2 was chemically stable with Na_2O and the addition of MnO_2 did not change the stoichiometry between Al and Na in the $\beta''\text{-Al}_2\text{O}_3$ phase. Therefore, it can be concluded that the addition of MnO_2 was not as effective as that of TiO_2 for densification of $\beta''\text{-Al}_2\text{O}_3$.

The shrinkage of the boehmite/YSZ sample with the help of 2 mol% TiO_2 was around 10.1%, which was higher compared to boehmite itself with 2 mol% TiO_2 . It might be related to the relatively lower densification temperature of the YSZ phase in the composite, considering that YSZ typically has a relatively lower sintering temperature [34]. Adding 5 mol% MnO_2 into the boehmite/YSZ composite containing 2 mol% TiO_2 further densified the sample, leading to an overall shrinkage rate of 12.4% at 1550°C, as shown in Fig. 4 and Table 1. According to the discussion above, MnO_2 was not helpful for the sintering of $\beta''\text{-Al}_2\text{O}_3$ so the obvious improvement in the densification of the $\beta''\text{-Al}_2\text{O}_3$ /YSZ composite containing 2 mol% TiO_2 may be related to the densification of YSZ phase by MnO_2 , which caused further shrinkage of the sample. MnO_2 been widely reported as a sintering aid to assist the densification of YSZ [34-36] and it may have a similar effect towards the sintering of YSZ in current study.

Fig. 4 also showed the sintering behavior of $\beta''\text{-Al}_2\text{O}_3$ /YSZ composite containing 2 mol% TiO_2 and 5 mol% MnO_2 at 1400 and 1500°C with a hold time of 10 h. The shrinkage

rate of the sample was 9.0 and 11.7% at 1400 and 1500°C, respectively. With a period of 10 h at these temperatures, the final shrinkage rate reaches 12.5 and 12.8%, respectively. Compared to the results at 1550°C, it can be seen that a lower firing temperature with a certain time can achieve similar sintering performance as that at a higher temperature without a hold time. From the curves in Fig. 4, it also can be seen the first 5 h is more critical during the 10-h hold time at 1400 and 1500°C as more of the shrinkage happened during this period of time.

The microstructures of the boehmite and boehmite/YSZ samples sintered at different temperatures are compared in Fig. 5 and 6. The corresponding density was calculated and listed in Table 2. As seen in Fig. 5a, pores with the size of 40-50 μm were observed for the sample with the starting mixture of boehmite, NaNO_3 , and LiNO_3 after sintered at 1400°C for 5 h. According to Fig. 1, single phase of $\beta''\text{-Al}_2\text{O}_3$ was achieved; however, the relative density of sample was as low as 37.9% (see Table 2). With the addition of 2 mol% TiO_2 to the mixture, the pore size decreased and the density enhanced accordingly with a value of 60%, which clearly showed that TiO_2 was effective as a sintering aid of $\beta''\text{-Al}_2\text{O}_3$. The boehmite/YSZ composite sample showed a relative density of 83% with the help of 2 mol% TiO_2 . Further adding 5 mol% MnO_2 to the composite led to a full dense of $\beta''\text{-Al}_2\text{O}_3/\text{YSZ}$ with a relative density of 98.3%, as seen in Fig. 5a. Furthermore, fine $\beta''\text{-Al}_2\text{O}_3$ grain with the size less than 10 μm was observed, which was owed to the lower sintering temperature.

The microstructure and relative density of the samples sintered at 1500°C were shown in Fig. 6 and Table 2. Compared to those at 1400°C, similar trends in the microstructure and density were observed with the addition of sintering aids. The notable difference was that coarsening of both the YSZ and $\beta''\text{-Al}_2\text{O}_3$ particles was observed at

1500°C due to relatively high sintering temperature. All of these results were generally in agreement with the sintering behavior of the samples in Fig. 4 and clearly proved the effectiveness of the sintering aids of TiO₂ and MnO₂ in helping densification of β"-Al₂O₃ and β"-Al₂O₃/YSZ.

The fracture strength of the full dense β"-Al₂O₃/YSZ sintered at 1400 and 1500°C was 464 and 507 MN M⁻², respectively. The strength of pure β"-Al₂O₃ and β"-Al₂O₃/ZrO₂ composites are listed in Table 3 for comparison. It can be seen that the strength of pure β"-Al₂O₃ was around 120-260 MN M⁻² [37-39]. Addition of 15 vol% doped ZrO₂ to β"-Al₂O₃ increased the strength up to 356 MN M⁻² [11,40,41]. The strength of β"-Al₂O₃/YSZ (volume ratio of 70 to 30) fabricated through a vapor phase process was as high as 514 MN M⁻² [42]. From these results, it can be seen that the β"-Al₂O₃/YSZ (volume ratio of 70 to 30) fabricated at lower temperatures in current study showed excellent mechanical strength, which is comparable with that via the vapor phase process.

3.2 Electrochemical performance

The ionic conductivity of the β"-Al₂O₃/YSZ electrolyte was measured through a symmetric cell with Na-Cs alloy (molar ratio of 1:4) as the electrodes. According to our previous study, the addition of cesium to sodium can remarkably improve the sodium wettability on the surface of β"-Al₂O₃, which, therefore, thoroughly modifies the electrode/electrolyte interface and ensures intimate contacts between the components [31]. The resistivity of the β"-Al₂O₃/YSZ electrolyte sintered at 1400 and 1500°C was 20.17 and 25.01 Ω cm at 300°C. These results are compared with those of pure β"-Al₂O₃ and other β"-Al₂O₃/YSZ composites in Table 4. It can be seen that the resistivity of the β"-Al₂O₃/YSZ composite electrolyte in current study was slightly lower than that of

β'' -Al₂O₃/YSZ via the vapor phase process. However, both of them were 4 to 5 times higher compared to those of pure β'' -Al₂O₃, according to Table 4. The interior electrical performance of the composite electrolytes was believed to be related the addition of YSZ. It is well-known that YSZ or doped ZrO₂ is a sodium-ion insulating phase so the addition of them to β'' -Al₂O₃ would deteriorate its electrical performance. As seen in Table 4, addition of 15 vol% doped ZrO₂ to β'' -Al₂O₃ led to a resistivity of 7.7-9 Ω cm at 300°C, which was almost twice as those of pure β'' -Al₂O₃. Adding 30 vol% YSZ to β'' -Al₂O₃ further increased its resistivity, as shown in Table 4. Incorporation of YSZ or doped ZrO₂ into β'' -Al₂O₃ significantly increased its mechanical strength (see Table 3) while, at the same time, deteriorated the electrical performance. Optimization of the β'' -Al₂O₃/YSZ composite in current study to further improve the electrical performance while maintaining favorable mechanical properties will be carried out in future.

The performance of the β'' -Al₂O₃/YSZ electrolyte sintered at 1400°C was further verified in a Na-NiCl₂ cell at 190°C. The cell was charged under a constant current of 20 mA (a rate of C/6) until a cut-off voltage of 2.8 V. During discharge, a constant power of 225 mW was employed, which was equivalent to an average current of 110 mA and a rate of $\sim$ 1C, and the discharge was stopped at 1.8 V. Fig. 7 showed the cycling performance of the cell. It can be seen that the cell capacity was slightly increased in the initial 50 cycles and it was stabilized afterwards. A fade rate in cell capacity less than 3% was observed over around 250 cycles, which clearly demonstrated the excellent stability of this β'' -Al₂O₃/YSZ composite materials as the electrolyte for sodium batteries.

Conclusion

The effects of sintering aids such as TiO₂ and MnO₂ on the sintering behavior of

β'' -Al₂O₃ and β'' -Al₂O₃/YSZ composite electrolyte were studied. It was found that TiO₂ was extremely helpful for the sintering of β'' -Al₂O₃, which was probably because of the formation of liquid phases between TiO₂ and Na₂O during sintering. Even though MnO₂ is a good sintering aid for YSZ, it appeared to be ineffective for β'' -Al₂O₃ in current study. The addition of 2 mol% TiO₂ and 5 mol% MnO₂ was found to significantly densify the β'' -Al₂O₃/YSZ composite at as low as 1400°C, which was believed to be related to densification of the β'' -Al₂O₃ and YSZ phases by the addition of TiO₂ and MnO₂, respectively. This study demonstrated an alternative approach to fabricate high-performance β'' -Al₂O₃/YSZ electrolyte. Compared to the traditional high-temperature method, it represented a simple, inexpensive and high-yield process.

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Figure Captions:

Fig. 1 XRD patterns of the mixture of boehmite, NaNO_3 , and LiNO_3 fired in air at various temperatures.

Fig. 2 XRD patterns of the mixture of boehmite, NaNO_3 , and LiNO_3 containing (a) 2 mol% TiO_2 and (b) 5 mol% MnO_2 fired in air at various temperatures.

Fig. 3 XRD patterns of the mixture of boehmite, YSZ, NaNO_3 , and LiNO_3 containing (a) 2 mol% TiO_2 , and (b) 2 mol% TiO_2 and 5 mol% MnO_2 fired in air at various temperatures.

Fig. 4 Sintering curves of boehmite and boehmite/YSZ pellets with and without the addition of sintering aids of TiO_2 and MnO_2 .

Fig. 5 Microstructures of samples of (a) boehmite, (b) boehmite + 2 mol% TiO_2 , (c) boehmite/YSZ + 2 mol% TiO_2 , and (d) boehmite/YSZ + 2 mol% TiO_2 + 5 mol% MnO_2 sintered in air at 1400 °C for 5 h.

Fig. 6 Microstructures of samples of (a) boehmite, (b) boehmite + 2 mol% TiO_2 , (c) boehmite/YSZ + 2 mol% TiO_2 , and (d) boehmite/YSZ + 2 mol% TiO_2 + 5 mol% MnO_2 sintered in air at 1500 °C for 5 h.

Fig. 7 Performance of a Na- NiCl_2 Cell using the β "- Al_2O_3 /YSZ composite as the electrolyte at 190°C: (a) cell voltage profiles during the 1st, 50th, 100th, 150th, 200th, and 247th cycles; (b) charge/discharge capacities during cycling.

Fig. 1 XRD patterns of the mixture of boehmite, NaNO_3 , and LiNO_3 fired in air at various temperatures.

(a)

(b)

Fig. 2 XRD patterns of the mixture of boehmite, NaNO_3 , and LiNO_3 containing (a) 2 mol% TiO_2 and (b) 5 mol% MnO_2 fired in air at various temperatures.

(a)

(b)

Fig. 3 XRD patterns of the mixture of boehmite, YSZ, NaNO₃, and LiNO₃ containing (a) 2 mol% TiO₂, and (b) 2 mol% TiO₂ and 5 mol% MnO₂ fired in air at various temperatures.

Fig. 4 Sintering curves of boehmite and boehmite/YSZ pellets with and without the addition of sintering aids of TiO_2 and MnO_2 .

Fig. 5 Microstructures of samples of (a) boehmite, (b) boehmite + 2 mol% TiO_2 , (c) boehmite/YSZ + 2 mol% TiO_2 , and (d) boehmite/YSZ + 2 mol% TiO_2 + 5 mol% MnO_2 sintered in air at 1400 °C for 5 h.

Fig. 6 Microstructures of samples of (a) boehmite, (b) boehmite + 2 mol% TiO₂, (c) boehmite/YSZ + 2 mol% TiO₂, and (d) boehmite/YSZ + 2 mol% TiO₂ + 5 mol% MnO₂ sintered in air at 1500 °C for 5 h.

(a)

(b)

Fig. 7 Performance of a Na-NiCl₂ Cell using the β'' -Al₂O₃/YSZ composite as the electrolyte at 190°C: (a) cell voltage profiles during the 1st, 50th, 100th, 150th, 200th, and 247th cycles; (b) charge/discharge capacities during cycling.

Table 1 Shrinkage of various samples calculated from Fig. 4.

Sample	Shrinkage (%)
boehmite	2.0%
boehmite + MnO ₂	2.4%
boehmite + TiO ₂	7.5%
boehmite/YSZ + TiO ₂	10.1%
boehmite/YSZ + TiO ₂ + MnO ₂	12.4%
boehmite/YSZ + TiO ₂ + MnO ₂ held at 1400°C for 10 h	12.5%
boehmite/YSZ + TiO ₂ + MnO ₂ held at 1500°C for 10 h	12.8%

Table 2 Relative density of various samples sintered in air at 1400 and 1500°C for 5 h.

Sample	Relative density (%)	
	1400 °C	1500 °C
boehmite	37.9%	39.2%
boehmite + TiO ₂	60.0%	60.1%
boehmite/YSZ + TiO ₂	83.0%	85.5%
boehmite/YSZ + TiO ₂ + MnO ₂	98.3%	98.5%

Table 3 Fracture strength of β'' -Al₂O₃/YSZ in current study compared with pure β'' -Al₂O₃ and other β'' -Al₂O₃/ZrO₂ composites.

Composition	Fracture strength (MN m ⁻²)	References
β'' -Al ₂ O ₃	120-260	[37-39]
β'' -Al ₂ O ₃ + 15 vol% doped ZrO ₂	226-356	[11,40,41]
β'' -Al ₂ O ₃ + 30 vol% YSZ (fabricated via vapor phase process)	514	[42]
β'' -Al ₂ O ₃ + 30 vol% YSZ (this study)	464-507	

Table 4 Resistivity of β'' -Al₂O₃/YSZ in current study compared with pure β'' -Al₂O₃ and other β'' -Al₂O₃/ZrO₂ composites.

Composition	Resistivity (Ω cm)						References
	300°C	250°C	200°C	150°C	100°C	50 °C	
β'' -Al ₂ O ₃ + 30 vol% YSZ (this study)	20.2 ^a 25.0 ^b	24.2 ^a 34.8 ^b	50.4 ^a 59.9 ^b	98.8 ^a 110.6 ^b	325.9 ^a 371.5 ^b	806.6 ^a 887.3 ^b	
β'' -Al ₂ O ₃ + 30 vol% YSZ (fabricated via vapor phase process)	26.0	41.2	62.0	120.4	247.8	-----	[42]
	9.0	-----	-----	-----	-----	-----	[11]
β'' -Al ₂ O ₃ + 15 vol% doped ZrO ₂	7.7	11.2	-----	-----	-----	-----	[40]
	8.5	11.4	-----	-----	-----	-----	[41]
	4.2	-----	10.0	-----	60.0	-----	[43]
β'' -Al ₂ O ₃	3.8	5.0	-----	-----	-----	-----	[40]
	4.8	-----	-----	-----	-----	-----	[9]

^a β'' -Al₂O₃ + 30 vol% YSZ sintered at 1400°C
^b β'' -Al₂O₃ + 30 vol% YSZ sintered at 1500°C

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