A Duplex β'' -Al₂O₃ Solid Electrolyte Consisting of A Thin Dense Layer and A Porous Substrate

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Abstract

To improve the performance of Na-beta batteries at intermediate temperatures ($\leq 200^\circ\text{C}$) where much improved cyclability and reduced degradation can be achieved, there is a need to lower the resistance/polarization originated from β'' -Al₂O₃ solid electrolyte (BASE) while maintaining its good strength. In this paper, the concept of a duplex BASE consisting of a thin dense electrolyte and a porous support was proposed as a solution to achieve low area-specific resistance (ASR) with good mechanical strength supported by the porous substrate. The effects of various factors including porosity, composition, and homogeneity of ingredients on the flexural strength of duplex BASEs were examined. In summary, lower porosity, higher YSZ content in the structure, and attrition milling of raw powders resulted in improved strength. The ASR measurement exhibited that the resistance of duplex BASEs was mainly originated from a dense layer. Overall, the maximum strength of 260 MPa and the ASR value of $0.31\ \Omega\cdot\text{cm}^2$ (at 350°C) was achieved from a duplex BASE consisting of a 50 μm thick dense layer (Al₂O₃: YSZ

= 7:3 in volume) and a 500 μm thick porous support (Al_2O_3 : YSZ = 4:6 in volume with 19% open porosity). The effects of various factors on the properties of duplex BASEs will be discussed in detail.

Keywords: Na beta batteries; duplex BASEs; flexural strength; area-specific resistance (ASR)

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1. Introduction

Na-beta batteries (NBBs) consisting of a sodium anode and a Na^+ -conducting β or β'' alumina solid electrolyte membrane have received a growing interest in large-scale batteries which enable the integration of renewable energy into the grid [1]. NBBs such as Na-S and Na-metal halide (ZEBRA) batteries are typically operated at relatively high temperatures (300-350°C) to minimize electrical resistance and achieve satisfactory electrochemical activity [2,3].

Even though significant progress has been achieved in the NBB technologies during the past few decades, the batteries are still facing challenges in cost and battery performance for broad market penetration. Recently, it was reported by us that the operation of NBBs at intermediate temperatures ($\leq 200^\circ\text{C}$) resulted in much improved cyclability and reduced degradation [4-7]. The reduced operating temperature may also allow for low cost materials of construction and high throughput manufacturing methods such as polymer seals. However, it has been recognized that the power densities at intermediate temperatures (150 to 250°C) will most likely be limited by the resistivity of the solid electrolyte [8]. To improve the performance of NBB's further especially at intermediate temperatures, there is a need to decrease resistance/polarization coming from BASEs while maintaining good strength. This requires that the material becomes more conductive for an electrolyte of the same thickness, or that the thickness of BASEs gets reduced in order to decrease area-specific resistance (ASR). Increasing the conductivity of BASEs is extremely difficult for mass production, requiring that the BASE is nearly a single crystal or at least reduces the anisotropy between grains [9]. On the other hand, decreasing the thickness of the BASE layer is relatively easy if the thin electrolyte can endure a load applied in a cell. Therefore, there is a limitation to reduce the thickness of BASEs under a certain critical thickness where the material no longer has the strength enough to function. This

issue related to the mechanical strength of thin BASE can be overcome by creating a duplex structure, in which a thin dense BASE layer is integrated with a thick porous support layer that adds strength to the dense BASE layer, yet does not increase the resistivity.

In this paper, we will demonstrate the concept of a planar duplex BASE which consists of a thin dense BASE and a porous ceramic substrate. Effects of various factors including conversion, pore former content (or porosity), composition, and homogeneity of ingredients on the flexural strength of duplex BASEs will be discussed. The influence of a porous support on the area-specific resistance will be also described.

2. Experimental

2.1 Duplex BASE fabrication

In this study, duplex BASEs were fabricated using the vapor phase approach [10-12], following the procedure shown in Figure 1. First, powders of α -alumina (α -Al₂O₃, Almatix Premium Alumina, 99.8wt%) and 5 mol% yttria stabilized zirconia (5YSZ, Imerys Fused Minerals, 5.4 wt% Y₂O₃) were mixed to the desired volume ratios. 5 mol% yttria stabilized zirconia was chosen since it shows no phase transformation due to the presence of a monoclinic phase while showing good mechanical strength [13]. To examine the effects of homogeneity of two powders on the mechanical strength, attrition milling was also performed in iso-propanol to eliminate large agglomerates and compositional non-uniformity until achieving a median particle size (d_{50}) less than 0.5 μ m. Slurries prepared for the tapes of dense and porous layers were prepared by mixing powders with solvents (methyl ethyl ketone, ethanol, emphos PS-136), a binder (polyvinylbutyral, B-79), and a plasticizer (benzyl butyl phthalate) followed by tape

casting to desired thicknesses. For a porous support tape, a sacrificial pore former (Superior Graphite, SLC1512P) was added to a slurry to create voids in the porous substrate during sintering.

After a single layer of a dense electrolyte tape was placed on top of multiple layers of porous-support tapes, entire tapes were vacuum bagged and run through a hot roll laminator (ChemInstruments HL-100) at 135°C to create a monolithic laminate from which out a number of pieces were cut for sintering. After cutting laminated tapes to a desired size, pieces were sintered at 1600°C for 2 hrs, with multiple holds to allow burning out the binder and pore formers (190°C for 2 hrs, 400°C for 1 hr, and 700°C for 1 hr). To investigate the effects of compositions and pore-former contents on the flexural strength of porous supports, only porous support tapes were also laminated to fabricate porous supports only.

The sintered parts were subjected to the conversion process in which α -Al₂O₃ in the structure was converted to β'' -Al₂O₃ in a packing bed of β'' -Al₂O₃ powder with additional 10 wt% NaAlO₂. The packing powder acts as the source of β'' -Al₂O₃ stabilizers such as Na and Li to convert the sintered α -Al₂O₃ in the parts to β'' -Al₂O₃. The conversion process was conducted in a dedicated furnace at 1400°C for 10 hrs.

2.2 Characterization

Flexural strength was measured using the ball-on-ring (BOR) technique [14, 15]. The BOR test is a simple variation of ring-on-ring test (ASTM C1499) which is useful to measure flexural strength of thin samples. BOR testing was performed by placing a round sample onto a support ring of a known size and using a single ball to apply load at the center of the sample (on the dense surface in the case of duplex samples). Since it is not possible to measure the

Poisson's ratio of duplex BASEs when the dense electrolyte was combined with a porous support layer, the Poisson's ratio of 0.25 is used, as the Poisson's ratio for the fully dense versions of materials used in this work was measured at 0.288 to 0.312. This may underestimate strength, adding a small safety factor to the measurement, but should provide a fairly representative strength value for all alumina:YSZ ratios examined.

For the current work, a series of 10 balls equally spaced around a 1 inch diameter circle were used as a support ring. At this diameter, the stress applied to the sample between balls was considered to be uniform, thus the 10 balls work as well as a full contact ring for this size sample. A converted sample was placed onto the support ring and centered. The load was applied to the sample at a constant rate of 0.5mm/min. A load cell (Bionix 400) was used to measure the load applied to the sample as the crosshead moved toward the sample. The maximum load applied on the breakage of the sample was used to calculate the flexural strength of the sample. Broken pieces of the sample were used for SEM/EDS analysis.

Flexural strength was calculated using the following formula [14]:

$$S = \left(\frac{3P(1 + \nu)}{4\pi t^2} \right) * \left\{ 1 + 2 \left[\ln\left(\frac{a}{b}\right) \right] + \left[\frac{(1 - \nu)a^2}{(1 + \nu)R^2} \right] \left[1 - \left(\frac{b^2}{2a^2} \right) \right] \right\}$$

Where **P** is load, **t** is the thickness of a sample, **a** is the radius of the sample support, **b** is the radius of the region of uniform loading at the center of the sample, **R** is the radius of the sample and ν is Poisson's ratio.

Microstructural comparisons were conducted using a Scanning Electron Microscope (SEM, JEOL 5900) with a backscattered electron (BSE) detector to collect images. BSE images were used to show compositional differences by which β'' -Al₂O₃ and YSZ grains were easily

distinguished. Samples were coated with gold to provide a conductive layer prior to placing them in the SEM.

Open and total porosity was measured using the Archimedes method following a procedure described in the ASTM standard #C20. Area-specific resistance (ASR) was measured using the electrochemical impedance spectroscopy (EIS) [16]. First, both sides of a planar duplex BASE were sealed on alumina tubes, filled with a Na-Cs alloy which was liquid at ambient temperature. Once this apparatus was heated to 350°C, it was kept under vacuum so as to infiltrate the Na alloy liquid into the porous layer. The resistance was then measured at 350°C using an impedance analyzer. ASR was calculated by multiplying the measured resistance by active area.

3. Results and Discussion

Figure 2 shows the microstructure of typical duplex BASEs processed with different contents of a pore former. The thickness of a dense layer and a porous support was ~20 μm and ~500 μm , respectively. In the back-scattered electron images (Figs. 2b, 2d, and 2f), the brighter particles are YSZ while the darker phases are alumina, indicating the uniform distribution of two materials. The size of pores was 10~20 μm regardless of pore-former contents, governed mainly by the size of a pore former. As expected, the porosity increased with the pore-former content, leading to the open porosity in the porous support in the range of 20 % (for 35 vol% pore former in the tape) to 48 % (for 58 vol% pore former in the tape). In these samples, the closed porosity was quite minimal (<2 %). In the cases of a porous support processed with 30 vol% pore former, the open porosity dropped down to ~7%.

One of the factors which influence the flexural strength of duplex BASEs was the conversion process. Since a huge change in crystal structure and volume occurred during the conversion of α -Al₂O₃ to β'' -Al₂O₃, the strength of converted BASEs was significantly lower compared to as-sintered samples (refer to Figure 3). Therefore, a decrease in strength after conversion was more for a porous support prepared with a higher content of alumina (51% decrease with Al₂O₃:YSZ=7:3 in volume vs. 33% decrease with Al₂O₃:YSZ=4:6 in volume). The impact of the conversion process on flexural strength was also larger for a porous support (51% decrease for Al₂O₃:YSZ=7:3 composition) compared with a dense layer (41% decrease for Al₂O₃:YSZ=7:3). This result can be expected since a YSZ network in the porous support is relatively weaker due to the presence of porosity and cannot hold the structure as strongly as the dense layer during conversion.

There are several other factors which can affect the strength of converted duplex BASEs including total porosity (or pore-former contents), composition, homogeneity of ingredients, etc. Effects of these factors on the flexural strength of the porous supports were closely examined.

The most influential one was the total porosity. Figure 4 shows the relationship between total porosity in the converted duplex BASEs and flexural strength measured by BOR tests. Overall, the strength was inversely proportional to the exponential of total porosity similar to the equation proposed by Ryshkevitch [17].

$$S = 656.23 \exp(-3.868p)$$

where S is the flexural strength of duplex BASEs, p is the total porosity. The strength of a dense layer in the equation (656.23 MPa when $p=0$) is similar to the measured value (697.4 MPa) in Figure 3. In this plot, a deviation of data from the equation can be attributed to other factors such as composition, homogeneity of ingredients, and empirical errors.

The effects of porosity and composition (volume fraction of Al_2O_3 to YSZ) on the strength of porous supports are shown in Figure 5. As shown in Figure 5a, the porosity was almost linearly proportional to the amount of a pore former added into tapes regardless of the alumina/YSZ compositions. Even though the bend strength of porous supports generally follows inverse exponential distribution with respect to porosity, the effects of compositions are clearly observed (refer to Figure 5b). Overall, the higher YSZ contents lead to the higher strength at a given porosity due to the stronger network of YSZ which are unchanged during the conversion process. The effects of composition (Al_2O_3 /YSZ ratio) on strength are more clearly seen in Figure 5c. When YSZ content increases from 30 vol% to 60 vol%, the flexural strength increases ~40% regardless of the pore-former content (38% increase for duplex BASEs with 50 vol% pore former and 39% increase for ones with 40 vol% pore former). This result indicates that the composition and porosity independently influences the strength of porous substrates.

The effects of homogeneity on flexural strength were also examined by comparing parts made from attrition-milled powder and low-speed ball-milled powder (refer to Figure 6). In the case of a dense layer only (500 μm thick), flexural strength increases 41% from 495.6 (low-speed ball-milled) to 697.4 MPa (attrition-milled). The effects of attrition milling on strength were smaller for porous supports (only 18% increase) compared to the dense layer. This is possibly related to a YSZ network in each layer. For a dense layer, improvement in homogeneity maximizes the YSZ network by eliminating the coarse agglomerates. On the other hand, the enhancement of the YSZ network due to the attrition milling is limited in porous substrates since the YSZ network is by and large restricted by porosity. In this study, the maximum strength of 213 MPa (when the porous substrate was in under tension) and 260 MPa (when the dense layer was under tension) was achieved from a duplex BASE consisting of a 50 μm thick dense layer

(Al₂O₃: YSZ = 7:3 in volume, processed with attrition-milled powder) and a 500 μm thick porous support (Al₂O₃: YSZ = 4:6 in volume, 19% open porosity, prepared with attrition-milled powder).

Table 1 lists the area-specific resistance (ASR) of a duplex BASE consisting of a 250 μm thick dense (Al₂O₃: YSZ = 7:3 in volume) and a 250 μm thick porous support (Al₂O₃: YSZ = 7:3 in volume). For the comparison, a standard BASE (Ionotec, D70-2-LNZ, 2 mm thick β'' -Al₂O₃) and a 250 μm thick dense only BASE processed using the same process as duplex BASEs were also tested. While the standard BASE shows the ASR of $1.16 \Omega\cdot\text{cm}^2$ at 300°C a duplex BASE with a 250 μm thick dense layer reveals the smaller ARS value ($0.66 \Omega\cdot\text{cm}^2$) at the same temperature. This value is comparable with the ASR value of a 250 μm thick dense only BASE ($0.78 \Omega\cdot\text{cm}^2$), indicating that the ASR of duplex BASEs are mainly coming from the dense layer. It should be noted that ionic conductivity of a dense layer itself is higher than the standard BASE possibly due to the existence of YSZ in the dense layer and the imperfect optimization of a conversion process which controls the composition of β'' -Al₂O₃. Therefore, there is a more room to improve the ARS of duplex BASEs further. More optimization work will be performed in the future.

In this study, the minimum ASR value of $0.31 \Omega\cdot\text{cm}^2$ was achieved at 350°C from the duplex BASE with a 50 μm thick dense layer and a 500 μm thick porous support (refer to Fig. 7). These results demonstrate that the duplex BASEs consisting of a thin dense layer and a thick porous support can be a feasible solution to provide low ASR and good mechanical strength for intermediate temperature applications.

4. Conclusions

A duplex BASE consisting of a thin dense electrolyte and a porous support was demonstrated as a solution to achieve low area-specific resistance while maintaining good mechanical strength. To enhance the mechanical strength, YSZ was added to the structure to form a β'' -Al₂O₃/5YSZ composite.

The strength of duplex BASEs was mainly governed by the amount of overall porosity following an inverse exponential distribution suggested by Ryshkevitch. The conversion process in which α -Al₂O₃ was converted to β'' -Al₂O₃ decreased flexural strength due to the huge change in crystal structure and volume. The impact of the conversion process on strength was larger for the porous support compared to the dense layer due to the inferior YSZ network in the porous support. The higher YSZ content was used, the higher strength was achieved even though these effects are independent of the influence of porosity on strength. The attrition milling used to improve the homogeneity of ingredients also enhanced flexural strength especially for a dense layer. Overall, the maximum strength of 260 MPa was achieved from a duplex BASE consisting of a 50 μ m thick dense layer (Al₂O₃: YSZ = 7:3 in volume) and a 500 μ m thick porous support (Al₂O₃: YSZ = 4:6 in volume with 19% open porosity).

The ASR measurements revealed that the resistance of duplex BASEs mainly came from the dense layer. In this study, the minimum ASR value of 0.31 $\Omega\cdot\text{cm}^2$ was achieved at 350°C from the duplex BASE with a 50 μ m thick dense layer and a 500 μ m thick porous support. These results demonstrate the feasibility of duplex BASEs for intermediate temperature applications of NBBs, which require low ASR and good mechanical strength.

Acknowledgments

This work was supported by the International Collaborative Energy Technology R&D Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted by financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea. (No. 20128510010070). PNNL is operated by Battelle Memorial Institute for the United States Department of Energy (U.S. DOE) under Contract DE-AC06-76RLO 1830.

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Table 1 Area specific resistance (ASR) of duplex BASEs compared with standard BASE measured at 300°C

	Standard BASE*	Dense Only (250 μm thick)	Duplex BASE (250 μm thick dense + 250 μm thick porous)
ASR ($\Omega\cdot\text{cm}^2$)	1.16	0.78	0.66

*Standard BASE was procured from Ionotec (D70-2-LNZ, 2 mm thick)

Fig. 1 A flowchart showing a procedure to fabricate duplex BASEs

Fig. 2 SEM micrographs collected from the fracture surfaces of duplex BASEs with a 20 μm thick dense layer and $\sim 500 \mu\text{m}$ thick porous supports processed with; (a) 58 vol% (SE), (b) 58 vol% (BSE), (c) 40 vol% (SE), (d) 40 vol% (BSE), (e) 30 vol% (SE), and (f) 30 vol% (BSE) pore formers in the porous support tapes.

Fig. 3 Effects of the conversion process on the flexural strength of porous supports with different compositions and a dense layer.

Fig. 4 Relationship between flexural strength and total porosity

(a)

(b)

(c)

Fig. 5 Effects of porosity and compositions on the flexural strength of porous supports: (a) pore porosity vs. former content, (b) flexural strength vs. porosity, and (c) flexural strength vs. YSZ content.

Fig.6 Effects of attrition-milling on the flexural strength of a porous support and a dense layer after conversion.

0.31Ωcm² @ 350°C

(2013 record: 0.66 Ωcm² @ 350°C)

Fig.7 Impedance plot of a duplex BASE with 50 μm thick dense layer measured at 350°C