Impact of nanostructured anode on low-temperature performance of thin-film-based anode-supported solid oxide fuel cells

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Graphical Abstract

HIGHLIGHTS

- The impact of a nanostructured Ni-YSZ anode on LT-SOFC is evaluated.
- The full SOFCs with and without the nanostructured anode are compared.
- The full-cell test revealed the contribution of the nanostructured anode at LT.
- The TPB increase by nanostructured anode improved charge transfer at the anode.
- Nanostructured anodes secure both the structural integrity and LT-performance.

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Abstract

The impact of a nanostructured Ni-\textdaggerstroked yttria-stabilized zirconia (Ni-\textdaggerstroked YSZ) anode on low-temperature solid oxide fuel cell (LT-SOFC) performance is investigated. By modifying processing techniques for the anode support, anode-supported SOFCs based on thin-film (~1 \textmu m) electrolytes (TF-SOFCs) with and without the nanostructured Ni-\textdaggerstroked YSZ (grain size ~100 nm) anode are fabricated and a direct comparison of the TF-SOFCs to reveal the role of the nanostructured anode at low temperature is made. The cell performance of the nanostructured Ni-\textdaggerstroked YSZ anode significantly increases as compared to that of the cell without it, especially at low temperatures (500 \degree C). The electrochemical analyses confirm that increasing the triple-phase boundary (TPB) density near the electrolyte and anode interface by the particle-size reduction of the anode increases the number of sites available for charge transfer. Thus, the nanostructured anode not only secures the structural integrity of the thin-film components over it, it is also essential for lowering the operating temperature of the TF-SOFC. Although it is widely considered that the cathode is the main factor that determines the performance of LT-SOFCs, this study directly proves that anode performance also significantly affects the low-temperature performance.

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1. Introduction

Solid oxide fuel cells (SOFCs) are promising next-generation power sources because they have higher efficiency than other competing energy conversion technologies [1–3]. However, the
high operating temperature of SOFCs (≥700–800 °C) has limited the development and deployment of this technology because it induces fast degradation and poor reliability. Therefore, lowering the operating temperature is a major issue in SOFC research, and it has been actively studied over the past decade [3–6]. Reduced operating temperatures can prevent unwanted chemical reactions between the cell components and thermal degradation. It also enables the use of less expensive materials, e.g., stainless steel interconnectors. Low-operating-temperature SOFCs (LT-SOFCs) can be applied both as portable power sources and in automotive applications because the system size can be reduced [7–10]. However, the electrode activity of SOFCs, which is thermally activated, deteriorates significantly with decreasing operating temperature. Therefore, the performance of SOFCs is predominantly determined by polarization losses induced by the electrode reaction at low temperatures [6].

The electrode performance of SOFCs is strongly affected by its microstructural characteristics, such as porosity, grain size, and connectivity. Therefore, the relation between microstructural characteristics and the electrochemical performance of an electrode has been actively studied [11–17]. In terms of the grain size of the electrode, nanostructured electrodes have been applied intensively to significantly improve performance and enhance activity [18,19]. This is because the rate of charge transfer in the electrode is influenced by the particle size and area surface of the catalyst. Thus, nanostructured electrodes have an increased rate of electrode reaction, which effectively reduces the polarization resistance at the electrodes at low temperatures [6,13,18,19]. However, the particle size obtained from conventional powder processing is on the order of micrometers because of the size of the raw powder and coarsening during high-temperature sintering. Therefore, novel nano-techniques, such as sputtering, pulsed-laser deposition (PLD), spray pyrolysis, metal organic deposition, and so on, have been employed to realize nanostructured SOFC electrodes [20–23].

In general, nanostructured cathodes have been intensively studied for low-temperature operation because it is known that the polarization loss at the cathode is the most significant factor in the poor low-temperature performance of SOFCs [24–26]. Nonetheless, the loss at the anode at low temperatures (≤600 °C) is predicted to become as significant as that at the cathode [27]. Therefore, it can be said that studies on nanostructured anodes are as important as those on the cathode for low-temperature operation. However, it is more difficult to fabricate nanostructured anodes because they mainly use metals as catalysts. Metal–phase agglomeration at SOFC operating temperatures eventually leads to serious problems such as the reduction of the triple-phase boundary (TPB) length and the loss of conductivity and thus to degradation of the cell stability [28,29]. In spite of the difficulty, in our previous study, a very uniform nanostructured Ni–yttria-stabilized zirconia (Ni–YSZ) anode with fine grain sizes of approximately 100 nm was successfully fabricated by using PLD [30]. The nanostructured layer was designed to suppress Ni agglomeration and to support thin-film electrolytes with a thickness of approximately 1 μm or less. Based on three-dimensional (3D) tomographic analyses, a recent paper reported that this nanostructured Ni–YSZ had a much higher TPB density, reaching almost 20 times that of conventional Ni–YSZ anodes [13].

Still, it is difficult to experimentally discern the impact of the nanostructured anode functional layer (nano-AFL) on full-cell performance for two reasons. One is that the nano-AFL is so thin (2–3 μm) that the catalyst amount in the layer is minute in comparison to that of the whole anode support, and thus it is difficult to exclude the participation of the top portion of the anode support in the anode reaction. If we can build thin-film electrolytes and cathodes directly over the anode support without the nano-AFL, then we can compare the properties of the cells with and without the nano-AFL and elucidate the impact of nano-AFL at least qualitatively. However, due to the surface conditions of powder-processed anode supports, such as a large pore size, high porosity, etc., it has been extremely difficult to build thin electrolytes directly over anode supports [30]. This is the second reason why it has been difficult to demonstrate the impact of the nano-AFL on the performance of LT-SOFCs with thin-film electrolytes (TF-SOFCs) experimentally.

However, by modifying the processing technique of the anode supports, we have been successful in obtaining a tape-cast anode support with satisfactory surface conditions by inducing more shrinkage in the bottom anode tape layer by means of pore formers. Now it is possible to build TF-SOFCs with and without nano-AFL and to elucidate the effect of the nanoscale grain size of the AFL more precisely, especially by electrochemical analyses. In this study, therefore, we investigated the electrochemical properties of TF-SOFCs at low temperatures as a function of the grain size of the Ni–YSZ composite anode. The output power and impedance spectra at various cell operating conditions were analyzed to compare the electrode reaction mechanism as affected by the grain size of the anode in the full-cell test.

2. Experimental

We prepared two different unit cells, one with an anode with a nano-scale AFL and one with an anode of micron-scale grain sizes. The cell with the nano-scale Ni–YSZ AFL is denoted as the NS-cell and that without the nano-AFL is denoted as the MS-cell hereafter. A 2 cm × 2 cm and 1-mm-thick NiO–YSZ (NIO/8YSZ = 56:44 wt%) anode support was fabricated by tape casting. 150-μm-thick NIO–YSZ tapes with poly(methyl methacrylate) (PMMA) as a pore-forming agent and 30-μm-thick NIO–YSZ tapes without PMMA were also fabricated by tape casting. Then, seven layers of the 150-μm-thick tape and one layer of the 30-μm-thick tape were laminated at 75 °C under a uniaxial pressure of 15 MPa. The laminated substrate was sintered at 1300 °C for 4 h to fabricate a completely rigid substrate. For the NS-cell, a 2-μm-thick NIO–YSZ AFL was deposited onto the tape-cast anode support by PLD at 700 °C and an ambient oxygen pressure (Pamb) of 6.67 Pa. The support with the deposited nano-AFL was post-annealed at 1200 °C in air for 1 h [30]. This induces the grain growth of NiO-YSZ from several nm to around 200 nm level and it would stabilize the nano-NIO-YSZ structure by strengthening the oxide network and preventing uncontrollable Ni agglomeration [30–32]. Then, a 1-μm-thick YSZ electrolyte and 200-nm-thick gadolinia-doped ceria (GDC) buffer layers were deposited using PLD at a substrate temperature of 700 °C and a Pamb of 6.67 Pa. A 3-μm-thick lanthanum strontium cobaltite (LSC) layer with a 1 cm × 1 cm area was deposited onto the GDC by PLD at room temperature and a Pamb of 13.3 Pa, followed by post-annealing at 650 °C in air for 1 h to crystallize the cathode. The detailed physical and electrochemical properties regarding the cathode by this process are reported elsewhere [33–36]. The MS-cell was also prepared in an anode-supported configuration, the same as the NS-cell except for the nano-AFL (Fig. 1). The electrolyte, buffer, and cathodes were directly formed on the tape-cast anode support under identical fabrication conditions as those of the NS-cell.

Electrochemical characterization was performed by the full-cell measurement. During the fuel cell operation, air and humidified H2 (3% H2O) were used as the oxidant and fuel, respectively. A detailed cell test configuration is described in our previous study [37]. The cell operating temperature varied from 650 to 500 °C at intervals of 50 °C, and the electrochemical impedance spectra (EIS) and current–voltage–power (I–V–P) curves were obtained at each
temperature. Each EIS was observed over a frequency range of $10^2$ Hz $- 10^{-1}$ Hz. The AC amplitude of the impedance measurement was 50 mV. An Iviumstat electrochemical analyzer (Iviumstat, Ivium Technologies) was used to obtain these EIS and $I-V-P$ curves. Additionally, to more clearly discern the cathode and anode reactions, the electrochemical properties of the SOFC electrodes were characterized by AC impedance measurements using a half-cell test. In the anode half-cell, a 1-mm-thick, dense YSZ substrate was used as the electrolyte support. 1-μm-thick NiO–YSZ nano-AFL thin films were deposited on both sides of the support and post-annealed, the same as with the full-cell anode fabrication. In the cathode half-cell, a 2-mm-thick, dense GDC substrate was used as the electrolyte support. A silver paste was applied to one side of the GDC as a counter electrode and a 1-μm-thick LSC thin film was fabricated on the other side as a working electrode, the same as with the full cell. A Pt wire was wound in the middle of the GDC substrate between the working and counter electrodes as the reference electrode [36]. The operating temperature was varied from 650 to 500 °C at intervals of 50 °C. The anode half-cell was measured in humidified H$_2$ (3% H$_2$O) and the cathode half-cell was measured in air. The EIS change was observed at an open-circuit voltage (OCV) in the frequency range of $10^3$ Hz $- 10^{-1}$ Hz.

The microstructures of each full cell after the cell test were observed using scanning electron microscopy (SEM). The composite structures of the nano- and micron-scale Ni–YSZ were visualized by using focused ion beam (FIB).

3. Results and discussion

In Fig. 2, cross-sectional SEM images of each cell after the cell test are shown. The cross-sectional SEM images show the thicknesses and microstructural characteristics of the LSC cathode, GDC buffer layer, YSZ electrolyte, and Ni–YSZ anode, from top to bottom. In the NS-cell [Fig. 2(a)], an LSC cathode with crack-like vertical pores and a fully dense and hetero-epitaxial YSZ/GDC bi-layer electrolyte and a nanostructured Ni–YSZ AFL (nano-AFL) with a grain size of approximately 100 nm formed over the anode support with the micron-scale particle sizes. In the MS-cell [Fig. 2(b)], a cathode and a bi-layer electrolyte identical in thickness and microstructure to those of the NS-cell formed directly over the anode support, without the nano-AFL. The Ni–YSZ composite structure of each cell is shown by the corresponding FIB images. The dark grains are YSZ and the bright grains are Ni. Both the nanoscale Ni–YSZ and the micron-scale Ni–YSZ have well-interconnected structures of each component. The size difference is clearly observable in the FIB figures. Except for this anode difference, since both cells have almost identical dimensions for the bi-layer electrolyte and the cathode, it is reasonable to assume that differences in the cell performance originate from the existence of the nanostructured Ni–YSZ AFL.

To investigate the effect of the nanostructured Ni–YSZ AFL on the full-cell performance, $I-V-P$ curves of the two cells at 650 °C and 500 °C were compared, as shown in Fig. 3(a) and (b), respectively. The peak power density of the NS-cell at 650 °C reached 1775 mW cm$^{-2}$, which was slightly better than that of the MS-cell, which reached 1650 mW cm$^{-2}$. At 500 °C, the performance of the NS-cell exceeded that of the MS-cell. However, there was a significant difference in performance ratios at 650 °C and 500 °C. The power density at 0.7 V and the peak power density of both cells at each tested temperature are listed in Table 1. The ratio of the performance ($I_{NS-cell}/I_{MS-cell}$) continuously increased with decreasing temperature, and the performance of the NS-cell at 0.7 V was more than two times higher than that of the MS-cell at 500 °C. These results indicate that the effect of the nano-AFL on the full-cell performance increases with decreasing temperature. From Fig. 3(b), it is also noticed that the $I-V$ drop of the MS-cell is much faster at lower current density, which indicates that the activation loss from the electrode is significant in the MS-cell.

To analyze the effect of the nano-AFL on what part the electrode reaction, the Bode plots for each temperature at OCV conditions are compared in Fig. 4. Fig. 4(a) shows the Bode plots of the NS-cell and Fig. 4(b) shows those of the MS-cell. In Bode plots, capacitance variations with respect to the frequency are displayed. Therefore, the rate-determining process can be identified because each frequency range is allocated to a particular electrochemical process. The impedance in the frequency range of $10^2$ Hz $\leq f \leq 10^4$ Hz is considered to be the major contributor to the total impedance of both cells and to exhibit a significant temperature dependency. However, it seems that the impedance in this range comes from the overlap of the resistance of two processes, Freq. 1 ($10^2$ Hz $\leq f \leq 10^3$ Hz) and Freq. 2 ($10^3$ Hz $\leq f \leq 10^4$ Hz). The resistance variation of both cells in the Freq. 1 range is larger as the temperature change. However, the variation of the resistance of the MS-cell in the Freq. 2 range by the temperature change is larger than that of the NS-cell. Eventually, the performance difference between the both cells occurs by the reaction process in the Freq. 2 range.

Bode plots of the EIS for both cells at OCV, 0.75 V, and 0.55 V at 500 °C are compared in Fig. 5. At low cell voltages such as the 0.75 V and 0.55 V (high current density) range, the impedance in the Freq. 2 range becomes the major contributor. The impedance in the Freq. 1 range, which was the major resistance component at OCV, is significantly reduced. In terms of the microstructure, the critical difference between the cells is the TPB density difference in the nano-AFL region adjacent to the electrolyte. If a change in the microstructure is reflected in the EIS, it is postulated that the impedance in the Freq. 2 range is associated with the charge transfer at the TPB inside the nano-AFL and at the interface between the nano-AFL and the electrolyte.

Because the electrode reactions at both the cathode and the
anode are reflected in the full-cell test results above, further analyses are required to discern which reaction is mainly affected by the anode. To analyze the identity of the reaction mechanism in the Freq. 1 and Freq. 2 ranges, we additionally performed the half-cell test about the cathode and anode. The Bode plots of the cathode and the anode half-cells are shown in Fig. 6(a) and (b), respectively, measured at each operating temperature at OCV. When the temperature was decreased from 650 °C to 500 °C during the cathode half-cell test, the impedance in the Freq. 1 range significantly increased. This result indicates that the impedance in the Freq. 1 range is mainly related to the electrode reaction at the cathode. The impedance in the Freq. 2 range did not exhibit significant temperature dependence at the cathode. On the other hand, when the temperature was decreased during the anode half-cell test, the impedance in the Freq. 2 range significantly increased. This result suggests that the impedance in the Freq. 2 range is related to the electrode reaction at the anode region. To enhance the visibility of the difference, normalized $-Z$ values of the impedance measured at 500 °C from each half-cell are overlapped in Fig. 6(c), and a dotted line is drawn to show the shape of the impedance measured from the MS-cell at 500 °C. The figure clearly shows that the impedance in the Freq. 1 range is affected by the cathode, whereas the impedance in the Freq. 2 range is affected by the anode. This half-cell test result supports the aforementioned results shown in the

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Peak power density (power density at 0.7 V) [mW cm$^{-2}$]</th>
<th>Power density ratio $P_{NS-cell}/P_{MS-cell}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>650 °C</td>
<td>NS-cell: 1775 (1707)</td>
<td>1.08 (1.22)</td>
</tr>
<tr>
<td></td>
<td>MS-cell: 1650 (1396)</td>
<td>1.26 (1.53)</td>
</tr>
<tr>
<td>600 °C</td>
<td>NS-cell: 1443 (1237)</td>
<td>1.49 (1.89)</td>
</tr>
<tr>
<td></td>
<td>MS-cell: 1149 (811)</td>
<td>1.69 (2.16)</td>
</tr>
<tr>
<td>550 °C</td>
<td>NS-cell: 958 (674)</td>
<td>1.89 (2.37)</td>
</tr>
<tr>
<td></td>
<td>MS-cell: 645 (357)</td>
<td>2.16 (3.00)</td>
</tr>
<tr>
<td>500 °C</td>
<td>NS-cell: 462 (302)</td>
<td>2.37 (3.50)</td>
</tr>
<tr>
<td></td>
<td>MS-cell: 274 (140)</td>
<td>3.00 (4.60)</td>
</tr>
</tbody>
</table>

Table 1 Power density values of each cell and $P_{NS-cell}/P_{MS-cell}$ ratio at each operating temperature.

(a) SEM images of cross-sectional microstructures of (a) NS-cell and (b) MS-cell. The corresponding FIB pictures below show the Ni–YSZ composite structure of each.

![SEM images](image1)

![FIB pictures](image2)

Fig. 2. SEM images of cross-sectional microstructures of (a) NS-cell and (b) MS-cell. The corresponding FIB pictures below show the Ni–YSZ composite structure of each.

![FIB pictures](image3)

Fig. 3. $I$–$V$–$P$ curves of each cell at (a) 650 °C and (b) 500 °C.
Fig. 4. Bode plots of the impedance at OCV of (a) NS-cell and (b) MS-cell at each temperature.

Fig. 5. Bode plots of (a) NS-cell and (b) MS-cell with various cell voltages at 500 °C.

Fig. 6. Bode plots of EIS values measured from (a) cathode half-cell and (b) anode half-cell at each temperature at OCV. (c) Normalized $-Z$ values at 500 °C from each half-cell. The small dots show the shape of the Bode plot of the MS-cell measured at 500 °C.
full-cell measurements, in which the Freq. 2 range is related to the electrode reaction at the anode, more specifically to the charge transfer, which is affected by the TBP density.

In the Bode plots of the NS- and MS-cells, the contributions from the Freq. 1 and Freq. 2 ranges are deconvoluted, and Arrhenius plots of the ASR of the Freq. 1 and Freq. 2 ranges for each cell are presented in Fig. 7. As shown in the Arrhenius plots, the resistance values of both cells in the Freq. 1 range are almost the same. Because the impedance in the Freq. 1 range is related to the electrode reaction of the cathode, it can be recognized that there is no significant difference in the resistances of the two cells in this range because both cells have almost identical cathodes. Nonetheless, the resistance value of each cell in the Freq. 2 range is quite different, even though the slope of the plot is similar, which indicates that the resistance of the reaction is different but the reaction mechanism is the same. It is obvious that the resistance of the anode reaction is much smaller in the NS-cell than in the MS-cell due to the small particle size of the nano-AFL. In comparing Fig. 7(a) and (b), it is noticeable that the MS-cell has comparable ASR values from the Freq. 1 and Freq. 2 ranges, whereas the NS-cell has ASR values several factors lower in the Freq. 2 range as compared to the Freq. 1 range. Therefore, it can be concluded that in the MS-cell, both the cathode and the anode reaction contribute to the electrode impedance, whereas in the NS-cell, the impedance from the anode is significantly reduced. Thus, the performance improvement in the NS-cell in comparison to that of the MS-cell at lower temperatures is owing to the facilitation of the charge transfer at the anode. These results directly prove that the anode performance can significantly affect the cell performance at low temperature.

On the other hand, at higher temperatures, the cell performance seems to be affected by other electrode mechanisms. Fig. 8 shows the Bode plots of the EIS for the NS-cell and MS-cell at OCV, 0.75 V, and 0.55 V at 650 °C. Unlike at the low-temperature range, the contribution of the impedance in the frequency range of 10 Hz < f < 10^4 Hz (Freq. 1 and Freq. 2) decreased somewhat. As a result, the impact of the impedance in the very low frequency range of 0.1 Hz < f < 10 Hz on the cell performance increased. It has been reported that this range is associated with mass transport and is influenced by the electrode microstructure and the reactant gas supply [35,38,39]. Because the electrode microstructure differs only at the top portion of the anode of the two cells, these phenomena are considered to originate at the anode. The charge transfer of the NS-cell at the interface was improved as compared to that of the MS-cell owing to the nanostructures. However, due to the nanostructured pores, the poorer mass transport at the anode of the NS-cell hindered further improvement in the performance as compared to the MS-cell. It is thus confirmed that the impedance of the low-frequency range is more substantially increased in the high current density range (low cell voltage, 0.55 V), which is typical for the mass transport domination. The gas transport becomes a more significant impeding factor at higher temperatures because the viscosity of the gas increases. At low temperatures, because the charge transfer at the interface is a major resistance contributor and the effect of the gas transport is less important, the performance difference becomes more significant with nanostructured anodes.

4. Conclusions

We confirmed the effect of a nanostructured Ni–YSZ AFL on the anode-supported full-cell low-temperature performance through electrochemical analyses. The cell performance was significantly increased by adopting a nanostructured Ni–YSZ AFL as compared
to the performance of a cell without it, especially at the low operating temperatures. The electrochemical analyses revealed that increasing the TPB density near the electrolyte and anode interface increased the number of sites available for the charge transfer by the nano-AFL, leading to an enhancement in the cell performance. At relatively higher temperatures, other electrode reaction mechanisms, which are affected by the microstructure, such as gas transport, appear to affect the impedance more significantly, which leads to less of a discrepancy in the cell performance.

Although it is widely considered that the cathode is the main factor that determines the low-temperature performance of SOFCs, this study directly proves that the anode performance also significantly affects the cell performance at low temperatures. Even if it is possible to fabricate thin-film electrolytes without the nano-AFL, it is important to minimize the grain size of Ni–YSZ in order to obtain reasonable cell performance at low temperatures. The nanostructured anode not only secures the structural integrity of the thin-film components over it, it is also essential for lowering the operating temperature of SOFCs.

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