Effects of nickel oxide impurities on the microstructure and electrical properties of a nickel–yttria-stabilized zirconia anode

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Abstract

Understanding the impact of raw materials on electrode microstructures is important for improving the electrical performance of fuel cells. In this study, two similar NiO powders with different amounts of impurities were used to prepare an anode support for Ni–yttria-stabilized zirconia (Ni-YSZ) anodes. The anodes fabricated with high-purity NiO and with commercial grade NiO with a high impurity concentration are denoted anode-1 and anode-2, respectively. The nano-CT technique was used to reconstruct the anode support and AFL microstructures and to calculate several structural parameters, such as the triple phase boundary, Ni and YSZ particle

sizes and pore sizes. In addition, the electrical properties of the cells fabricated with anode-1 and anode-2 were measured and compared. The electrical performance of the cell fabricated with anode-1 is higher than that of the cell fabricated with anode-2 because the anode-1 microstructure is more suitable for this application. Further investigations indicate that the differences in the microstructures and electrical properties of anode-1 and anode-2 are primarily due to anode-2 over-sintering. The anode-2 sintering temperature is lower than the anode-1 sintering temperature due to MgO impurities introduced by the anode-2 raw material, which results in the observed over-sintering phenomenon. When anode-2 is sintered at a lower temperature, its microstructure and electrical performance is similar to that of anode-1.

Keywords: Solid oxide fuel cell; Nano-computed tomography; Impurity; NiO powder

1. Introduction

A solid oxide fuel cell (SOFC) is a highly efficient device for transforming the chemical energy of various fuels directly into electricity. These fuel cells exhibit fuel flexibility and have low emissions. An SOFC essentially consists of two porous electrodes separated by a dense electrolyte. The porous electrodes exhibit electrical conductivity and preferably ionic conductivity at the SOFC operating temperature.

One typical SOFC design, the anode-supported design, has received much attention due to its many advantages, such as low ohmic and activation polarization, high mechanical strength, a larger reaction zone and lower operating temperatures [1-5]. Nickel–yttria-stabilized zirconia (Ni–YSZ) cermet is the most widely used SOFC anode

material due to its good electrocatalytic properties and low cost [6]. The anode support thickness in the anode-supported design is typically greater than 0.5 mm. During the burnout process, organic pore formers are employed to produce large additional pores that form continuous gas diffusion paths [7]. However, these large pores reduce the triple phase boundary (TPB) length of the anode. To improve the ceramic anode performance, an anode functional layer (AFL) containing fine particles is placed between the porous anode and dense electrolyte to increase the TPB length and reduce the interfacial polarization losses [8-10]. Previous studies indicated that the AFL microstructure and composition can affect the electrochemical performance of the entire anode [9, 11]. The AFL and anode support have different microstructures and morphologies tuned to their specific roles in the anode. It had reported that during co-sintering process the mismatch of the shrinkage or stress between the different layers may result in serious problems such as cracks in the half-cells. Thus the introduction of AFL may lead to similar issues. Laurencin et al. investigated the interfacial interactions between the AFL and anode support during Ni-YSZ reoxidation and found that a high compressive stress is produced in the AFL layer when it is reoxidized, which might cause delamination at the AFL-anode support interface [12]. Therefore, the anode support might influence the AFL microstructure during co-firing.

To further lower the high cost of SOFCs for large-scale production, industrial grade raw materials, which inevitably contain impurities, should be employed to prepare the anodes. Several studies have reported that impurities in electrodes negatively affect the electrode performance. In particular, the impurity phase can migrate to and accumulate

at the anode-electrolyte interface, causing serious damage to the YSZ electrolyte [13, 14]. Jensen et al. reported that NiO impurities became concentrated in the Ni-YSZ interfacial region, resulting in high resistances at the interface [15]. Oishi et al. studied the effects of impurities on SOFC cathode properties and found that the amount of impurities that could be incorporated into $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ cathodes without affecting their properties varied significantly depending on the element [16]. As mentioned previously, decreasing the cost of the raw materials will help reduce the cost of SOFCs. Therefore, to determine the optimal trade-off between the cost and performance, the effects of raw material impurities on the electrode performance must be investigated further. However, few studies have investigated this problem at the 3D microscale level.

Recently, the 3D microstructures of SOFC electrodes were studied by focused ion beam/scanning electron microscopy (FIB/SEM) [17-21] and X-ray nano-computed tomography (nano-CT) [22-32]. Currently, the spatial resolution of FIB/SEM is 10 nm [33], whereas that of transmission X-ray microscopy is 15-20 nm [34, 35]. Nelson et al. used nano-CT and FIB/SEM to reconstruct the 3D microstructure of an SOFC cathode at spatial resolutions of 45 nm and 10 nm, respectively. The microstructural parameters of the cathode were quantitatively calculated from the data obtained by these two techniques. A comparison of the calculated parameters indicated that nano-CT is a viable quantitative characterization technique for investigating SOFC cathode microstructures [33]. Moreover, nano-CT is non-destructive, i.e., cross-sectional imaging can be performed without cutting the sample, is chemically and elementally

sensitive and has potential for in situ studies of real samples. In other work, Cronin et al. reconstructed an entire SOFC using full-field transmission X-ray microscopy [36], and Shearing et al. studied the microstructural evolution of the cathode during heating and in situ operation using synchrotron X-ray nano-CT [37].

In this study, the effects of raw material impurities on the Ni-YSZ anode support and AFL microstructures in an anode-supported SOFC during co-firing were determined by nano-CT measurements. The 3D structural parameters of the anode support and AFL were quantitatively calculated based on 3D reconstructions. The electrochemical properties of anode-supported SOFCs fabricated from the studied anodes were also measured, and the results are discussed in terms of the microstructural changes.

2. Materials and methods

2.1. Sample preparation and cell tests

In this study, two different NiO powders were used to fabricate anode supports. The key properties of these NiO powders are listed in Table 1. As shown in Figure 1, the average particle size of the NiO-1 powder is slightly smaller than that of NiO-2. Although the NiO-1 and NiO-2 powders have different particle sizes and specific surface areas, they have a similar median particle size (0.9 μm for NiO-1 vs 1 μm for NiO-2) after sintering. In addition, these NiO powders contain different amounts of impurities, which were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and are given in Table 2. The NiO-1 powder was prepared by decomposing thermally pure $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (Sinopharm Chemical Reagent

Ltd., Shanghai, China) at 600 °C. NiO-2 is an industrial grade raw material containing some impurities.

Table 1

Properties of the studied NiO powders.

Sources	Abbr.	Color	Average grain size (μm)	BET surface area ($\text{m}^2\cdot\text{g}^{-1}$)
Sinopharm Chemical Reagent Ltd.	NiO-1	Gray-green	93	3.769
Jinchuan Ltd.	NiO-2	Gray-green	110	5.939

Table 2

Main impurities (wt.%) in the studied NiO powders measured by ICP-AES.

	NiO-1	NiO-2
Fe	0.0044%	0.0249%
SiO ₂	0.0068%	0.0555%
Co ₂ O ₃	0.129%	—
CaO	—	0.1516%
MgO	—	0.142%

Figure 1 SEM images and particle size distributions of (a) NiO-1 and (b) NiO-2.

The cell preparation process was described in detail in a previous report [38] and is briefly summarized in this paper. The AFL was prepared by a suspension spray method. Specifically, 8YSZ (Tosh, TZ-8Y, Japan) and fine NiO (J.T. Baker, USA) powders (YSZ:NiO = 50:50 vol.%) were mixed and ball-milled to obtain a slurry, which was then sprayed onto a polythene membrane to form a green AFL layer. The anode support layer was prepared using the tape-casting method. The NiO-1 and NiO-2 powders were separately mixed with the same 8YSZ powder in a 50:50 volume ratio to obtain the anode support slurries. Then, these slurries were cast on dry green AFL layers. After drying, the green tapes were sintered at 1400 °C for 5 h to form two different anodes, which are denoted anode-1 and anode-2. In addition, the green tapes were sintered at 1250, 1300 and 1350 °C to investigate the effect of the sintering temperature on the

anode-2 microstructure. The support and functional layers were 500 μm and 20 μm thick, respectively. A thin, dense YSZ (Tosoh, Japan) electrolyte film was deposited on the NiO-YSZ anode support by a mid-frequency reactive magnetron sputtering system (ASC-800, Shincron Co., Ltd.) and then sintered at 1250 $^{\circ}\text{C}$ for 4 h. Finally, an LSM (($\text{La}_{0.8}\text{Sr}_{0.2}$) $_{0.95}\text{MnO}_3$, Nextech, USA)-YSZ (TZ-8Y, Tosoh, Japan) cathode was screen-printed on the YSZ electrolyte to a thickness of 30 μm and then sintered at 1150 $^{\circ}\text{C}$ for 3 h. The active cell area was $20 \times 20 \text{ mm}^2$. The cells fabricated with anode-1 and anode-2 are denoted cell-1 and cell-2, respectively.

Initially, the NiO-YSZ anode was reduced under an H_2 (3% H_2O) atmosphere at 750 $^{\circ}\text{C}$ for 2 h. The single cell performance was measured at 700, 750 and 800 $^{\circ}\text{C}$ using a direct current electronic load (N3300, Agilent) with a two-electrode and four-wire setup. The fuel and oxidant were 300 sccm humidified H_2 (2-3% H_2O) and compressed air, respectively. The electrochemical impedance spectra of the single cells were measured on an electrochemical workstation (IM6eX, Zahner) over a frequency range of 0.1-10⁵ Hz with an alternating current signal amplitude of 20 mV under open-circuit conditions from 700 to 800 $^{\circ}\text{C}$.

2.2. Nano-CT experiments

Synchrotron X-ray nano-computed tomography experiments were performed at beamline 4W1A at the Beijing Synchrotron Radiation Facility (BSRF), China [39]. This system utilizes a full-field imaging technique in which elliptical capillary condensers are coupled with zone plate optics to perform absorption contrast imaging. The X-ray beam is focused on the sample by an elliptical capillary condenser. Then, the objective

zone plate produces a magnified image of the sample on a scintillator crystal. The resulting visual image is further enlarged with a microscope objective lens and captured by a 16-bit 1024×1024 CCD camera with a resolution of 30 nm. Due to the tunable photon energy of the synchrotron source, nano-CT can provide chemical phase mapping information by imaging near elemental X-ray absorption edges [40].

In this study, the anode supports and AFLs of the Ni-YSZ anode-1 and anode-2 were imaged. The samples were polished using a polishing machine to obtain a small anode specimen with a thickness of several tens of microns. Then, the polished samples were cleaned using an ultrasonic machine. Finally, an imaging location near the top of the specimen (less than twenty microns) was chosen. One hundred eighty-one projections were collected at 1° increments over a 180° range using 8.4 keV (above the Ni K-edge) X-ray illumination. At each angle, a projection image was collected with an exposure time of 30 seconds. The reconstructions was carried out using the software based on filtered back-projection algorithm from Xradia Inc. (Now Carl Zeiss X-ray Microscopy Inc.). Each tomographic data set was reconstructed using a filtered back-projection algorithm to generate a 3D volume. The voxel size of the reconstructed volume was 60 nm after 2×2 pixel binning. In this study, two different locations on each sample were selected for imaging and reconstruction.

3. Results and discussion

3.1. Electrochemical performance analysis

Figure 2 Electrochemical performances of (a) single cell-1 and (b) single cell-2 at different temperatures.

Figures 2a and b show the performances of cell-1 and cell-2, respectively, in the temperature range of 700 to 800 °C. Their electrical performances differ significantly. To ensure that the observed differences in the electrochemical performances are not due to variations in the cell construction or sealing, three samples of each composition were tested. Table 3 shows the open-circuit voltages and maximum power densities of cell-1 and cell-2 in the temperature range of 700 to 800 °C. The open-circuit voltages (OCVs) at 700, 750 and 800 °C are 1.096 ± 0.002 , 1.093 ± 0.005 and 1.096 ± 0.007 V, respectively, for cell-1 and 1.091 ± 0.002 , 1.092 ± 0.003 and 1.091 ± 0.004 V, respectively, for cell-2. The OCVs of all the cells are higher than 1 V and approach the theoretical values over the entire temperature range studied. This result indicates that the YSZ electrolytes of the two cells are dense and gas-tight. In addition, the maximum power densities of single cell-1 at 700, 750 and 800 °C are higher than those of single cell-2 at the same temperatures. For example, at 750 °C, cell-1 and cell-2 have maximum power densities of approximately 0.69 ± 0.04 W·cm⁻² and 0.17 ± 0.05 W·cm⁻², respectively. This result indicates that the performance of cell-1 is higher than that of

cell-2.

Table 3

Electrochemical performances of cell-1 and cell-2 at different temperatures.

	Open-circuit voltage (V)			Max power density ($\text{W} \cdot \text{cm}^{-2}$)		
	700 °C	750 °C	800 °C	700 °C	750 °C	800 °C
Cell-1	1.096 ± 0.002	1.093 ± 0.005	1.096 ± 0.007	0.42 ± 0.04	0.69 ± 0.04	0.91 ± 0.02
Cell-2	1.091 ± 0.002	1.092 ± 0.003	1.091 ± 0.004	0.09 ± 0.05	0.17 ± 0.05	0.23 ± 0.04

Figure 3 Electrochemical impedance spectra of (a) single cell-1 and (b) single cell-2 at different temperatures.

The electrochemical impedance spectra of cell-1 and cell-2 at different temperatures under open-circuit conditions are shown in Figure 3. The impedance spectra can be separated into the total ohmic resistance (R_{Ω}) and total electrode polarization resistance (R_p) [41, 42]. The R_{Ω} and R_p values obtained from the impedance spectra at different operating temperatures are listed in Table 4. Both R_{Ω} and R_p increase as the operating temperature decreases. However, R_p , which accounts for most of the total cell impedance, is much more sensitive to the operating temperature than R_{Ω} . As shown in

Table 4, the cell-1 R_p values of 0.46, 0.19 and 0.13 $\Omega\cdot\text{cm}^2$ are much smaller than the corresponding cell-2 R_p values of 8.64, 4.67 and 1.90 $\Omega\cdot\text{cm}^2$ at 800, 750, and 700 $^{\circ}\text{C}$, respectively. The ionic and electrical conductivities of cell-1 and cell-2 given Table 4 were calculated using the equation $\sigma_i = L/AR_i$, where L is the sample thickness and A is the electrode area [43]. As shown in Table 4, the electrical conductivities of cell-1 are much larger than those of cell-2 at all operating temperatures tested. It should be noted that all of the cells were fabricated by the same procedure using the same LSM-YSZ composite cathode and YSZ electrolyte. Only the NiO-YSZ anodes are different because they were prepared from two different NiO powders. Therefore, the difference in the cell impedances should be related to the NiO-YSZ anodes. In other words, the significant difference in the maximum power densities of these two cells might be caused by microstructural differences in the anodes due to differences in the NiO powder quality. Therefore, the effects of the NiO raw materials on the anode microstructures must be studied.

Table 4

Resistances and conductivities of cell-1 and cell-2 at different operating temperatures.

	Cell-1			Cell-2		
	700 $^{\circ}\text{C}$	750 $^{\circ}\text{C}$	800 $^{\circ}\text{C}$	700 $^{\circ}\text{C}$	750 $^{\circ}\text{C}$	800 $^{\circ}\text{C}$
R_{Ω} ($\Omega\cdot\text{cm}^2$)	0.29	0.16	0.10	1.06	0.92	0.89
R_p ($\Omega\cdot\text{cm}^2$)	0.46	0.19	0.13	8.64	4.67	1.90
Ionic conductivity ($\text{mS}\cdot\text{cm}^{-1}$)	5.17	9.37	15.0	1.41	1.63	1.68
Electrical conductivity ($\text{mS}\cdot\text{cm}^{-1}$)	119.5	298.4	423.0	6.36	11.7	28.9

3.2. Microstructural characterization

Cross-sectional SEM images of the half-cells with different anode supports are shown in Figure 4. The 15 μm -thick electrolyte layer is sufficiently dense after sintering at 1400 $^{\circ}\text{C}$. The porosity of the NiO-1 anode support (Figure 4a) is higher than that of the NiO-2 anode support (Figure 4b). Thus, although the anode-1 and anode-2 AFLs were fabricated using the same raw materials and preparation method, their microstructures are different. In addition, the anode-1 AFL is denser than the anode-2 AFL. Therefore, the SEM images show that the NiO powders affect the anode support and AFL microstructures. To quantitatively analyze the impact of the NiO impurities on the microstructure, the 3D nano-CT data were used to determine the microstructural parameters.

Figure 4 SEM images of the half-cells with (a) anode-1 and (b) anode-2.

Figure 5 Radiographs of the (a) anode-1 and (b) anode-2 AFLs and (c) anode-1 and (d) anode-2 supports. The scale bar is 2.5 μm .

The 2D radiographs of the anode supports fabricated from different NiO powders and the corresponding AFLs are shown in Figure 5. Significant differences between the anode supports and AFLs are observed. The segmentation process began with the conversion of the 3D reconstructed data into stacks of 2D BMP images. The thresholds were choose based on the Ni phase showing a strong absorption to the X-ray above K-shell absorption edge of Ni and pore phase showing a weak absorption to the X-ray. Sharp changes in contrast at the respective phase boundaries can assist us to select the

appropriate threshold values. Although at present this procedure is a more appropriate way to carry out the segmentation [29, 40], it has a limitation that the visual inspection was used to set thresholds. Thus it is necessary to develop improved methods of segmentation in future works. To further demonstrate the 3D visualization method, the renderings of anode-1 and anode-2 are shown in Figure 6. The 3D views of the microstructures reveal differences in the pore volume fractions.

Figure 6 Reconstructed volumes of the (a) anode-1 and (b) anode-2 AFL regions and (c) anode-1 and (d) anode-2 supports.

3.3. Quantitative microstructural analysis

To better understand the impact of the NiO powder impurities on the anode microstructure, the key structural parameters were calculated based on the 3D

reconstructions using previously described methods [40] and are listed in Table 5.

Table 5

Key structural parameters calculated for the AFLs and anode supports sintered at 1400 °C.

	Anode-1 AFL	Anode-2 AFL	Anode-1 support	Anode-2 support
Ni volume fraction (%)	33.8 ± 0.6	30.2 ± 0.4	24.5 ± 0.4	26.6 ± 1.4
YSZ volume fraction (%)	48.9 ± 1.1	46.2 ± 0.2	36.4 ± 0.7	40.1 ± 0.1
Pore volume fraction (%)	17.3 ± 0.9	23.6 ± 0.7	39.1 ± 1.3	32.3 ± 1.2
Ni connectivity (%)	98.7 ± 0.6	94.8 ± 1.3	98.5 ± 0.7	93.3 ± 0.8
YSZ connectivity (%)	99.0 ± 0.3	99.2 ± 0.2	97.8 ± 0.4	99.6 ± 0.1
Pore connectivity (%)	94.3 ± 0.2	94.7 ± 1.3	99.2 ± 0.3	96.5 ± 1.4
Total TPB density (μm^{-2})	4.61 ± 0.16	2.42 ± 0.71	2.19 ± 0.23	1.20 ± 0.50
Active TPB density (μm^{-2})	3.57 ± 0.27	1.67 ± 0.22	1.36 ± 0.04	0.68 ± 0.14

The pore volume fractions of the anode-1 and anode-2 supports are $39.1\% \pm 1.3\%$ and $32.3\% \pm 1.2\%$, respectively, indicating that the anode-2 support is denser than the anode-1 support. It should be noted that the AFL porosities are significantly different ($17.3\% \pm 0.9\%$ for anode-1 vs $23.6\% \pm 0.7\%$ for anode-2), although the anode-1 and anode-2 AFLs were prepared by the same preparation method using the same raw materials. This result further indicates that during co-sintering, the anode support microstructure has a significant effect on the AFL. Moreover, the pore volume fractions of the two anode-1 layers are significantly different, increasing from $17.3\% \pm 0.9\%$ for the AFL to $39.1\% \pm 1.3\%$ for the anode support. The high porosity of the anode support allows for sufficient mass transport to compensate for the higher gas diffusion polarization [44].

The Ni, YSZ and pore connectivities are given in Table 5. The YSZ-phase connectivities of the anode-1 AFL, anode-2 AFL, anode-1 support and anode-2 support are $99.0\% \pm 0.3\%$, $99.2\% \pm 0.2\%$, $97.8\% \pm 0.4\%$ and $99.6\% \pm 0.1\%$, respectively,

indicating a high level of connectivity ($\geq 97.8\%$). The Ni-phase connectivities in anode-1 ($98.7\% \pm 0.6\%$ for the AFL and $98.5\% \pm 0.7\%$ for the anode support) are higher than those in anode-2 ($94.8\% \pm 1.3\%$ for the AFL and $93.3\% \pm 0.8\%$ for the anode support). The pore phases in both the anode-1 and anode-2 supports exhibit higher connectivity than those in the AFLs. In addition, the pore-phase connectivity of the anode-1 support is higher than that of the anode-2 support ($99.2\% \pm 0.3\%$ vs $96.5\% \pm 1.4\%$). The lower pore connectivities of the AFLs result from the proportionally lower AFL porosities.

The triple phase boundary (TPB) is of particular importance for the electrochemical performance of the anode. Two parameters are associated with the TPB length of the anode: the total and active TPB lengths. The total TPB length includes the boundaries where the Ni, YSZ and pore phases meet. However, these TPBs are only active when all three phases belong to a percolating network that enables reactant species transport. In the 3D processed images, each voxel was assigned a certain value to identify it as Ni, YSZ or a pore. If the three different phases shared an edge (i.e., three neighboring voxels had three different values), the shared edge (line segment surrounded by the three voxels) was defined as a TPB and marked in the image. This system was applied to the entire 3D volume, that is, to the slices in all three directions (x, y, z). The total TPB length was calculated by counting the total number of marked line segments and multiplying it by the line segment length (60 nm in this study). Only TPBs located at the boundaries connecting the Ni, YSZ and pore phases were included in the active TPB length calculation. However, the TPB lengths determined based on the voxelized structures are overestimated because the TPBs can be oriented in any direction relative

to the voxel edges in real electrodes. Therefore, more accurate TPB densities were obtained by dividing the calculated TPB densities by the correction factor (1.455) proposed by Wilson et al. [45].

The total and active TPB densities are reported in Table 5. For both anodes, the AFLs exhibit higher total and active TPB densities than the anode supports, which is desirable. Both the total and active TPB densities of anode-1 are higher than those of anode-2. For example, the total TPB density of the anode-1 AFL is $4.61 \pm 0.16 \mu\text{m}^{-2}$, whereas that of the anode-2 AFL is $2.42 \pm 0.71 \mu\text{m}^{-2}$. Therefore, anode-1 might exhibit a higher performance than anode-2 due to its higher TPB densities, indicating that the NiO powder used to prepare the anode support affects the anode support microstructure and the AFL performance. This result explains the differences in the cell-1 and cell-2 performances revealed in Table 3.

The volume-normalized surface area (surface area normalized to the reconstructed volume) of each anode phase was calculated based on the 3D reconstructions as described in detail elsewhere [40]. A brief summary of the procedure follows: the volume-normalized surface area of a given phase was calculated by summing over all the voxel faces between that phase and the complementary phases. However, it should be noted that the surface areas calculated from the voxel surfaces are overestimated; therefore, a corrective factor of 0.5 was employed in this study [46]. The volume-normalized surface areas of the Ni, YSZ and pore phases in the anode-1 and anode-2 AFLs and supports are given in Table 6.

Table 6

Volume-normalized surface areas and average diameters of the Ni, YSZ and pore phases of the anodes sintered at 1400 °C.

	Anode-1 AFL	Anode 2 AFL	Anode-1 support	Anode-2 support
$S_{Ni} (\mu m^{-1})$	2.93 ± 0.17	1.97 ± 0.29	1.36 ± 0.09	1.24 ± 0.04
$S_{YSZ} (\mu m^{-1})$	4.43 ± 0.22	3.27 ± 0.14	3.04 ± 0.30	3.10 ± 0.27
$S_{Pore} (\mu m^{-1})$	2.15 ± 0.13	1.81 ± 0.03	1.61 ± 0.02	1.85 ± 0.02
$D_{average, Ni} (\mu m)$	0.70 ± 0.03	0.94 ± 0.15	1.08 ± 0.09	1.27 ± 0.11
$D_{average, YSZ} (\mu m)$	0.67 ± 0.07	0.85 ± 0.04	0.73 ± 0.09	0.78 ± 0.07
$D_{average, Pore} (\mu m)$	0.50 ± 0.11	0.78 ± 0.01	1.45 ± 0.07	1.04 ± 0.03

The volume-specific surface area of the Ni phase plays an important role in hydrogen oxidation [47]. The Ni volume-specific surface area of the anode-1 AFL is higher than that of the anode-2 AFL ($2.93 \pm 0.17 \mu m^{-1}$ vs $1.97 \pm 0.29 \mu m^{-1}$). This result suggests that anode-1 is superior to anode-2. Moreover, all of the Ni, YSZ and pore volume-specific surface areas of anode-1 are higher than those of anode-2, except for the YSZ and pore surface areas of the anode support. This result indicates that the particle and pore sizes are smaller in anode-1 than in anode-2. To confirm this assumption, the particle and pore sizes were calculated.

The particle and pore sizes were analyzed using the Brunauer-Emmett-Teller (BET) formula: $d = 6V/S$ [48], where d , V and S are the average size, volume and surface area, respectively. Table 6 lists the average Ni and YSZ particle sizes and pore diameters. For both anodes (anode-1 and anode-2), the particle and pore sizes of the anode support are larger than those of the AFL, as observed in the 3D reconstructions (Figure 6). The larger difference in the Ni particle sizes is due to the different Ni particle sizes of the powders used to fabricate the anode supports and AFLs. The use of pore formers during sample preparation results in the formation of large pores in the substrate after sintering.

The average anode-1 and anode-2 particle and pore diameters are different in both the AFLs and anode supports. The anode-1 AFL has a smaller average Ni particle size than the anode-2 AFL ($0.70 \pm 0.03 \mu\text{m}$ vs $0.94 \pm 0.15 \mu\text{m}$) after sintering, although the same NiO raw material was used to fabricate both the anode-1 and anode-2 AFLs. Therefore, the AFL microstructure might be affected by the anode support during co-sintering. The average YSZ particle sizes of the anode-2 AFL and support are $0.85 \pm 0.04 \mu\text{m}$ and $0.78 \pm 0.07 \mu\text{m}$, respectively, and are larger than those of the anode-1 AFL and support ($0.67 \pm 0.07 \mu\text{m}$ and $0.73 \pm 0.09 \mu\text{m}$, respectively). Zupan et al. reported that the average YSZ grain size increased as the sintering temperature increased [49]. Therefore, it is concluded that a sintering temperature of 1400°C is too high for anode-2, as demonstrated by its over-sintering at this temperature. However, this sintering temperature is suitable for anode-1.

3.4. Effects of the impurities on the anode microstructure

As previously mentioned, although the NiO-1 and NiO-2 powders have a similar appearance, their average grain sizes are different (93 nm for NiO-1 vs 110 nm for NiO). The particle size of the NiO powder starting material has a significant effect on the SOFC performance [50, 51]. However, in this study, the difference in the grain sizes of NiO-1 and NiO-2 is very small, as shown in Figure 1. Therefore, it is assumed that the SOFC performance is not significantly affected by the grain size of the NiO powder starting material, which is consistent with previously reported results [52]. As shown in Table 2, these two powders contain different impurities. Specifically, NiO-2 contains 0.0249 wt.% Fe, 0.0555 wt.% SiO_2 , 0.152 wt.% CaO and 0.142 wt.% MgO, and NiO-

1 contains 0.0044 wt.% Fe, 0.0068 wt.% SiO₂ and 0.129 wt.% Co₂O₃. Therefore, the microstructural differences between anode-1 and anode-2 might be caused by the different types of impurities or different impurity levels in the NiO powders. Previous reports indicated that Fe, MgO and Co₂O₃ dopants can effectively reduce the sintering temperature and accelerate the YSZ densification rate. However, CaO can increase the 8YSZ sintering temperature and inhibit YSZ densification [53]. The ability of the impurities to effectively alter the YSZ sintering behavior is often determined by the doping amounts. For example, ≤ 1 wt.% Fe₂O₃ or CaO did not affect the densification of YSZ powder compacts [54]. In contrast, Wu et al. reported that 0.024-0.168 wt.% MgO plays an important role in YSZ densification [55]. Radford et al. reported that 0.24 wt.% MgO lowered the sintering temperature by 190 °C and increased the relative YSZ density by 6% [56]. The densification occurred by a solid-state sintering mechanism. Therefore, it is assumed that the 0.142 wt.% MgO impurity in the NiO-2 powder might cause the over-sintering of the anode-2 support in this study. The microstructural changes caused by the over-sintering lead to a decrease in the TPB length (Table 5). Furthermore, during co-sintering, the thick over-sintered anode support layer might affect the thin AFL layer microstructure in anode-2, also resulting in a decrease in the TPB length (Table 5). This result is closely related to the electrochemical performance of the anode. The total and active TPB lengths of anode-1 are approximately twice those of anode-2, as shown in Table 5. However, a four-fold difference in the cell-1 and cell-2 power densities is observed, as shown in Table 3, possibly due to the different TPB site distributions in the anodes. Jørgensen et al.

reported that the TPB site distribution in the anode can substantially affect the SOFC performance [57].

Figure 7 Cross-sectional morphologies of the NiO-2 double-layer anodes sintered at (a) 1250 °C, (b) 1300 °C, (c) 1350 °C and (d) 1400 °C.

Therefore, anode over-sintering must be avoided. In theory, this problem can be solved by reducing the sintering temperature. To confirm this hypothesis, the microstructures of anodes sintered at different temperatures were examined. Figure 7 shows SEM images of NiO-2 anodes fabricated by the same preparation method but sintered at different temperatures. The sintering temperature has a significant impact on the microstructure of the entire anode. Sintering at 1250 °C results in a less dense, porous structure, and thus, it is not obvious that anode-2 is actually sintered at this temperature. As the sintering temperature is increased to 1350 °C, the AFL porosity

decreases significantly, as shown in Figure 7c, indicating that sintering occurs. When the sintering temperature is increased to 1400 °C, over-sintering occurs in anode-2 (Figure 7d). A comparison of the SEM images of the anodes shown in Figures 4a and 7c shows that anode-1 sintered at 1400 °C and anode-2 sintered at 1350 °C have similar microstructures and morphologies. The electrochemical performance of the SOFC with the NiO-2-based electrode sintered at 1350 °C is shown in Figure 8. The maximum SOFC power density at 800 °C increases to approximately 0.7 W·cm⁻², showing that the SOFC performance of the NiO-2-based electrode is significantly improved when it is sintered at 1350 °C. Therefore, the 0.142 wt.% MgO impurity in the NiO-2 powder might be the main reason for decreasing the sintering temperature by 50 °C.

Figure 8 Electrochemical performance of the SOFC with the NiO-2-based electrode sintered at 1350 °C.

4. Conclusions

The effects of the raw material impurities on the Ni-YSZ anode microstructure and cell electrical properties were studied. Nano-CT was employed to reconstruct the 3D microstructures of Ni-YSZ anodes prepared with two different NiO powders. Some key structural parameters of the anodes were calculated based on the reconstructions. A comparison of the calculated parameters indicates that over-sintering occurs in anode-

2. Moreover, during the over-sintering, the thick anode substrate influences the microstructural evolution of the thin anode functional layer. Based on the experimental results, calculated data and previously reported results, the MgO impurity is assumed to be the main cause of the anode-2 over-sintering. These results provide insight that might be useful for optimizing the anode microstructure by employing appropriate preparation conditions with commercial raw materials. Therefore, additional studies will be performed to quantify the effects of the impurities on the anode microstructure and SOFC electrical properties.

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