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Electrochemical and Microstructural Properties of Ni-(Y₂O₃)_{0.08}(ZrO₂)_{0.92}-(Ce_{0.9}Gd_{0.1})O_{1.95} Anode-supported Microtubular Solid Oxide Fuel Cells

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Abstract

The nickel-zirconia cermet is widely used as an anode of solid oxide fuel cells (SOFCs). On the other hand, the nickel-ceria based anode indicates high electrochemical activity for hydrogen oxidation and hydrocarbon reforming. In this study, Electrochemical and microstructural properties of microtubular SOFCs with Ni-based composite anodes containing yttria-stabilized zirconia (YSZ) and gadolinia-doped ceria (GDC) are investigated electrochemically using impedance spectroscopy (EIS) and microstructurally using focused ion beam-scanning electron microscopy (FIB-SEM). The solid solution of YSZ and GDC was easily formed after mechanical mixing and sintering at 1400°C. The electrical conductivity and mechanical strength for the Ni-YSZGDC composite anodes are low relative to Ni-YSZ due to poor sinterability. The GDC-containing anodes show improved electrochemical activity for hydrogen oxidation, despite having lower three-phase boundary densities. Distribution of relaxation times (DRT) analysis of the EIS data shows that the concentration polarization is lower for the Ni-GDC anode, due to a higher measured pore volume. The maximum power density for the cell with the Ni-YSZGDC composite anode was higher than those with the Ni-YSZ and Ni-GDC anodes.

1. Introduction

Solid oxide fuel cells (SOFCs) are generally operated at high temperatures above 600°C using oxide-ion conductors (e.g. yttria-stabilized zirconia (YSZ) and gadolinia-doped ceria (GDC)) as an electrolyte [1]. In principle, SOFCs are able to use directly not only hydrogen but also hydrocarbon fuels such as methane, propane, butane, and ethanol [2]. Generally, steam reforming is conducted to prevent carbon deposition on SOFCs. For small-scale applications, it would be desirable to reduce costs and simplify the SOFC system by directly utilizing hydrocarbons, *i.e.*, without adding substantial steam to the fuel. However, hydrocarbons are unstable under these conditions, leading to carbon deposition and degradation of the SOFC anode due to the deactivation of nickel catalyst and the inhibition of fuel diffusion [3]. In general, ceria-containing anodes have been found to reduce the tendency for carbon deposition. Park *et al.* [4] found the Cu-GDC anode indicated high durability against carbon deposition in butane at low steam/carbon (S/C) ratios. Direct butane utilization was previously demonstrated using Ni-GDC anodes [5, 6]. A part of ceria can be reduced from Ce^{4+} to Ce^{3+} , which promotes the reforming of hydrocarbon and the electrochemical oxidation of deposited carbon.

$\text{ZrO}_2\text{-CeO}_2$ solid solutions are of interest to replace YSZ or GDC in Ni-based anodes, since they are well known as hydrocarbon combustion catalysts with high oxygen storage capacity [7, 8]. Tetragonal (*t'*) and cubic (*c*) single phase structures are metastable over a wide compositional range for the $\text{ZrO}_2\text{-CeO}_2$ solid solutions [9, 10]. Takahashi *et al.* [11] reported that the performance of cells with $\text{Ni-(Y}_2\text{O}_3)_{0.08}(\text{CeO}_2)_x(\text{ZrO}_2)_{0.92-x}$ increased with an increase in CeO_2 content up to $x = 0.08$. On the other hand, the ionic conductivity of $\{(\text{Y}_2\text{O}_3)_{0.08}(\text{ZrO}_2)_{0.92}\}_x\{(\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9})_{1-x}\}$ solid solutions exhibits a minimum at $x = 0.5$ due to increase in the scattering of mobile oxide ions [12].

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5 In this study, Ni-YSZ, Ni-GDC, and Ni-YSZGDC composite anodes were prepared by
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7 mechanical mixing, incorporated into anode-supported microtubular SOFCs, and their
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9 electrochemical and microstructural properties investigated. The sintering behavior of the
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11 composite anodes affects the crystal structure, electrical and mechanical properties [13]. To
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13 evaluate the electrode performance precisely, the distribution of relaxation times (DRT) analysis
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15 was conducted for the microtubular cells with the Ni-YSZGDC composite anodes with reference
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17 to the previous reports [14-17]. Furthermore, focused ion beam-scanning electron microscopy
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19 (FIB-SEM) provides three-dimensional (3D) microstructural information such as volume
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21 fractions, surface areas and three-phase boundary (TPB) lengths. [18-26]. A new method is used
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23 to obtain statistically significant microstructural data for these anodes that have a wide range of
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25 pore sizes. The FIB-SEM microstructures of Ni-YSZ and Ni-GDC anodes were correlated to the
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27 DRT-analyzed electrode performance in this study.
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36 2. Experimental

37 2.1. Sample preparation

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39 Anode microtubes were made from NiO (Sumitomo metal mining), $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ (YSZ;
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41 Tosoh), $(Ce_{0.9}Gd_{0.1})O_{1.95}$ (GDC; Shin-Etsu Chemical), pore former (acrylic resin; Sekisui Plastic)
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43 and binder (Cellulose; Yuken Kogyo) powders. The weight ratio of NiO to oxide was 6:4, and the
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45 molecular ratios of YSZ to GDC were 100:0 (Ni-100YSZ), 50:50 (Ni-50YSZ-50GDC), 25:75
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47 (Ni-25YSZ-75GDC) and 0:100 (Ni-100GDC). The volume ratios of Ni:YSZGDC after reduction
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49 were 44.5:55.5, 47.3:52.7, 48.2:51.8 and 49.2:50.8 for Ni-100YSZ, Ni-50YSZ50GDC,
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51 Ni-25YSZ75GDC and Ni-100GDC, respectively. A pore former of acrylic resin with a grain size of
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53 ca. 5 μm was added before sintering to increase anode porosity. These powders were mixed
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mechanically by kneading machine with adding the proper amount of water for 2 h. The anode microtubes were extruded using a piston cylinder with a metal hole of 2.4 mm (outside diameter) and 1.4 mm (inside diameter). After extrusion, the tubes were dried overnight in air at room temperature. An electrolyte slurry was prepared by mixing YSZ, a binder (polyvinyl butyral; Sekisui Chemical) a dispersant (tallow propylene diamine; Kao) and a plasticizer (dioctyl adipate; Wako Pure Chemical Industries) into ethanol and toluene solvents for 48h. The YSZ electrolyte was formed by dip-coating at a pulling rate of 2 mm/s. The YSZ thin-film electrolyte and NiO anode microtube were co-sintered in air for 3 h at 1400°C. The interlayer of GDC and the cathode of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\text{GDC}}$ were coated by a similar manner. The weight ratio of LSCF to GDC was 7:3. The GDC interlayer was introduced between the electrolyte and the cathode, using a similar dip-coating method, to prevent chemical reactions with these materials. The pulling rates of the dip-coater were 1 and 2 mm/s for the interlayer and the cathode, respectively. The interlayer and cathode thin-film layers were sintered sequentially in air for 2 h at 1250°C and for 1 h at 950°C, respectively. The outside diameter of microtube was 1.8 mm, and the cathode length was 30 mm after sintering. The thicknesses of the anode, electrolyte, interlayer and cathode were ca. 200, 5, 1 and 20 μm , respectively. The Ni-YSZGDC anodes were reduced for 2 h at 700°C in 20% H_2 -80% N_2 before electrochemical and microstructural measurements.

2.2.Ni-YSZGDC anode characterization

Crystal structures of Ni-YSZGDC powders were evaluated with an X-ray diffractometer (Rigaku RINT-2200) using $\text{Cu-K}\alpha$ radiation at room temperature in air. Sintering behaviors were measured with thermomechanical analyzer (Rigaku TMA-8310). A green NiO-YSZGDC microtube after extrusion with 20 mm in length was set, and the change in length was measured

during heating and cooling between room temperature and 1400°C at 4°C/min in air. Radial crushing strengths of oxidized NiO-YSZGDC anode microtubes were evaluated by a method based on ISO-2739 “Determination of radial crushing strength for sintered metal bushings” at room temperature in air. Five microtubes with 10 mm in length after sintering were set in compression testing machine, and the radial crushing strength, S , was calculated from the following equation:

$$S = \frac{F(D-t)}{Lt^2}$$

where F is the maximum load, D is the outside diameter, t is the thickness, and L is the length of tube. Electrical conductivity of Ni-YSZGDC microtubes were measured from room temperature to 700°C in 20% H_2 – 80% N_2 measured by four-terminal method applying an AC voltage of 10 mV.

2.3. Electrochemical evaluation

The characteristics of power generation and AC impedance were evaluated with a potentiostat/galvanostat built in an impedance analyzer (Autolab PGSTAT302). Platinum paste TR-7905 (Tanaka Kikinzoku Kogyo) was used as a current collector on the LSCF-GDC cathode [27]. A mixture of $H_2:H_2O:N_2 = 20:3:77$ was supplied as fuel at a flow rate of 100 mL/min to the anode side, and air was supplied as oxidant at 100 mL/min to the cathode side. The operating temperature was 600°C. Current-voltage (i-V) characteristics were measured from open circuit voltage (OCV) to 0.4 V at a sweep rate of 5 mV/s. The AC impedance was measured at OCV in the frequency range from 1 MHz to 0.1 Hz with 20 steps per logarithmic decade. The DRT analysis was done as described in detail in Refs. [14-17]. The polarization processes are considered as an equivalent circuit composing an infinite series connection of parallel RC elements. The inductance components were removed by the same method as described in Ref.

[17] before DRT analysis for the impedance spectra in this study. The software package FTKREG [28] was used to solve an ill-posed inverse problem in DRT analysis by Tikhonov regularization.

2.4. Microstructural Measurements

In preparation for 3D tomography, the microtubular cells with Ni-100YSZ and Ni-100GDC anodes were fractured. The pores within the anodes were infiltrated with a low viscosity epoxy [29] prior to the observation. The serial sectioning and imaging was carried out using a Zeiss 1540XB dual beam FIB-SEM system with a 1-1.5 kV electron beam energy and the in-lens detector. The image resolution was 30×30 nm and the spacing between images was 30 nm. The total volume reconstructed was ~1200 μm^3 for the Ni-100GDC and ~1500 μm^3 for the Ni-100YSZ. The area imaged was located close to the anode/electrolyte interface and the milling direction was perpendicular to the tube axis. Ni-YSZ anode has been 3D reconstructed by many groups previously, and the nature of the contrast is well known. For Ni-GDC anode, which has not been imaged for 3D reconstruction previously, the contrast was not known *a priori* so SEM-EDS analysis was carried out in a Hitachi SU8030 microscope with an Oxford X-max 80 SDD EDS detector to ensure that the image segmentation accurately assessed which contrast corresponded to Ni, GDC, and pore.

2.5. Image Processing and Microstructural Quantification

Two different methods were used for the segmentation, due to a variation in image quality between the two anodes. The Ni-100YSZ anode was segmented using the same thresholding method as described elsewhere [26]. For the Ni-100GDC anode, the areas of highest quality

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5 were selected and cropped. An edge detection code was run to isolate interfaces between
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7 phases. Then a connected component labeling algorithm was used to identify each independent
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9 region defined by the interfaces. Segmentation was then carried out using thresholding based on
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11 the average greyscale value of each independent region.
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14 Macrohomogeneous morphological information including phase volume fraction, particle
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16 size distributions, phase connectivity and TPBs, were calculated from the 3D data sets using
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18 methods described elsewhere [22, 30-32]. Algorithms were written in-house for the image
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20 process programming language, Interactive Data Language (IDL). Tortuosity was computed as
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22 described elsewhere [33]. The values reported here correspond to an average in all directions
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24 since no anisotropy was observed.
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31 **3. Results and Discussion**

32 **3.1. Anodes Characterization**

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37 Figure 1 shows the x-ray diffraction (XRD) patterns of the Ni-YSZGDC powders, after
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39 reduction treatment, measured with CuK α radiation at room temperature in air. The XRD pattern
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41 of the Ni-100YSZ consisted of a face-centered cubic nickel and a fluorite type tetragonal (t') or
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43 cubic YSZ. While the peak positions and intensities of nickel were unchanged by the substitution
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45 of GDC with YSZ, the peak positions of YSZ were shifted to the lower diffraction angles with an
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47 increase in GDC contents. The diffraction peaks of YSZ and GDC were not separated for the
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49 Ni-50YSZ50GDC and Ni-25YSZ75GDC. Figure 2 shows the lattice parameters of nickel and
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51 oxide as a function of GDC/(YSZ+GDC) molecular ratio for the Ni-YSZGDC. While the lattice
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53 parameter of nickel was unchanged with GDC content, that of the oxide increased linearly with
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55 GDC content. This result suggested that the mechanical mixing and sintering at 1400°C for the
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Ni-YSZGDC composites resulted in the formation of a YSZ-GDC solid solution. The lattice parameter of the YSZ-GDC solid solution is the same as that reported by Tsoga et al. [12]. While the peaks of YSZ-GDC solid solutions were broader, and that of GDC was sharper than that of YSZ as shown in Figure 1. The YSZ-GDC solid solutions had smaller crystallite sizes.

Sintering behavior affects the mechanical and electrical properties for anode-supported microtubular SOFCs. Figure 3 shows the length changes in the NiO-YSZGDC anode microtubes during heating and cooling between room temperature and 1400°C in air, when a green microtube after extrusion with 20 mm in length was set in a thermomechanical analyzer. The data around 300-380°C were disturbed during heating procedure, because the pore former of acrylic resin was burnt rapidly [13]. Keeping and raising temperature slowly around 300-380°C is very important during co-sintering procedure to obtain a dense YSZ electrolyte. The NiO-YSZGDC anode microtubes started to shrink at 810-910°C. The linear sintering shrinkage percentages of the NiO-100YSZ, NiO-50YSZ50GDC, NiO-25YSZ75GDC and NiO-100GDC anodes were 21.3, 18.6, 16.5 and 20.4%, respectively. That is, the composites of nickel oxide and the YSZ-GDC solid solution were less sintered than the NiO-100YSZ and NiO-100GDC anodes. On the other hand, the lengths of NiO-YSZGDC anode microtubes decreased linearly during cooling procedure. The thermal expansion coefficients of the NiO-YSZGDC anodes were $12.6\text{-}13.1 \times 10^{-6} \text{ K}^{-1}$.

Table 1 shows the radial crushing strength of the NiO-YSZGDC anode microtubes evaluated by a method based on ISO-2739 at room temperature in air. The NiO-100YSZ anode was stronger than the NiO-100GDC anode, because the mechanical strength of YSZ was higher than that of ceria [34]. The NiO-25YSZ75GDC and NiO-50YSZ50GDC anodes were weaker than the NiO-GDC anode. The low shrinkage percentages of the composites of nickel oxide and the YSZ-GDC solid solution resulted in a higher porosity structure with lower mechanical strength.

Figure 4 shows the electrical conductivity of the Ni-YSZGDC anode microtubes from room temperature to 700°C in 20%H₂ – 80%N₂. The temperature dependence of electrical conductivity was negative for the all samples. The ionic conductivity of the YSZ-GDC solid solution was lower than those of pure YSZ and GDC [12]. However, the metallic behavior supports that electron conduction through nickel network is dominant for the Ni-YSZGDC anodes. The electrical conductivities were the following sequence; Ni-25YSZ75GDC < Ni-50YSZ50GDC < Ni-100YSZ < Ni-100GDC. The low shrinkage percentages of the composites of nickel oxide and the YSZ-GDC solid solution resulted in lower electrical conductivity.

3.2. Electrochemical properties of Ni-YSZGDC anodes

Figure 5 shows the current-voltage and power characteristics for the microtubular cells with the Ni-YSZGDC anodes at 600°C in 20%H₂ – 3%H₂O – 77 %N₂ / air. The maximum power density was 0.16 W.cm⁻² for the cell with the Ni-100YSZ anode. While the power density increased to 0.17 W.cm⁻² for the cell with the Ni-50YSZ50GDC anode, it decreased with further increases in GDC content. Figure 6 shows the Nyquist plot of AC impedance for the microtubular cells with the Ni-YSZGDC anodes at 600°C in 20%H₂ – 3%H₂O – 77%N₂/ air measured between the anode and cathode at OCV. The ohmic losses, which were derived from the intersections of the impedance arcs at high frequency with the real axis, for Ni-25YSZ75GDC and Ni-50YSZ50GDC anodes increased by 0.05-0.07 Ω.cm² compared to Ni-100YSZ and Ni-100GDC anodes because of low ionic conductivity for YSZ-GDC solid solution [12]. While the impedance at high frequencies was relatively large for the Ni-100YSZ anode as shown in the Bode plots in Figure 7, it decreased significantly for the anodes containing GDC. On the other hand, a new impedance response appeared at low frequency for the Ni-100GDC anode.

Because of the overlaps of the anode and cathode polarization responses, DRT analysis was applied to this impedance data to separate each response – the results are shown in Figure 7. Six peaks were detected by the DRT analysis for all cells. It was previously reported that the peaks at 10-20 kHz (P_1^c) and 20-30 Hz (P_2^c) were ascribed to the ionic conduction process in the LSCF bulk and adsorption/desorption process on the LSCF surface, respectively, on the LSCF-GDC cathode for the microtubular cells [35]. The peaks of P_1^c and P_2^c seem to be overlapped with those of P_1^a and P_2^a for Ni-100YSZ. In consideration of these reasons, the cathode polarization resistances of P_1^c and P_2^c were almost the same among the cells. The DRT peaks at 2-4 kHz (P_1^a) and 200-300 Hz (P_2^a), which were ascribed to the fuel oxidation process [17]. Figure 8 show the inverse resistance (R_p^{-1}) and capacitance (C_p) for the processes of P_1^a and P_2^a as a function of GDC/(YSZ+GDC) molecular ratio for the Ni-YSZGDC anodes. For porous electrode in SOFCs, the R_p^{-1} and C_p are almost proportional to the active reaction area and the closely contacted electrode/electrolyte interface area, respectively [36]. The values of R_p^{-1} and C_p for Ni-100GDC were twice as large as those for Ni-100YSZ. Furthermore, the R_p^{-1} and C_p indicated the highest values for Ni-50YSZ50GDC or Ni-25YSZ75GDC anode. This means that the Ni-YSZGDC composite anodes have more active reaction area than the Ni-YSZ anode. The DRT peak at 1-2 Hz (P_3^a) was ascribed to the gas diffusion process in Ni-YSZ anodes [26]. The resistance of P_3^a was low for Ni-100GDC, which might be caused by the change in anode morphology. The peak around 0.1 Hz (P_4^a) was observed only for the GDC-containing anodes. The capacitances of P_4^a for Ni-50YSZ50GDC, Ni-25YSZ75GDC and Ni-100GDC were 7.61, 5.75 and 11.9 F cm⁻², respectively. The large pseudo-capacitance suggests the peak of P_4^a is ascribed to the oxygen nonstoichiometric variation process in GDC [37]. The oxygen nonstoichiometric variation process change, of course, is caused by the oxygen potential change due to the electrochemical reaction in the GDC-containing anodes.

3.3.FIB-SEM observation of Ni-YSZ and Ni-GDC anodes

Both the anode composition (*i.e.*, GDC content) and microstructure are expected to affect the anode activation and concentration polarization. Thus, in order to better understand the role of GDC content in anode characteristics, three-dimensional microstructure quantification was carried out with FIB-SEM. The Ni-100GDC anode was selected for 3D analysis because it appears to be typical of the GDC-containing anodes, which all behaved similarly electrochemically. Furthermore, Ni-100GDC is the most promising GDC-containing anode in terms of mechanical properties. Ni-100YSZ was also analyzed to provide a baseline for comparison. The reconstructed anode microstructures are presented in Figure 9. The TPB density is also rendered in Figure 10. Microstructural information obtained from the reconstruction is listed in Table 2.

Figure 11 shows the size distributions derived from the 3D data. Ni, YSZ, and GDC show clear single peaks in the feature size distributions below 1 μm , whereas pores show a single peak below 1 μm along with some isolated larger features. The clear peak at smaller sizes mainly corresponds to pores created by the reduction of NiO to Ni, whereas the larger features result from the pore former. Both the small and larger pores are readily seen in Figure 9. The random nature of the pore size distribution at larger sizes is a direct result of the smaller number of large pores sampled in the measured volumes.

The present anodes present a problem for accurate tomographic measurements because there are two much-different length scales – the $\sim 10 \mu\text{m}$ pores and the sub-micron Ni, YSZ/GDC, and pores. This problem did not arise in prior work on 3D tomography of Ni-YSZ anodes [22], where all features had a similar size. Specifically, the average particle size to voxel size ratio should be large enough to accurately image the particles and thereby obtain small

errors in the microstructural parameters derived from the data [38]. Prior calculations indicate that the ratio of ~16 in the present data sets yields an ~2% error [32]. In addition, the length of the reconstructed volume has to be at least 15 times the average particle size in order to keep the statistical error below 3% [39]. This condition is satisfied for the nickel and YSZ particles, as well as the smaller pores, where the ratio is 17 for Ni-100GDC and 19 for Ni-100YSZ, as well as the smaller pores. However, the larger pores present a ratio of reconstruction length to particle size of ~3, indicating substantial statistical error. That is, there are too few pores within the measured volumes to provide statistically significant results. For example, if a given measured volume has fewer large pores than the average, the overall pore volume will be too small while the solids volumes will be too large.

In order to address this problem, a procedure was developed to correct the statistical errors in the parameters obtained from the 3D data sets. In order to obtain a statistically accurate large-pore volume, large areas of electrode were imaged in two dimensions and stereological analysis used to determine the large-pore volume fraction, determined to be 25% for both the Ni-100YSZ and Ni-100GDC anodes. The measured large-pore volumes in the 3D data sets, 22.7% for Ni-100-GDC and 15.5% for Ni-100YSZ (Table 2), were corrected upwards to match the average value, 25%. The other microstructural parameters were corrected proportionately. Note that the larger pores were quantified separately from the smaller pores using an expansion-dilation method [39]. The small-pore volume fractions were estimated to be 29.7% and 22.6% for the Ni-100GDC and the Ni-100YSZ, respectively. The change in YSZ or GDC tortuosity was less than 10 % after the correction. The connectivity and TPB were almost unchanged by the correction, since no anisotropy was observed for Ni-100YSZ and Ni-100GDC in this study. The corrected data in Table 2 are believed to be more statistically accurate representations of the actual electrodes.

The 3D reconstructed data in Figure 9 suggests that the pore distribution is quite different between Ni-100YSZ and Ni-100GDC. The small-pore volume fraction was larger, and the pore tortuosity smaller, for the Ni-100GDC compared to the Ni-100YSZ as shown in Table 2. This is consistent with the decrease in the gas diffusion resistance (DRT peak P_3^a in Figure 7) for Ni-100GDC.

Table 2 also indicates that the TPB density in the Ni-GDC anode is ~ 15% lower than that in the Ni-YSZ anode. Despite this, the Ni-GDC anode shows a lower resistance associated with the anode impedance responses at ~ 100 – 1000 Hz (P_1^a and P_2^a in Figure 7), which are believed to be the fuel oxidation processes occurring at TPBs. This is probably explained by a lower characteristic resistance associated with Ni-GDC-fuel TPBs compared to Ni-YSZ-fuel TPBs, because GDC is a mixed ionic-electronic conductor and reactions may occur on the oxide surface near the TPB. Although there appear to be no Ni-GDC TPB resistance measurements available in the literature, it is often observed that SOFCs with Ni-GDC anodes provide low polarization resistance at $\leq 600^\circ\text{C}$ [40], whereas SOFCs with Ni-YSZ anodes generally show much larger resistance [15]. Kikuchi et al. [41] reported that the anode activation polarization for Pt-samaria doped ceria (SDC) patterned electrode was estimated to be almost 10 times smaller than that for Pt-YSZ with the same TPB length.

The present active TPB density is similar to values previously measured for anode functional layers in anode-supported planar SOFCs [27]. However, the presence of larger pores in the functional layer region in these microtubular cells reduced the percentage of TPB density somewhat compared to planar SOFC anode functional layers that typically do not contain pore formers. Thus, inserting a functional anode layer without pore formers can improve the percentage of active TPBs, and thereby improve the performance of anode-supported microtubular SOFCs.

4. Conclusions

In this study, the electrochemical and microstructural properties of Ni-YSZGDC composite anodes in anode-supported microtubular SOFCs were investigated. It was confirmed with XRD that the YSZ-GDC solid solution was formed after mechanical mixing and sintering at 1400°C for the Ni-YSZGDC composite anodes. The Ni-YSZGDC composite anodes had relatively low mechanical strength and electrical conductivity, due to reduced sintering compared to Ni-YSZ and Ni-GDC. The anodes containing GDC showed high electrochemical activities for the fuel oxidation process, even though measured TPB densities were lower for Ni-GDC, presumably because of a low Ni-GDC-fuel TPB resistance. The gas diffusion polarization was lower for the GDC-containing anodes compared to Ni-YSZ, which was consistent with a higher small-pore volume and lower pore tortuosity measured for the Ni-GDC anode. Overall, the highest maximum power density was observed for the cell with the Ni-50YSZ50GDC anode.

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Table & Figure captions

Table 1 Radial crashing strength of the NiO-YSZGDC anode microtubes evaluated by a method based on ISO-2739 at room temperature in air.

Table 2 Summary of the measured 3D structural data. Small pores were mainly created by the reduction of NiO to Ni, whereas the large features result from the pore former.

Figure 1 XRD patterns of the Ni-YSZGDC anodes after reduction treatment measured with CuK α radiation at room temperature in air.

Figure 2 Lattice parameters of nickel and oxide as a function of GDC/(YSZ+GDC) molecular ratio for the Ni-YSZGDC anodes.

Figure 3 Length changes in the NiO-YSZGDC anode microtubes during heating and cooling between room temperature and 1400°C in air.

Figure 4 Electrical conductivity of the Ni-YSZGDC anode microtubes from room temperature to 700°C in 20 %H₂-80 %N₂.

Figure 5 Current-voltage and power characteristics for the microtubular cells with the Ni-YSZGDC anodes at 600°C in 20 %H₂-3 %H₂O-77 %N₂/air.

Figure 6 Nyquist plot spectra for the microtubular cells with the Ni-YSZGDC anodes at 600°C in 20 %H₂-3 %H₂O-77 %N₂/air.

Figure 7(a-b) AC impedance and (c) DRT spectra for the microtubular cells with the Ni-YSZGDC anodes at 600°C in 20 %H₂-3 %H₂O-77 %N₂/air measured between the anode and cathode under OCV state.

Figure 8 Inverse resistance and capacitance for the processes of P_1^a and P_2^a as a function of GDC/(YSZ+GDC) molecular ratio for the Ni-YSZGDC anodes.

Figure 9 3D Reconstruction of the anode functional layer for the Ni-100GDC (left) and Ni-100YSZ (right) anodes.

Figure 10 3D Reconstruction of the TPB density for the Ni-100GDC (left) and Ni-100YSZ (right) anodes.

Figure 11 Particle Size Distribution for the for the Ni-100GDC and Ni-100YSZ anodes.

Tables

Table 1

NiO-100YSZ	115.3 ± 14.5 MPa
NiO-50YSZ50GDC	48.0 ± 4.1 MPa
NiO-25YSZ75GDC	38.0 ± 11.2 MPa
NiO-100GDC	72.2 ± 3.8 MPa

Table 2

	Raw Data		Corrected Data	
	Ni-100GDC	Ni-100YSZ	Ni-100GDC	Ni-100YSZ
Total Reconstructed Volume (μm^3)	1204	1491	1204	1491
Volume fraction Ni (%)	24.6	27.2	23.8	24.0
Volume fraction YSZ / GDC (%)	22.3	32.4	21.5	28.4
Volume fraction Small-pore (%)	30.3	24.8	29.7	22.6
Volume fraction Large-pore (%)	22.7	15.5	24.9	24.9
YSZ / GDC Tortuosity	1.7	1.3	1.7	1.4
Pore Tortuosity	1.2	1.3	1.2	1.3
Ni Connectivity	99.5	98.3	99.5	98.3
YSZ / GDC Connectivity	92.5	99.3	92.5	99.3
Pore Connectivity	99.6	96.7	99.6	96.7
Total TPB density (μm^{-2})	3.09	3.62	3.09	3.62
% Active TPB	78	78	78	78

Figures

Fig1

Fig2

Fig3

Fig4

Fig5

Fig6

Fig7

Fig8

Fig9

Fig10

Fig11