

Synthesis and characterization of conjugated core-shell structured YSZ@Ni-GDC anode materials for solid oxide fuel cells

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Yttria-stabilized zirconia (YSZ) powders covered by conjugated catalysts of Ni-Ce_{0.8}Gd_{0.2}O_{1.9} (GDC) were synthesized by glycine nitrate process. The conjugated core-shell structured YSZ@Ni-GDC anodes exhibited better electrochemical performance than conventionally mixed Ni-YSZ anode. The core-shell structure extends the triple-phase boundary length, and GDC as a co-catalyst provides catalytic activity. The maximum power density of a single cell with the NGY-601030 anode exhibited the highest maximum power density of 324.9 mW/cm² at 800 °C, which is higher than that of the conventionally mixed Ni-YSZ anode (212.7 mW/cm²).

Key words: Solid oxide fuel cell, Anode, Core-shell, Triple-phase boundary.

Introduction

One of the main advantages of solid oxide fuel cells (SOFCs) is the use of non-precious metal or oxide catalysts, due to their high operational temperature [1-3]. The state-of-the-art anode material for SOFC anode is Ni-yttria stabilized zirconia (YSZ) [4, 5]. Ni plays the main role of catalyst for oxidation of the fuel, and YSZ acts as a support to hold the porous structure, and prevent Ni coarsening [5]. Additionally, YSZ also acts as an ionic conductor, which transfers oxygen ions to the reaction site to finish the catalytic cycle. The hydrogen oxidation reaction can only occur at the limited site, which is called the triple-phase boundary (TPB), where the electrolyte, gas, and electrically connected electrode meet [6]. Therefore, extension of the TPB can enhance performance. Microstructure and connectivity of the composite anode must be controlled to extend the TPB [7-8].

Many research works have been carried out in order to extend the TPB length, such as the use of nano-sized particles to increase the surface area [9-12]. Although nano-sized anode particles can enhance the electrochemical performance, the nano-sized particles also agglomerate easily. This grain growth of nano-sized catalysts causes reduction of the reaction sites, and leads to consequent reduction in performance [13, 14]. In this regard, we adopted the conjugated core-shell structure, where the YSZ core and conjugated

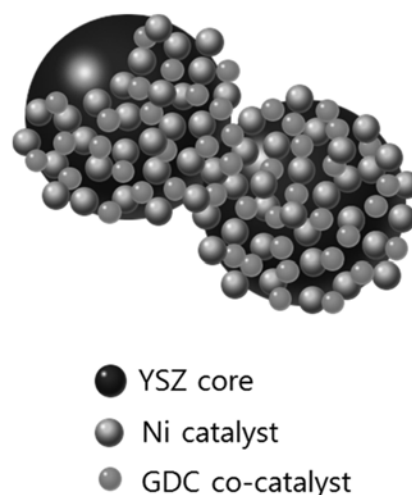


Fig. 1. A schematic of the core-shell structure, with YSZ core and conjugated Ni-GDC shell. anodes in humidified H₂ at 800 °C.

Ni-Ce_{0.8}Gd_{0.2}O_{1.9} (GDC) shell act as an anchor and a catalyst, respectively. The conjugated core-shell structure of YSZ@Ni-GDC is illustrated in Fig. 1. YSZ core can suppress the grain growth of catalysts, and provide enough channels for the oxide ion to pass. In this work, the conjugated core-shell structured YSZ@NiO-GDC powders were synthesized by glycine nitrate process (GNP). Morphology, phase, and electrochemical performance of the conjugated core-shell structured anodes were investigated with various volume ratios of components.

Experimental Procedures

Conjugated core-shell structured YSZ@NiO-GDC

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powders were synthesized by glycine nitrate process (GNP). The starting materials of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 98%), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa aesar, 99% metal basis), $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa aesar, 99.9% REO), and glycine (Alfa aesar, 99%) were dissolved in deionized water. 8-YSZ ($\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{2-\delta}$, Tosoh) as a core seed was added into the prepared solution. Ultrasonication was carried out to disperse the core seed. The prepared slurry was then heated at 240 °C to evaporate excess water, and started the combustion reaction. Ash remained after the combustion. The ash was calcined at 600 °C for 2 hrs to remove the residues of the combustion reaction. The calcined powders were then ball-milled with zirconia ball and ethanol for 24 hrs, followed by sieving process.

Phase analysis of the synthesized powders was identified by X-ray diffraction (XRD) with a scan rate of 4 °/min in the 2θ range of 20 ° to 80 °. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS or EDX) were used for the confirmation of the core-shell structured morphology. Particle size distribution of the as-synthesized powders was analyzed by ZETA-potential and particle size analyzer (ELS-6000, Otsuka Electronics). Electrochemical performance of the anode materials were evaluated by AC impedance analysis and current-voltage (I-V) test.

Electrolyte supported-type single cells were used for evaluation of the electrochemical performance. The electrolyte supporter was prepared with GDC pellets of 0.5 mm thickness, sintered at 1500 °C for 4 hrs. The anode and reference electrodes were deposited by screen-printing method. The paste of anode for screen-printing was made by mechanical mixing the prepared powder and ink vehicle (Heraeus V006). The weight ratio of powder to vehicle was 60 : 40 wt.%. The reference electrode at the anode side used the same composition as the anode, and was also printed next to the anode. The anode and the reference electrode printed on the GDC electrolyte pellets were sintered at 1250 °C for 2 hrs. The geometrical area of the anode and the reference electrode were 0.25 cm² and 0.125 cm², respectively. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}\text{-Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (BSCF-GDC) composite material was used as a cathode. The BSCF-GDC powder was synthesized by a modified sol-gel combustion method [15]. The paste of cathode was prepared in the same manner as the anode, and screen-printed on the GDC pellet at the opposite side of the anode. The printed cathodes were sintered at 1050 °C for 2 hrs. Platinum mesh and wire were attached with platinum paste on both electrodes and the reference for current collecting, and then fired at 950 °C for 2 hrs for adhesion. A PYREX® ring and paste were used for sealing between the alumina tube and GDC electrolyte supporter at the fuel side. Humidified H₂ (3% H₂O at room temperature) fuel and dry air were supplied to the anode and cathode side,

respectively, with a flow rate of 100 cc/min. AC impedance spectroscopy was carried out with a potentiostat (SP150, Biologic SAS, France) at 700, 750, and 800 °C in humidified H₂, respectively. The applied frequency was in the range of 1 mHz to 1 MHz, with a voltage amplitude of 10 mV. I-V measurement of the single cells was carried out, with the same configuration as the AC impedance analysis.

Results and Discussion

Compositions of the conjugated core-shell structured YSZ@Ni-GDC were designed in order to verify the effect of volume ratio of the components. The amount of Ni was fixed to 60 vol.% to provide the percolated structure, and the amount of core was held to at least 30 vol.%, in order to sustain the core-shell structure. Since the Ni content was fixed, the amount of core would decrease as the amount of GDC co-catalyst increased. The compositions of the conjugated core-shell structured YSZ@Ni-GDC with the fixed Ni (60 vol.%) and various GDC content are listed in Table 1. Conventional Ni-YSZ powder (Ni : YSZ = 60 : 40 vol.%) was also prepared by ball-milling process, in order to compare the electrochemical performance.

Fig. 2 shows XRD patterns of the as-synthesized

Table 1. Synthesized compositions and abbreviations of the YSZ@Ni-GDC composite anode materials.

Anode material	Composition		
	Shell		Core
	Ni (vol.%)	GDC (vol.%)	YSZ (vol.%)
NGY-600040	60	0	40
NGY-600535	60	5	35
NGY-601030	60	10	30

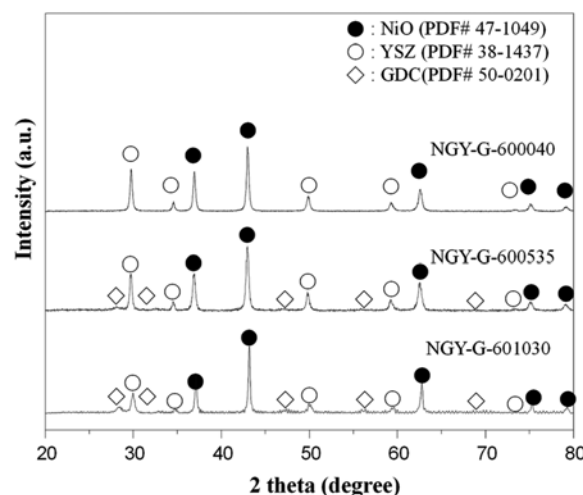


Fig. 2. XRD patterns of the as-synthesized YSZ@NiO-GDC powders calcined in air atmosphere at 600 °C for 2 hrs.

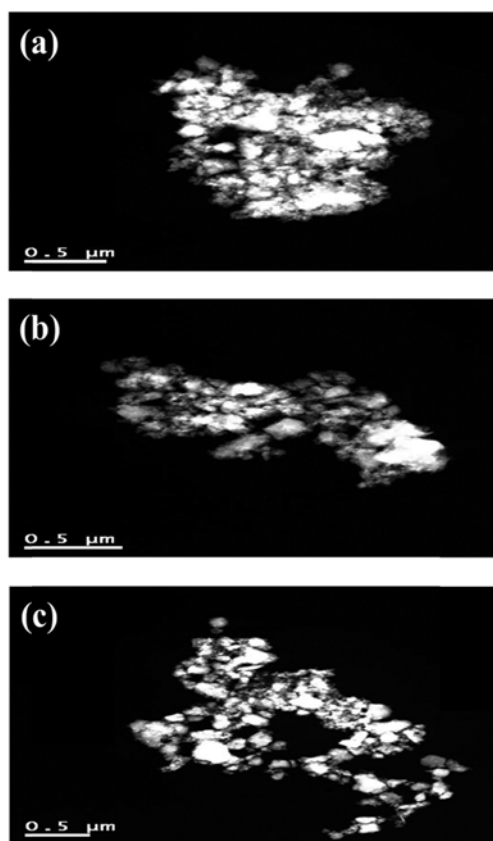


Fig. 3. TEM images of the conjugated core-shell structured YSZ@NiO-GDC powders with various compositions; (a) NGY-600040, (b) NGY-600535 and (c) NGY-601030.

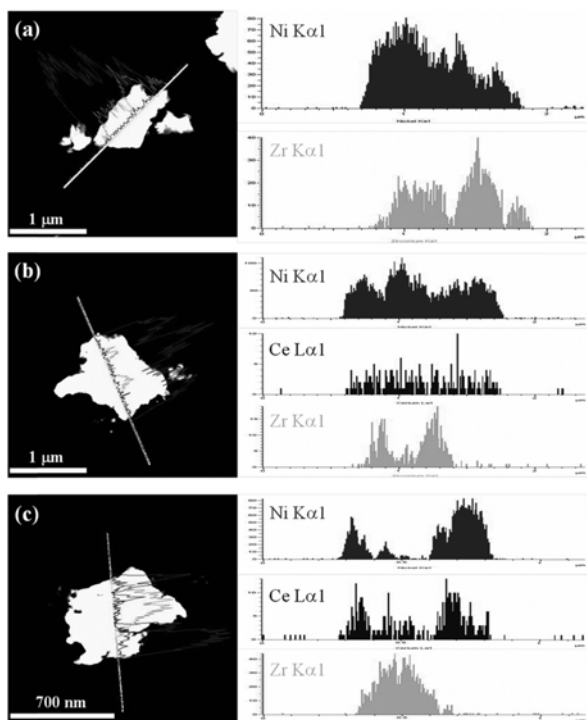


Fig. 4. EDS line-scanning data of the conjugated core-shell structured YSZ@NiO-GDC; (a) NGY-600040, (b) NGY-600535 and (c) NGY-601030.

conjugated core-shell structured YSZ@NiO-GDC powders with the fixed Ni (60 vol.%) and various GDC content. All the patterns match with NiO (JCPDF No. 47-1049), YSZ (JCPDF No. 38-1437), and GDC (JCPDF No. 50-0201), respectively, without any trace of impurity or reaction products.

Fig. 3 shows TEM images of the as-synthesized YSZ@NiO-GDC powders with conjugated core-shell structure. The bright colored parts increase with an increase in the amount of core. Therefore, it can be concluded that the bright colored particles corresponding to the YSZ core are surrounded by the cloud-like grey colored particles corresponding to the NiO-GDC shell. In order to confirm the core-shell structure and the conjugated NiO-GDC, EDS line-scanning was carried out. Based on the EDS line-scanning data in Fig. 4, both Ni and Ce spectra show almost the same patterns and positions. This indicates that NiO and GDC particles are conjugated. Meanwhile,

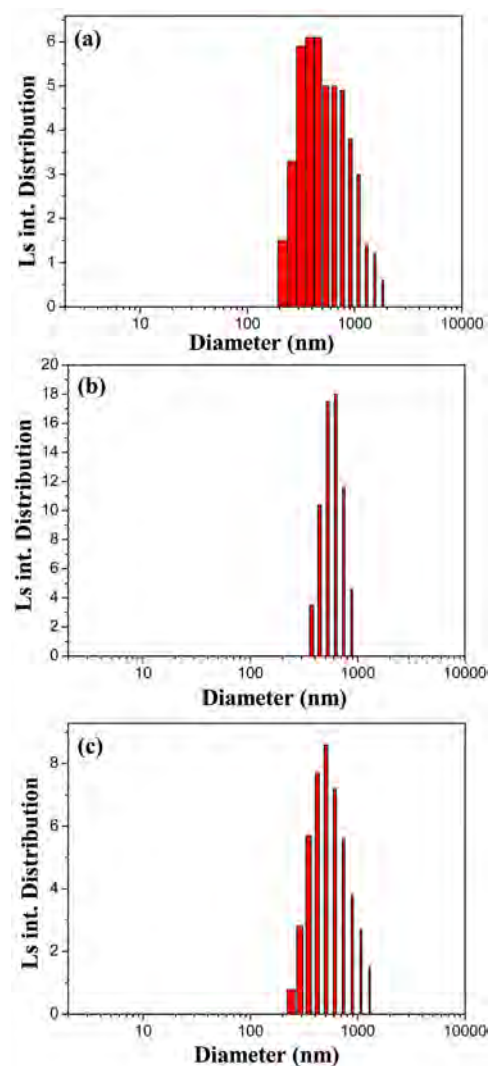


Fig. 5. Particle size distribution data of the conjugated core-shell structured YSZ@NiO-GDC; (a) NGY-600040, (b) NGY-600535 and (c) NGY-601030.

Ni and Ce spectra are spread wider than the YSZ spectrum, which means that the YSZ core is covered by the conjugated NiO and GDC particles. However, a large amount of core decreased the shell thickness and increased the overall size of the core, because a large amount of YSZ core seeds may suppress the dispersion of YSZ particles in the precursor solution, leading to agglomeration of the YSZ, and consequent increase in the size of core particles.

Meanwhile, there is no significant difference in the overall particle size distribution, as shown in Fig. 5. All compositions have a similar particle size, of less than 1 μm . However, the powders with a large amount of core show relatively broader particle size distribution, and larger particle size.

The typical AC impedance spectra of the conjugated core-shell structured YSZ@Ni-GDC anode with a GDC electrolyte at 800 $^{\circ}\text{C}$ are shown in Fig. 6. An equivalent circuit, consisting of an inductor (L), a resistor (R_o), and two RQ elements (R_1Q_1 and R_2Q_2), was employed to fit the impedance data. The left intercept with the impedance arc on the $\text{Re}(Z)$ real axis at high frequencies corresponds to the ohmic resistance, R_o , and the right intercept on the $\text{Re}(Z)$ real axis indicates the total resistance, R_{tot} . The polarization resistance, R_p , is the overall size of the arcs ($R_{\text{tot}} - R_o$). The calculated ohmic and polarization resistance values are listed in Table 2.

Since the amount of Ni catalyst for each composition is the same at 60 vol.%, the difference in electrochemical performance may be due to the morphology or the GDC co-catalyst effect. All the conjugated core-shell structured YSZ@Ni-GDC anodes exhibited better electrochemical performance than the conventionally mixed Ni-YSZ anode. In particular, compared with the NGY-600040 anode and Ni-YSZ anode with the same composition, the NGY-600040 anode showed much lower anode polarization. This may be due to the good dispersion of Ni onto the YSZ core, which results in the extension of the TPB length. The ohmic resistance

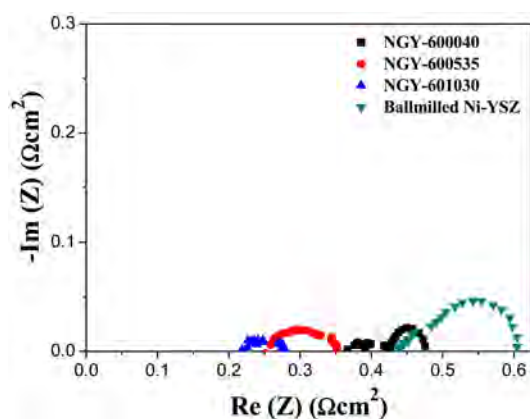


Fig. 6. Typical AC impedance spectra of the conjugated core-shell structured YSZ@Ni-GDC anodes and the conventionally mixed Ni-YSZ anodes in humidified H_2 at 800 $^{\circ}\text{C}$.

Table 2. Ohmic and polarization resistances of the YSZ@Ni-GDC composite anode materials in humidified H_2 at 800 $^{\circ}\text{C}$.

Anode material	Area specific resistance ($\Omega \cdot \text{cm}^2$)	
	R_o	R_p
NGY-600040	0.356	0.101
NGY-600535	0.251	0.085
NGY-601030	0.213	0.062
Ni-YSZ	0.434	0.171

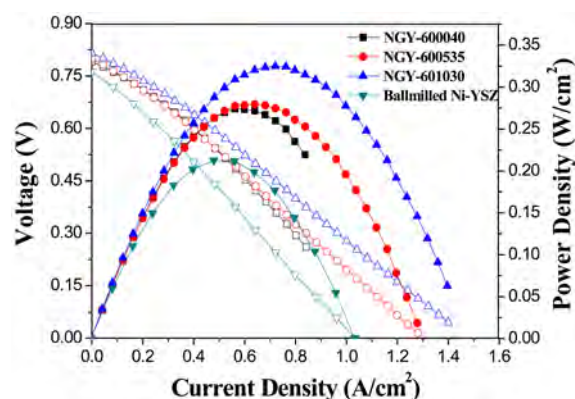


Fig. 7. Comparison of the I-V curves (open symbols) and power densities (closed symbols) of the conjugated core-shell structured YSZ@Ni-GDC anodes at 800 $^{\circ}\text{C}$.

of YSZ@Ni-GDC anodes increased with the amount of YSZ core, which is due to the lack of Ni percolation, which was hindered by large YSZ core particles. On the other hand, the polarization resistance values decreased with an increase in the GDC content in the shell. GDC is well known as a mixed ionic/electronic conductor in a reducing atmosphere, and may therefore provide certain catalytic activity.

The anode reaction in SOFCs is considered as a multiphase catalytic reaction, including gas diffusion, surface exchange (the adsorption/dissociation of hydrogen molecules), bulk diffusion of oxide ions, and charge transfer. Each reaction can be a rate-determining step. Considering surface exchange and bulk diffusion, it is clear that the conjugated GDC, which is a mixed ionic/electronic conductor in a reducing atmosphere, may enhance the overall catalytic activity of the composite anode. Moreover, GDC has much higher ionic conductivity than YSZ. Thus introduction of GDC to the Ni-YSZ based anode has a positive effect on the electrical performance.

The cell voltages and power densities with current density are also shown in Fig. 7. The open circuit voltages at 800 $^{\circ}\text{C}$ were 0.77 ± 0.02 V, due to the reduction of GDC electrolyte in a reducing atmosphere. The maximum power density of a single cell with the NGY-600040 anode was 274 mW/cm^2 , which was higher than that of single cells with the conventionally mixed Ni-YSZ anode (212.7 mW/cm^2). This result is consistent with the trend observed in the AC

impedance data. The maximum power density of the conjugated core-shell structured YSZ@Ni-GDC anode increased with the amount of GDC in the shell. The highest maximum power density of 323.9 mW/cm² was achieved at the NGY-601030 anode. Based on these results, it can be clear that the conjugated core-shell structure of YSZ@Ni-GDC is effective in enhancing the electrochemical performance to provide the extended TPB, as well as additional catalytic activity from the conjugated co-catalyst of GDC.

Conclusions

The conjugated core-shell structured YSZ@NiO-GDC anode powders were synthesized by GNP combustion method with YSZ core seed. Nano-crystalline NiO and GDC particles were conjugated on the YSZ core. The conjugated core-shell structured YSZ@Ni-GDC anodes showed better electrochemical performance than the conventionally mixed Ni-YSZ anode. The core-shell structure extends the TPB length, and GDC as a co-catalyst provides catalytic activity. It is confirmed that an increase in the GDC content decreased the anode polarization resistance, and consequently improved the overall single cell performance.

Acknowledgments

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