Characterization of Spherical NiO-YSZ Anode Composites for Solid Oxide Fuel Cells Synthesized by Ultrasonic Spray Pyrolysis

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ABSTRACT

Spherical NiO-YSZ particles were synthesized by ultrasonic spray pyrolysis (USP). The morphology of the synthesized particles can be modified by controlling parameters such as precursor pH, carrier-gas flow-rate, and temperature of the heating zone. The synthesized spherical NiO-YSZ particles have rough surface morphology at high carrier-gas flow-rates due to rapid gas exhaustion and insufficient particle ordering. The Ni-YSZ cermet anode synthesized by ultrasonic spray pyrolysis at a flow rate of 1 L/min, with precursor solution at pH4, showed a higher maximum power density of 256 mW/cm² compared to a conventionally mixed Ni-YSZ anode (185 mW/cm²) at 800°C. While the area-specific resistance of conventionally mixed Ni-YSZ anodes increases gradually with operation time (indicating performance degradation), the Ni-YSZ anode synthesized by USP does not exhibit any performance degradation, even after 500 h.

Key words : Solid oxide fuel cell, Anode material, Ultrasonic spray pyrolysis, Electrochemical performance, Long-term stability

1. Introduction

Solid-oxide fuel cells (SOFCs) are known as promising energy conversion systems due to their high efficiency. In addition, due to the high operating temperature of the fuel cells, hydrocarbon fuels can be used without external reforming. The primary reaction at the SOFC anode is the oxidation of a fuel. Nickel provides high catalytic activity for the oxidation of hydrogen gases to hydrogen ions. Usually, nickel is used with electrolyte materials such as yttria-stabilized zirconia (YSZ). The common term for this composite material is ‘ceramic metal composite’ (cermet). YSZ used in a Ni-YSZ cermet anode not only reduces the thermal expansion mismatch with the electrolyte but also provides ionic conductivity.

The oxidation reaction of the fuel at the anode occurs at the triple phase boundary (TPB—the three phase interface of gas, ionic conductor, and catalyst).¹⁾ Therefore, extension of the TPB length is the most important step for improving SOFC performance. Kinetically, a large TPB area can provide high performance. However, Ni in the Ni-YSZ cermet anode easily aggregates during long-term operation at high temperature. Such coarse Ni particles may reduce the TPB area. Moreover, the reduction of porosity due to the coarsening phenomenon suppresses gas diffusion. In this regard,

restraining Ni aggregation has been the focus of a great deal of research(e.g., infiltration of catalysts into a porous anode support, mechano-chemical mixing, and core-shell structure).^{2,3)} Meanwhile, the TPB length in the Ni-YSZ cermet anode is strongly influenced by initial morphological factors such as the grain size, connectivity between grains, and porosity. Therefore, the morphology of the starting powder is an important factor in control of the final microstructure of the cermet anode, which affects the overall electrochemical performance.

Spray pyrolysis is a popular synthesis method for producing spherical and uniform ceramic powders.⁴⁾ Ultrasonic spray pyrolysis (USP), in particular, allows modification of the powder morphology easily by controlling several parameters, including solution preparation, atomizing frequency, flow rate, and heating temperature.⁵⁻⁷⁾ Compared with powder particles prepared conventionally by solid state reaction, the powders synthesized using USP have a narrower particle-size distribution, a controllable particle-size range of 0.1–100 μm, and high purity. Moreover, good dispersion of the spherical particles, with a narrow particle-size distribution is very easy to achieve in any solvent, for preparation of stable paste or slurry, and may suppress abnormal grain growth during the high temperature sintering step.⁸⁾

In this study, spherical NiO-YSZ composite powder particles were synthesized using ultrasonic spray pyrolysis (USP) with various precursor pH and carrier-gas flow-rates. Morphology, phase, and performance of the anodes were investigated.

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2. Experimental Procedure

Spherical NiO-YSZ composite powder particles were synthesized by ultrasonic spray pyrolysis using the multi-zone furnace illustrated in Fig. 1. $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Alfa Aesar, 98%), $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Daejung Chemical), and $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Kanto Chemical) were used as starting materials. All compositions of the NiO-YSZ powders were designed with 60 vol% of Ni and 40 vol% of YSZ after final reduction of NiO to Ni. A calculated amount of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in de-ionized water to make up the 0.25 M precursor solution. In another beaker, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ for YSZ, were also dissolved in de-ionized water. Nitric acid was added into the nitrate solutions to adjust the pH. The prepared Ni and YSZ precursor solutions were mixed by stirrer. The mixed solution was atomized to a mist by an ultrasonic atomizer. The generated mists were then carried into the multi-zone furnace with 200°C , 400°C , 800°C , and 1000°C heating zones by a carrier-gas of air at flow rates of 1 L/min, 3 L/min, and 5 L/min. During passage through the furnace, the mists decomposed and the decomposed powders collected on filter paper. The collected powder particles do not need any further heat treatment.

The decomposition and reaction temperatures of the precursors were determined by thermogravimetric analysis (TGA, Q600, TA instrument Ltd., USA). Phase analysis for the as-synthesized powders was carried out by X-ray diffraction (XRD). The morphology was investigated by scanning electron microscopy (SEM) and field emission scanning electron microscopy (FE-SEM) with energy-dispersive X-ray spectroscopy (EDX).

Electrolyte-supported-type single cells were used for the evaluation of electrochemical performance. $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) electrolyte pellets 0.5 mm thick were sintered at 1500°C for 4 h in air. The anode and reference electrodes were deposited by the screen-printing method. The anode paste used for screen-printing was made by mechanical mixing of the prepared powder and an ink vehicle (Heraeus V006). The weight ratio of powder to ink vehicle was 60 : 40 wt%. A reference electrode with the same composition as the anode was also printed next to the anode. The anode and reference electrodes printed on the GDC electrolyte pellet were sintered at 1250°C for 2 h. The geometrical area of

the anode and the reference electrode was 0.25 cm^2 and 0.125 cm^2 , respectively. The cathode was the composite material of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}\text{-Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (BSCF-GDC). The BSCF-GDC powder was synthesized by a modified sol-gel combustion method.⁹⁾ The cathode paste was prepared in the same manner as for the anode, and then printed on the GDC pellet, on the opposite side from the anode. The printed cathode was sintered at 1050°C for 2 h.

The electrochemical performance of the anode materials was evaluated by AC impedance analysis and a current-voltage (I-V) test, with a single cell. A PYREX[®] ring and paste were used for sealing between the alumina tube and the GDC electrolyte at the anode side. Humidified hydrogen (3% H_2O at room temperature) and dry air were supplied to the anode and cathode sides, respectively, with a flow rate of 100 mL/min. NiO in the NiO-YSZ anode was reduced to Ni *in-situ* during the single-cell test. AC-impedance spectroscopy was carried out with a potentiostat (SP150, Biologic SAS, France) which analyzes frequency response at 800°C in humidified H_2 . The applied frequency was in the range of 1 mHz to 1 MHz with a voltage amplitude of 10 mV.

3. Results and Discussion

A TGA plot of the mixed-precursor solution of Ni acetate, Y nitrate, and Zr nitrate-oxide-dehydrate, is shown in Fig. 2. The weight loss around 220°C corresponds to the decomposition of Ni acetate, and the weight loss around 394°C corresponds to the decomposition of Y and Zr nitrates. Based on these results, the first, second, and third heating zones were set at 200°C , 400°C , and 800°C , respectively. Since particle ordering is critical to forming spheres, the heating zone at 800°C was extended to provide enough time for the particles to stay in the heating zone for a sufficient interval. The temperature of the last zone was held at 1000°C in order to get crystalline YSZ. It is well known that YSZ exists in an amorphous phase below 1000°C . Meanwhile, two different pH values (2 and 4) were used for the precursor solution, because precipitation occurred when pH was over 4.

Fig. 1. Illustration of ultrasonic spray pyrolysis (USP) with multi-zone furnace.

Fig. 2. TGA data of the precursor solution of Ni acetate, Y nitrate, and Zr nitrate oxide dehydrate mixture.

XRD patterns of the as-synthesized NiO-YSZ powders are shown in Fig. 3. All of the powders showed a single phase without any impurities, even without any post-heat treatment. All peaks of the as-synthesized powders well matched those of NiO (JCPDS card no. 47-1049) and YSZ (JCPDS card no. 38-1437), respectively. The crystallite sizes calculated by Scherrer's equation are listed in Table 1. It was confirmed that the as-synthesized powders consisted of very small crystallites of NiO and YSZ (~ 10 nm). Interestingly, there was no significant difference in the size of the NiO and YSZ crystallites.

Figure 4 shows SEM micrographs of the as-synthesized NiO-YSZ particles. All the particles have spherical shapes of less than $1\ \mu\text{m}$ diameter. The particle size of the as-synthesized powder decreased, with increasing pH of the precursor solution. Interestingly, the powders synthesized at pH4 have a rather rough surface morphology while those synthesized at pH2 were hollow spheres with a smooth surface. Kawano *et al.* reported that differences in the pH of the precursor solution affects the chemical environment in the vicinity of the cations, consequently leading to differences in the surface morphology of the as-synthesized powder.⁷⁾ In the high pH range, acetate counter ions were located close to cations (e.g., Ni^{2+} , Zr^{4+} , and Y^{3+}) and reacted with air exothermically during the drying and aggregation process. This

rapid exothermic reaction leads to a rough surface. On the other hand, in the low pH range, large numbers of nitrate ions associate with cations and decompose endothermically at a slow rate, which leads to a smooth surface.

Meanwhile, a non-uniform particle size distribution was observed at high flow-rates of the carrier gas. This was due to insufficient time for the particles to rearrange in the droplet, given the high flow-rate of the carrier gas. During the decomposition reaction of the precursor, gases such as H_2O , N_2 , NO , and CO_2 are produced, and push the metal-oxide particles to the outer surface of the particles. Therefore, there must be sufficient time in the reaction zone for the droplets to form fine particles with uniform size and smooth surface morphology.

FE-SEM images and EDS line-scanning spectra for the synthesized powders are shown in Fig. 5. The Zr and Ni spectra overlapped over the whole particle. Moreover, the intensity of the Zr and Ni spectra were similar. This indicates that NiO and YSZ particles were well mixed in the composite.

Figure 6 shows typical AC-impedance spectra and current-voltage (I-V) test results of the Ni-YSZ anode materials synthesized by USP at various pH values of the precursor solution, at a flow rate of 1 L/min, compared with the conventionally mixed Ni-YSZ anode, measured at 800°C . An equivalent circuit consisting of an inductor (L), a resistor (R_o), and two RQ elements (R_1Q_1 and R_2Q_2) was used to fit the AC impedance data. Meanwhile, the total polarization resistance (R_p) can be separated into R_1 and R_2 , which corresponds to the high-frequency and low-frequency arcs, respectively. The individual electrode reaction processes can be verified by comparing R_1 and R_2 values. Separated polarization-resistance values for the Ni-YSZ anodes from Fig. 6(a), are listed in Table 2. The Ni-YSZ anode prepared by USP shows a much lower R_p value than the conventionally mixed Ni-YSZ anode. The overall R_p value for the Ni-YSZ anode prepared by USP decreased with increasing pH

Fig. 3. XRD patterns of the NiO-YSZ particles synthesized by USP with multi-zone furnace.

Table 1. Calculated Size of NiO-YSZ Crystallites Synthesized by USP with Multi-zone Furnace

Precursor pH and flow rate of carrier gas	Component	Crystallite size (nm)
pH2, 1 L/min	NiO	12.9
	YSZ	10.8
pH2, 3 L/min	NiO	12.6
	YSZ	10.6
pH4, 1 L/min	NiO	14.3
	YSZ	10.2
pH4, 3 L/min	NiO	12.2
	YSZ	9.2

Fig. 4. SEM micrographs of the NiO-YSZ particles synthesized by USP with multi-zone furnace: (a) pH2, 1 L/min, (b) pH2, 3 L/min, (c) pH4, 1 L/min, and (d) pH4, 3 L/min.

Fig. 5. FE-SEM micrographs and EDX line scanning spectra of the NiO-YSZ particles synthesized by USP with multi-zone furnace: (a) pH2, 1 L/min, (b) pH2, 3 L/min, (c) pH4, 1 L/min, and (d) pH4, 3 L/min.

Fig. 6. (a) AC impedance spectra and (b) single-cell performance data of a Ni-YSZ anode synthesized by USP with precursor solutions of various pH, at a flow rate of 1 L/min, compared with a conventionally-mixed Ni-YSZ anode, measured at 800°C with humidified H₂ fuel.

of the precursor solution. It is well known that the high-frequency (R_1) and the low-frequency (R_2) arcs correspond to the activation and diffusion processes, respectively.¹⁰⁾ Interestingly, while the Ni-YSZ anode prepared by USP exhib-

Table 2. Electrochemical Performance a Ni-YSZ Anode Prepared by USP with Various pH of the Precursor Solution at a Flow Rate of 1 L/min Measured at 800°C with Humidified H₂ Fuel

Anode	Area specific resistance ($\Omega \cdot \text{cm}^2$)			Maximum power density (mW/cm^2)
	R_1	R_2	R_p	
Ni-YSZ (USP, pH2)	0.067	0.133	0.200	213
Ni-YSZ (USP, pH4)	0.065	0.100	0.165	256
Ni-YSZ (Ball-milled)	0.163	0.085	0.248	185

ited greater values for R_2 than for R_1 , the conventionally mixed Ni-YSZ anode exhibited an R_1 value considerably larger than for R_2 . This indicates that the charge-transfer reaction at the Ni-YSZ anode prepared by USP occurs much faster than that at the conventionally mixed Ni-YSZ anode. This might be due to well-dispersed nano-sized Ni and YSZ particles in the Ni-YSZ anode prepared by USP, with a consequent increase in the TPB area.

Cell voltages and power densities, with current density, are shown in Fig. 6(b). The open-circuit voltage of the single cells with Ni-YSZ-pH2, Ni-YSZ-pH4, and conventionally mixed Ni-YSZ anodes was 0.77, 0.81, and 0.78 V, respectively. The relatively lower open-circuit voltage, compared to that of the single cell with YSZ electrolyte, is due to the reduction of the GDC electrolyte in a reducing atmosphere. The maximum power densities of the single cells with Ni-YSZ-pH2, Ni-YSZ-pH4, and conventionally mixed Ni-YSZ anodes, were 213, 256, and 185 mW/cm^2 , respectively, at 800°C. This single-cell performance result is consistent with the trend observed in the AC-impedance data.

Figure 7 shows the area-specific resistance (ASR) values for the Ni-YSZ anodes synthesized by USP, with precursor solution at pH4, and a flow rate of 1 L/min; synthesized by the conventional ball-milling method, measured in humidified H₂ at 800°C for 500 h. ASR values at the initial stage increase significantly due to the reconstruction of a porous-electrode microstructure. In the case of the conventionally-mixed Ni-YSZ anode, the ASR value kept increasing with operation time, which indicates performance degradation. On the other hand, the Ni-YSZ anode synthesized by USP did not exhibit any performance degradation, even after 500 h. It is well known that degradation at the anode during long-term operation is mainly due to microstructural change caused by Ni coarsening and aggregation, consequently leading to a decrease in the TPB area.

In order to confirm the microstructural degradation, SEM observation was carried out before and after the long-term stability test. As shown in Fig. 8, there was no significant change in the microstructure of the Ni-YSZ anode synthesized by USP before or after the long-term stability test, compared to the microstructure of the conventionally-mixed Ni-YSZ anode. The well distributed nano-sized YSZ parti-

Fig. 7. Comparison of area-specific resistance (ASR) for the Ni-YSZ anodes synthesized by USP with precursor solution of pH4, at a flow rate of 1 L/min, synthesized by conventional ball-milling, and measured at 800°C with humidified H_2 fuel.

cles in the Ni-YSZ anode synthesized by USP may suppress Ni coarsening. On the other hand, coarse Ni particles were easily observed after long-term operation of the conventionally-mixed Ni-YSZ anodes.

4. Conclusions

The main advantage of using ultrasonic spray pyrolysis (USP) with a multi-zone furnace is to obtain NiO-YSZ powders continuously, without post-heat treatment. During the USP process, both NiO and YSZ primary particles, in the form of nano-size powder, are well-mixed and spherical. The Ni-YSZ cermet anode prepared by USP exhibited better electrochemical performance than the conventional Ni-YSZ mixed by ball-milling. This is due to a significant increase in the three-phase boundary (TPB) area caused by thorough dispersion of the nano-sized Ni and YSZ particles. Moreover, the well dispersed YSZ particles in the Ni-YSZ cermet anode prepared by USP can restrain Ni coarsening and the resulting microstructural change, which consequently leads to the stable electrochemical performance during even long-term operation, without significant degradation.

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Fig. 8. Back-scattered SEM micrographs of the Ni-YSZ anodes synthesized by (a, b) USP with precursor solution at pH4 at a flow rate of 1 L/min and (c, d) synthesized by conventional ball-milling, before and after a long-term test.

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