Ceramics International 42 (2016) 13715–13722

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Characterization of core-shell structured Ni@GDC anode materials synthesized by ultrasonic spray pyrolysis for solid oxide fuel cells

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ARTICLE INFO

Article history:
Received 27 April 2016
Received in revised form
25 May 2016
Accepted 26 May 2016
Available online 27 May 2016

Keywords:
Solid oxide fuel cell
Anode
Core-shell
Ultrasonic spray pyrolysis
Long-term stability

ABSTRACT

Core-shell structured NiO@GDC powders with NiO cores and GDC shells were synthesized by ultrasonic spray pyrolysis (USP) with a four-zone furnace. The morphology of the as-synthesized powders can be modified by controlling parameters such as the precursor pH, carrier gas flow rate, and zone temperature. At high carrier gas flow rates, the as-synthesized core-shell structured NiO@GDC powders have raisin-like morphology with a rough surface; this is due to fast gas exhaustion and insufficient particle ordering. The core-shell structured Ni@GDC anode showed considerable electrochemical performance enhancement compared to the conventionally-mixed Ni-GDC anode. The polarization resistance (R_p) of conventionally-mixed Ni-GDC anodes increases gradually as a function of the operation time. Alternatively, the core-shell structured Ni@GDC anode synthesized by USP does not exhibit any significant performance degradation, even after 500 h of operation. This is the case because the rigid GDC ceramic shell in the core-shell structured Ni@GDC may restrain Ni aggregation.

1. Introduction

Solid oxide fuel cells (SOFCs) are attractive because of their many advantages such as their high energy conversion efficiencies, low pollution emissions, and various environmental advantages compared with other energy conversion devices [1,2]. A high operating temperature is one of the features of SOFCs, where the direct internal reforming of hydrocarbon fuels at the anode side of the SOFC is possible [3]. Ni-yttria stabilized zirconia (YSZ) is commonly used as a SOFC anode material due to its high catalytic activity and high electronic conductivity [4–6]. The oxidation reaction of the fuel at the anode occurs at the triple phase boundary (TPB), which is the three phase interface between the gas, ionic conductor, and catalyst [7]. A large TPB area is kinetically favorable for increased performance. However, Ni in the Ni-YSZ cermet anode can easily aggregate during long-term operations at high temperatures [8,9]. Coarse Ni particles may reduce the TPB area. Moreover, the reduction of porosity, caused by coarsening, can suppress gas diffusion. In this regard, many techniques have been studied in order to restrain Ni aggregation. These include infiltration of catalysts into porous anode supports, electrodeposition, and fabricating core-shell structures [10–13]. Among these various approaches, core-shell structures with a Ni core and ceramic shell may be effective because the rigid ceramic shell can restrain Ni aggregation.

Spray pyrolysis is known to be a useful synthesis method for the production of spherical and uniform ceramic powders [14]. In particular, the ultrasonic spray pyrolysis (USP) method can be used to easily modify the powder morphology by controlling several parameters such as the solution preparation method, atomizing frequency, flow rate, and heating temperature [15–17]. In this study, we synthesized core-shell structured NiO@GDC powders using the USP method with various precursor pHs and carrier gas flow rates. The morphology, phase, and performance of the core-shell structured Ni@GDC anodes were investigated.

2. Experimental procedures

The core-shell structured NiO@GDC powders were synthesized by ultrasonic spray pyrolysis with a multi-zone furnace. A flowchart depicting the synthesis is shown in Fig. 1.

$Ni(CH_3COO)_2 \cdot 4H_2O$ (Alfa Aesar, 98%), $Ce(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99% metal basis), and $Gd(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99.9% Reo) were used as starting materials. All compositions of the NiO@GDC powders were designed with 60 vol% of Ni and 40 vol% of GDC. The calculated amount of $Ni(CH_3COO)_2 \cdot 4H_2O$ (for the NiO shell) was dissolved in deionized water to create a 0.25 M precursor solution for the core component. $Ce(NO_3)_3 \cdot 6H_2O$ and

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http://dx.doi.org/10.1016/j.ceramint.2016.05.170
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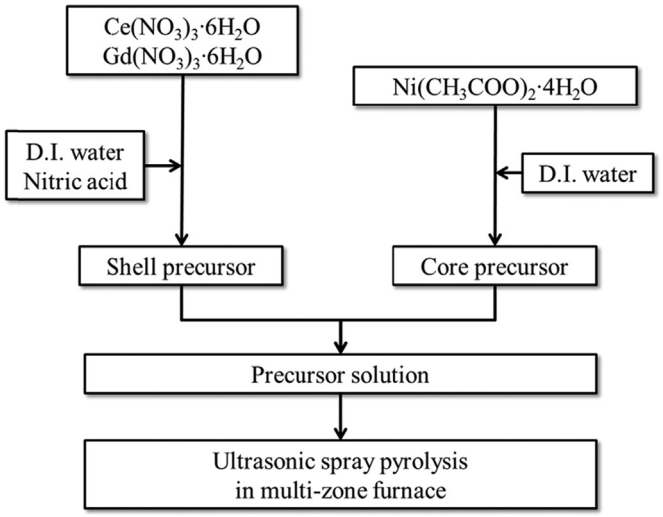

Fig. 1. Flowchart for the synthesis of the core-shell structured NiO@GDC powders using the USP method.

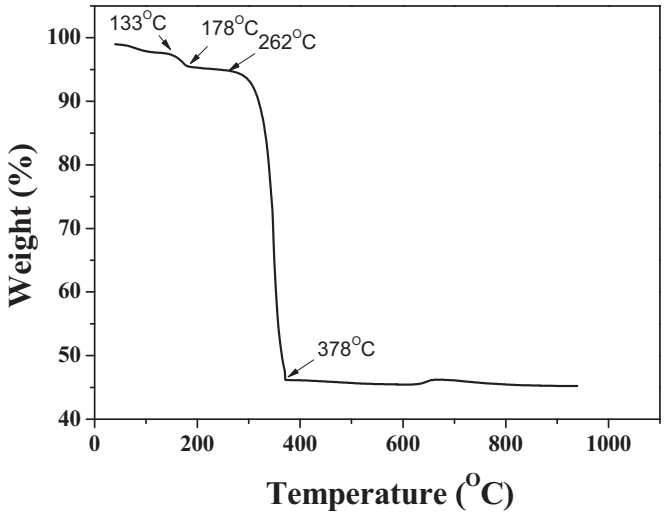

Fig. 2. TGA data for the precursor solution of the Ni acetate, Ce nitrate, and Gd nitrate mixture.

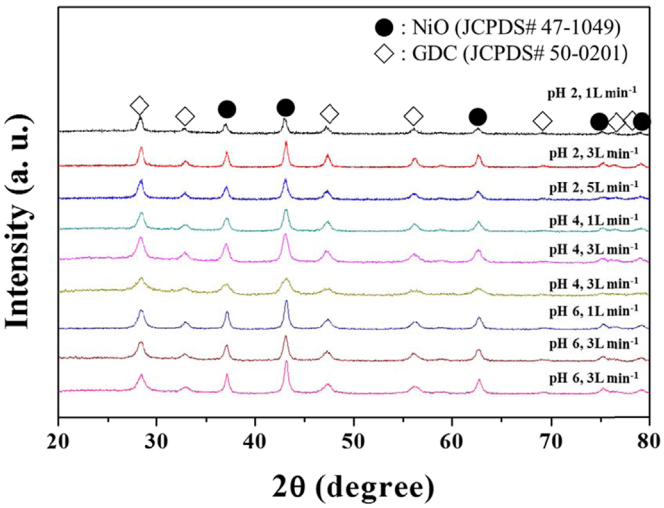

Fig. 3. XRD patterns of the NiO@GDC particles synthesized by USP with a multi-zone furnace at various pHs and carrier gas flow rates.

Table 1
Calculated crystallite size of the NiO@GDC synthesized by USP with a multi-zone furnace at various pHs and carrier gas flow rates.

Precursor pH and flow rate of carrier gas	Component	Crystallite size (nm)
pH 2, 1 L min^{-1}	NiO	18.1
	GDC	16.0
pH 2, 3 L min^{-1}	NiO	20.7
	GDC	16.8
pH 2, 5 L min^{-1}	NiO	15.8
	GDC	13.8
pH 4, 1 L min^{-1}	NiO	15.7
	GDC	12.5
pH 4, 3 L min^{-1}	NiO	14.6
	GDC	11.2
pH 4, 5 L min^{-1}	NiO	12.8
	GDC	12.5
pH 6, 1 L min^{-1}	NiO	18.3
	GDC	12.1
pH 6, 3 L min^{-1}	NiO	16.8
	GDC	10.8
pH 6, 5 L min^{-1}	NiO	18.8
	GDC	11.5

$Gd(NO_3)_3 \cdot 6H_2O$ (for the GDC shell) were also dissolved in deionized water in another beaker. Nitric acid was added into the nitrate solutions in order to adjust pH. The prepared core and shell precursor solutions were mixed by stirrer. The mixed solutions were atomized and turned into mists by an ultrasonic atomizer. These generated mists were then carried into the four-zone furnace (with temperature zones of 200 °C, 400 °C, 800 °C, and another 800 °C) by carrier gases of air at rates of 1 L min^{-1}, 3 L min^{-1}, and 5 L min^{-1}, respectively. While passing through the furnace, the mists were decomposed and the decomposed powders were collected by filter paper. The filtered powders do not require any further heat treatment.

The decomposition and reaction temperatures of the precursors were determined by thermogravimetric analysis (TGA, Q600, TA instrument Ltd., USA). Phase analyses of the as-synthesized powders were carried out by X-ray diffraction (XRD, MAX-2500, Rigaku, Japan). The core-shell structure and morphology were investigated by scanning electron microscopy (SEM, JSM-6400, JEOL, Japan) and field emission-scanning electron microscopy (FE-SEM, SUPRA 40VP, Carl Zeiss, Germany) with energy-dispersive X-ray spectroscopy (EDS or EDX). To view the inner texture of particles and confirm the core-shell structure, high-resolution TEM (HR-TEM, JEM-2010, JEOL, Japan) was also used. Particle size analyses of the as-synthesized powders were carried out using a particle size analyzer (PSA, ELS-6000, Otsuka Electronics, Japan). The electrochemical performance of the anode materials were evaluated by AC impedance analysis and current-voltage (I-V) measurements using electrolyte-supported-type single cells. 0.5-mm-thick $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) electrolyte pellets were sintered at 1500 °C for 4 h in air. A $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$-$Ce_{0.9}Gd_{0.1}O_{1.95}$ (BSCF-GDC) cathode powder was synthesized by a modified sol-gel combustion method. The electrode paste was produced by mixing the anode powder and binder (Heraeus V006) at a ratio of 60:40 wt%. The anode and cathode were deposited on opposite sides of the electrolyte by a screen-printing method. This was followed by firing at 1250 °C and 1050 °C for 2 h in air, respectively. The geometric area of both electrodes was 0.25 cm^2. A Pt mesh, placed onto the electrode with a spring-loaded alumina tube, was used as the current corrector. A seal between the single cell and the alumina tube was achieved with a Pyrex® glass ring and paste. Humidified H_2 (~3% H_2O at