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Effects of adding alumina to the nickel-zirconia anode materials for solid oxide fuel cells and a two-step sintering method for half-cells

Xiao Song, Xiaolei Dong, Ming Li, Haiqian Wang*

Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui 230026, PR China

HIGHLIGHTS

- A two-step sintering method for the fabrication of half cells is reported.
- The shrinkage of the NiO-YSZ anode material can be tailored by adding Al_2O_3.
- Al_2O_3 transiently promote the grain growth of NiO at low temperature.
- $NiAl_2O_4$ spinel suppresses the grain growth of NiO at high temperature.
- High performance flat cells have been demonstrated by adding 0.2 wt% Al_2O_3 into the anode.

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ABSTRACT

The co-sintering process of half-cells has an important effect on the flatness and performance of solid oxide fuel cells. In this study, we report a two-step sintering method to fabricate flat three-layer half-cells. The first sintering step is a freestanding sintering process at a low temperature (1280 °C). The second sintering step is a constrained sintering process at 1400 °C. The shrinkage of the anode support layer (ASL) and the curvature of the half-cell can be adjusted by adding Al_2O_3 into the ASL in the first sintering step. Effects of Al_2O_3 addition on the NiO-YSZ anode material are also studied. We find that NiO reacts with Al_2O_3 to form $NiAl_2O_4$ spinel at the early sintering stage. This reaction transiently promotes the grain growth of NiO. Once the reaction terminates and the $NiAl_2O_4$ spinel is formed, the grain growth of NiO will be suppressed, even at higher sintering temperatures. Our results indicate that by a proper amount (approximately 0.2 wt%) of Al_2O_3 addition, smaller NiO grains can be obtained while the side effects of $NiAl_2O_4$ are negligible, which is favorable to increase the conductivity and stability of the ASL, and can enhance the performance of SOFC.

1. Introduction

Solid oxide fuel cells (SOFCs) have attracted increasing attention as clean and efficient electrochemical devices to convert chemical energy into electrical energy [1]. Compared to electrolyte-supported SOFCs, anode-supported SOFCs (AS-SOFCs) have the advantages of lower cost, high power density at lower temperatures, better interfacial contact with other parts, and a longer three-phase boundary (TPB) when using a composite electrode [2,3].

The Ni-YSZ (yttria-stabilized zirconia) cermet is widely used for an AS-SOFC anode material because of its well-behaved electronic/ionic conductivity, chemical/structural stability, catalytic activity and compatibility with other SOFC components [4]. Because of its good oxygen ionic conductivity, chemical stability and proper thermal expansion coefficient (TEC), YSZ (8 mol% yttria) is commonly used as an electrolyte material paired with the Ni-YSZ anode [5].

The half-cell of a planar AS-SOFC is typically composed of a thick (500–1000 μm) anode support layer (ASL) and a thin (10–20 μm) electrolyte layer (EL). The performance of SOFC can be improved by inserting an anode functional layer (AFL) with a fine microstructure to extend the TPB [6–8]. The AFL material can be either the same as or different from that of the ASL.

Tape casting is the predominant method to produce the ASL of planar AS-SOFCs because of its low cost and mass producibility [9]. In a previous work, we reported a bi-layer wet powder spraying (WPS) method for the production of ELs and AFLs which is

* Corresponding author.
E-mail address: hqwang@ustc.edu.cn (H. Wang).

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compatible with the tape casting method for the ASL [10]. With this technique, ELs, AFLs and ASLs were successively prepared on a Mylar film, and the three-layer green tapes were cut into the desired size and sintered at a high temperature to obtain ceramic half-cells. The co-sintering process of the half-cells has an undoubtedly important effect on the final performance of SOFCs due to the multilayer feature and the different properties of the materials used for each layer [11].

When sintering multilayer ceramics with different materials, stress is known to occur because of the different TECs and shrinking rates of the adjacent layers [12–14]. Moreover, the sintering of green tapes is often accompanied by a very large amount of shrinkage. The mismatch of the shrinkage or stress between the different layers may result in curvature or even more serious problems such as cracks in the half-cells [15,16]. For planar SOFCs, the curvature of half-cells will cause difficulties in the preparation of the cathode, poor sealing of the cells, and bad contact with current collectors. Usually a plate-pressed sintering method is applied to abate the curvature of a half-cell instead of freestanding sintering. However, this method is unfavorable at the early sintering stage of the green tapes because a pressing plate may (1) block the release of organics and carbon, (2) lead to distortions in the shape of the half-cells, thus introducing inhomogeneous cell performance, and (3) result in defects on the surface of the half-cells, such as dents, scratches, or even cracks, due to the large shrinkage and weak mechanical strength of the sintered body at the early sintering stage.

Another approach to obtain flat half-cells is to adjust the shrinking rate of one or more layers to compensate for the stresses between the different layers. Al_2O_3 is a common sintering aid for shaping the sintering behavior of ceramics. For SOFCs, Al_2O_3 can be used to modify the shrinking rate of NiO-YSZ anodes and thus regulate the curvature of half-cells. Cologna et al. indicate that the shrinking rate of a NiO/YSZ anode with 1.0 mol% Al_2O_3 is higher than that of the anode without Al_2O_3, which is beneficial for matching the shrinkage of the anode and the YSZ electrolyte [17]. Similar results reported by He et al. show that the density of a NiO-YSZ anode increases with increasing Al_2O_3 content up to 0.25 wt%, and the curvature of single cells can be tailored by adding Al_2O_3 into the anode [18,19].

In the present work, we report a two-step sintering method to fabricate flat three-layer half-cells. The first sintering step is a freestanding sintering process. Three-layer green tapes with Al_2O_3 added to the NiO-YSZ ASL, NiO-YSZ AFL and YSZ EL were sintered at 1280 °C to obtain pre-sintered half-cells. The shrinkage of the ASL and the curvature of the half-cell were adjusted by the Al_2O_3 content in the ASL during the first sintering step. The second sintering step is a constrained sintering process with pressing plates, by which the pre-sintered half-cells with reasonable flatness and mechanical strength were fully sintered at 1400 °C. High-performance and defect-free (i.e., free from dents or scratches) flat half-cells can therefore be obtained. The effects of the added Al_2O_3 on the sintering and electrical properties of the NiO-YSZ anode materials are also discussed.

2. Experimental

2.1. Materials

Commercial YSZ (TZ-8Y, Tosoh, Japan) and NiO (J.T.Baker, U.S.) powders were used for EL and AFL. On the other hand, for the ASL, a low-cost alternative YSZ powder with a purity of 99.8 wt% (BQ-8Y, Jiaozuo Weina, China) and NiO powder (purity of ~99.97 wt% with a main cation impurity of 0.02 wt% Co) were decomposed from basic nickel carbonate (HAITAI SCI-TECH, China) at 650 °C for 2 h Al_2O_3 (average grain size of ~50 nm, Shanghai Huaming Gona, China) was used as the additive for the ASL. The SOFC cathode was composed of LSM ($La_{0.2}Sr_{0.8}MnO_3$, Fuel Cell Materials, U.S.) and TZ-8Y.

2.2. Sample preparation

To examine the microstructures, Al_2O_3-NiO powders were prepared by mixing the NiO powder with 0, 0.36, 0.72 and 3.6 wt% Al_2O_3 and grinding with ethanol for 1 h. After drying, they were sintered at 1280 °C and 1400 °C for 2 h respectively. The Al_2O_3-YSZ powders were prepared by the same method except that the Al_2O_3 contents were 0, 0.44, 0.88 and 4.4 wt%. Thus, the volume fractions of Al_2O_3:NiO and Al_2O_3-YSZ are set to be the same for each pair of samples.

For the linear shrinkage measurement, the ASL green tapes with a NiO:YSZ weight ratio of 55:45 were prepared by the tape casting method. The slurries were obtained by mixing the ceramic YSZ and NiO powders (with 0–2 wt% Al_2O_3 of the total NiO-YSZ) with ethanol and butanone as solvents, triethanolamine as a dispersant, polyethylene glycol (PEG), dibutyl phthalate (DBP) and polyvinyl butyl (PVB) as plasticizers and binders, and graphite as a pore former. The green tapes were cut into 10 × 1 × 0.1 cm^3 bars for further measurements.

The three-layer (ASL/AFL/EL) half-cell green tapes were prepared by the WPS and tape casting methods. The EL and AFL were successively prepared on Mylar film by the WPS method, and then the ASL was cast on the green layer using a doctor blade. After drying, the three-layer green tapes were cut into 7 × 7 cm^2 square pieces for SOFC fabrication. Details on the preparation of the three-layer green tapes can be found in our previous work [12].

After the half-cells were sintered, the LSM-YSZ composite cathode functional layer (CFL) and the LSM cathode current collecting layer (CCCL) were screen printed on the half-cells with an active area of 4 × 4 cm^2 and sintered at 1150 °C for 5 h. The thicknesses of the ASL, AFL, EL, CFL, and CCCL of a single cell are approximately 700, 10, 15, 10, and 20 μm, respectively.

2.3. Two-step sintering method for the half-cells

The first sintering step is a freestanding sintering process. The half-cell green tapes were sintered at 1280 °C for 5 h without any physical constraint to exhaust the organic contents while achieving enough mechanical strength for the second sintering step. The second sintering step is a constrained sintering process with zirconia plates pressing the pre-sintered half-cells. In the second sintering step, the pre-sintered half-cells were sintered at 1400 °C for 5 h to densify the electrolyte and to obtain cells with high mechanical strength.

2.4. Characterization of samples

X-ray diffraction analysis (XRD) was performed using an X-ray diffractometer (TTR III, Rigaku Co., Japan) in the range of $2\theta = 10$ - 80°. The microstructures of samples were obtained using scanning electron microscopy (SEM, JSM-6301F, Hitach, Japan). The compositional analysis was performed by an inductively coupled plasma – atomic emission spectrometer (ICP-AES, Optima 7300 DV, PerkinElmer, Inc., U.S.).

The sintering curve was measured by a thermal dilatometer (DIL 402C, Netzsch, Germany). Before the measurement, the green tape was presintered at 800 °C to attain sufficient mechanical strength. Then, the samples were cut into rectangular bars with a height of 5 mm and scanned from room temperature to 1400 °C with a heating rate of 5 °C/min.

The linear shrinkage and curvature were measured by a caliper.