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Anode-supported SOFCs based on $Sm_{0.2}Ce_{0.8}O_{2-\delta}$ electrolyte thin-films fabricated by co-pressing using microwave combustion synthesized powders

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Abstract

Decreasing the electrolyte thickness is an effective approach to improve solid oxide fuel cells (SOFCs) performance for intermediate-temperature applications. $Sm_{0.2}Ce_{0.8}O_{2-\delta}$ (SDC) powders with low apparent density of 32 ± 0.3 mg cm^{-3} are synthesized by microwave combustion method, and SDC electrolyte films as thin as ~10 μm are fabricated by co-pressing the powders onto a porous NiO–SDC anode substrate. Dense SDC electrolyte thin films with grain size of 300–800 nm are achieved at a low co-firing temperature of 1200 °C. Single cells based on SDC thin films show peak power densities of 0.86 W cm^{-2} at 650 °C using 3 vol% humidified H_2 as fuel and ambient air as oxidant. Both the thin thickness of electrolyte films and ultra-fine grained anode structure make contributions to the improved cell performance.

Keywords: A. Films; D. CeO_2; E. Fuel cells; Microwave combustion

1. Introduction

Solid oxide fuel cells (SOFCs) have attracted great attentions as alternative power generation systems due to their high energy conversion efficiency, low pollutant emission, and excellent fuel flexibility [1–8]. However, commercialization of SOFCs technologies has been constrained by many difficulties associated with the high operation temperatures (800–1000 °C). Thus, it is necessary to reduce the operating temperature to less than 700 °C [9]. The operating temperature can be reduced by using electrolyte of high ionic conductivity at reduced temperatures, and decreasing the electrolyte thickness. Doped-ceria, such as $Sm_{0.2}Ce_{0.8}O_{2-\delta}$ (SDC), has been regarded as the most promising electrolytes for intermediate temperature solid oxide fuel cells (IT-SOFCs) due to its superior ionic conductivity at reduced temperatures [10,11]. Meanwhile, intense research work has been conducted to the development of IT-SOFCs based on thin-film electrolytes of doped ceria, which showed much higher ionic conductivities than the state-of-the-art yttria-stabilized zirconia (YSZ) electrolytes at reduced temperatures [12–17]. Compared with some physical and chemical vapor deposition methods for film fabrication, the co-pressing and co-firing process is a more simple and inexpensive approach to fabricate dense electrolyte thin-film on a porous anode. The critical step for fabrication of SDC electrolyte thin-film by co-pressing is the synthesis of SDC powders with relatively low apparent density [12,18].

SDC powders with low apparent density are usually fabricated by glycine–nitrate process (GNP) [19–22], in which precursor mixture containing the oxidizer (metal nitrate) and the fuel (glycine) undergoes an exothermic redox reaction at a certain temperature, thus leading to a combustion reaction. Conventional resistance heating mostly used to ignite the combustion reaction, however, usually forms an uneven temperature

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distribution on reaction mixtures [23]. In this context, microwave combustion method has emerged as a novel method to synthesize nanopowders [24], showing more rapid and uniform heating of materials, shorter processing time, and finer particle size [25,26]. In our previous work, [27] $MgO–Y_2O_3$ nanopowders have been successfully synthesized by microwave combustion method. To our best knowledge, no report on synthesis of SDC powders by microwave assisted GNP combustion method has been taken to this date.

In this paper, SDC nanopowders with low apparent density were synthesized by microwave combustion method, and dense SDC electrolyte thin-films were fabricated from the SDC powders using a co-pressing and co-sintering process. The single cells with electrolyte thin-films demonstrated excellent performance at intermediate temperatures.

2. Experimental

2.1. SDC powders synthesis

$Sm(NO_3)_3 \cdot 6H_2O$ (purity 99.9%) and $Ce(NO_3)_3 \cdot 6H_2O$ (purity 99.5%) with a molar ratio of 1:4 were dissolved in distilled water to get a concentration of 0.1 M, in which glycine was added with a stoichiometric glycine:nitrate molar ratio of 2:1. All chemicals were purchased from Alfa Aesar. After sufficiently stirring to allow complete complexation, the solution was transferred into an alumina crucible. The crucible was placed in a domestic microwave oven operating at 2.45 GHz, with output power of 700 W. The precursor solution mixture underwent boiling, drying and subsequent rapid combustion within several minutes. As a comparison, the SDC powders were also synthesized by conventional GNP combustion process on a hotplate. Finally, the resulted ashes were calcined at 600 °C for 2 h in a box furnace (SXW-1000, Shanghai Shi Yan Electric Furnace, Shanghai, China).

The phase compositions of the powders were examined using X-ray diffraction analysis (XRD, X'Pert PRO Alpha-1, Cu Ka radiation), and the morphologies of the powders were characterized using a field emission scanning electron microscopy (FE-SEM, LEO 1530). The apparent density of the powders was estimated using an oscillating funnel method as described elsewhere [12].

2.2. Single cell fabrication and characterization

The anode substrates containing NiO (synthesized by GNP method [28]), SDC (synthesized by microwave combustion method) and corn starch (purchased from Sigma) with weight ratio of 60:40:10 were fabricated by die pressing at 50 MPa, followed by co-pressing the SDC electrolyte powders onto the substrates at 400 MPa to form anode-electrolyte bi-layers with a diameter of 13 mm. The mass of SDC electrolyte powders for each sample was controlled to be ~14 mg. Subsequently, the bi-layer green pellets were co-sintered at 1200 °C for 5 h to densify the electrolyte thin-films. $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC)–SDC cathode ink with mass ratio of 70:30 was prepared by ball-milling SSC and SDC powders (both purchased from Alfa Aesar) with V-006 organic solvent (Heraeus) and acetone and then screen-printed on the SDC electrolyte, followed by firing at 950 °C for 2 h to form single cells. The effective area of cathode was 0.31 cm^2.

Each single cell was sealed on an alumina tube using a ceramic bond (purchased from Aremco). NiO paste and silver paste (both purchased from Heraeus) were employed as current collectors on the anode and the cathode side, respectively. Silver wires were used as the lead wires. The anode side was exposed to humidified hydrogen (~3 vol% H_2O) with a flow rate of 40 ml min^{-1} while the cathode was exposed to ambient air. The cells were first stabilized at 650 °C to allow complete reduction of NiO to Ni. Cell testing was carried out using an electrochemical workstation (Princeton Applied Research). The cell current and voltage characteristics were evaluated in the temperature range of 550–650 °C. Impedance measurement was performed for the cell under open-circuit conditions with the applied frequencies in the range of 0.1 Hz to 1 MHz with signal amplitude of 10 mV. The images of the single cells were taken using FE-SEM (LEO 1530).

3. Results and discussion

Shown in Fig. 1 are the XRD patterns of SDC powders synthesized by microwave and conventional combustion methods. All the XRD peaks are corresponding to a single-phase fluorite structure, and the broadening of these peaks indicates a nanocrystalline nature of the powders. The crystallite size of the powders, D_{xrd}, are calculated to be 12.45 nm and 14.67 nm according to the Scherrer equation performed on the (111) diffraction, for SDC powders synthesized by microwave and conventional combustion methods, respectively.

The morphologies of the powders are shown in Fig. 2. Both SDC powders appear highly porous structures with foam-like aggregates consisting of some primary particles. The microwave combustion synthesized powders show looser aggregates with bigger pore sizes (Fig. 2a), whereas conventional combustion powders show denser structures with smaller pore sizes due to the stronger agglomeration of primary particles and some degree of sintering (Fig. 2b). The difference can be attributed to the different heating mechanisms. For microwave

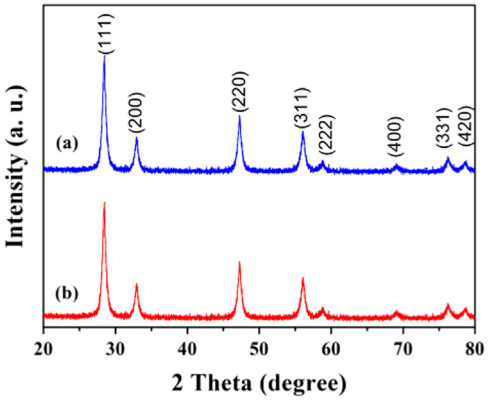

Fig. 1. XRD patterns of SDC powders synthesized by (a) microwave and (b) conventional combustion methods.