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Short communication

Extremely fine structured cathode for solid oxide fuel cells using Sr-doped $LaMnO_3$ and Y_2O_3-stabilized ZrO_2 nano-composite powder synthesized by spray pyrolysis

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HIGHLIGHTS

- LSM-YSZ nano-composite powder was synthesized by spray pyrolysis.
- Individual particles had spherical morphology with uniform size.
- Extremely fine cathode microstructure was achieved using the powder.
- SOFC with this cathode showed high power density and stable operation.

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ABSTRACT

A solid oxide fuel cell (SOFC) for high power density operation was developed with a microstructure-controlled cathode using a nano-composite powder of Sr-doped $LaMnO_3$ (LSM) and Y_2O_3-stabilized ZrO_2 (YSZ) synthesized by spray pyrolysis. The individual LSM-YSZ nano-composite particles, formed by crystalline and amorphous nano-size LSM and YSZ particles, showed spherical morphology with uniform particle size. The use of this powder for cathode material led to an extremely fine microstructure, in which all the LSM and YSZ grains (approximately 100–200 nm) were highly dispersed and formed their own network structures. This microstructure was due to the two phase electrode structure control using the powder, namely, nano-order level in each particle and micro-order level between particles. An anode-supported SOFC with the LSM-YSZ cathode using humidified H_2 as fuel and ambient air as oxidant exhibited high power densities, such as 1.29 W cm^{-2} under a voltage of 0.75 V and a maximum power density of 2.65 W cm^{-2} at 800 °C. Also, the SOFC could be stably operated for 250 h with no degradation, even at a high temperature of 800 °C.

1. Introduction

Anode-supported solid oxide fuel cells (SOFCs) have achieved high power densities because of their thin electrolytes [1–6]. The ohmic resistance in this type of cell is extremely low, resulting in the cell performance being dominated by the electrode polarization resistance. The current majority of cathode materials for SOFCs are mixed ionic-electronic conductors (MIECs) such as Sr-doped $LaCoO_3$, Sr-doped $LaFeO_3$, and Sr-doped $La(CoFe)O_3$ (LSCF) due to their high catalytic activity for electrochemical reaction in a wide temperature range (500–800 °C) [7–12]. In general, when these cathodes are used with ZrO_2-based oxide electrolytes such as Y_2O_3-stabilized ZrO_2 (YSZ) and Sc_2O_3-stabilized ZrO_2, a CeO_2-based oxide interlayer is needed to avoid reaction between the cathode and electrolyte [13–15]. However, both the bulk resistance of the interlayer and the contact resistance at the interlayer/electrolyte interface degrade the cell performance, particularly at high temperatures (≥800 °C) [16]. Although the intrinsic catalytic activity of Sr-doped $LaMnO_3$ (LSM) is inferior to that of MIECs, LSM is a commonly used cathode material in high temperature SOFCs due to its good chemical compatibility with ZrO_2-based oxides [7,13]. Due to poor ionic conductivity of LSM, however, the electrochemical

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reaction on LSM cathodes occurs only at the triple-phase boundary (TPB), where LSM, electrolyte, and oxygen are in contact. Therefore, LSM is generally used as a composite cathode with electrolyte material to extend the TPB [17–19].

In composite cathodes, the microstructure is an essential factor to improve the electrochemical performance. An attractive method to achieve a fine microstructure is using ceramic powder materials prepared by spray pyrolysis for the cathode. Spray pyrolysis enables control of the individual particle structure at nano-order level, thus yielding a nano-composite powder. Various particle structure can be designed by changing precursor type and spray pyrolysis parameters. Electrodes produced by using nano-composite powders generally have high surface area and uniform networks. In previous studies, many nano-composite powders for electrode materials have been proposed, and fine electrode microstructures have been realized [20–26].

In the present study, the objective was an extremely fine structured LSM-YSZ cathode that achieved the same level of high performance as MIEC cathodes. First, spray pyrolysis was used to synthesize an LSM-YSZ nano-composite powder for electrode starting material. Then, an anode-supported SOFC with a cathode made from the LSM-YSZ nano-composite powder was fabricated, and its electrochemical performance in a high temperature range (750–900 °C) was evaluated.

2. Experimental

An LSM-YSZ nano-composite powder was synthesized using the spray pyrolysis apparatus described in a previous study [26]. First, the starting solution for spray pyrolysis was a mixture of two nitrate solutions, $La_{0.6}Sr_{0.4}MnO_{3-\delta}$ (LSM) and 8 mol% Y_2O_3-ZrO_2 (YSZ), at a weight ratio of 45:55; (*i*) 0.1 mol L^{-1} LSM nitrate solution using $La(NO_3)_3 \cdot 6H_2O$ (99.99% purity, Kanto Chemical Co.), $Sr(NO_3)_2$ (98.0% purity, Kanto Chemical Co.), and $Mn(NO_3)_2 \cdot 6H_2O$ (98.0% purity, Kanto Chemical Co.); and (*ii*) 0.1 mol L^{-1} YSZ nitrate solution using $Y(NO_3)_3 \cdot 6H_2O$ (99.99% purity, Kanto Chemical Co.) and $ZrO(NO_3)_2 \cdot 2H_2O$ (99.0% purity, Kanto Chemical Co.). Then, this starting solution was atomized by an ultrasonic atomizer (1.75 MHz) and transported through a quartz tube by carrier gas (air at 5 L min^{-1}) into a heating section, in which three electric furnaces were respectively set at 300, 700, and 900 °C. Finally, the resulting synthesized LSM-YSZ nano-composite powder was captured by a PTFE filter.

An anode-supported planar SOFC was then fabricated as follows. NiO powder (Sumitomo Metal Mining Co.) and YSZ powder (TZ-8YS, Tosoh) at a weight ratio of 60:40 were mixed with pore former and binder. The pore former was a mixture of graphite carbon and cellulose at a weight ratio of 2:1, and was added at 33.8 wt% of the NiO and YSZ powders. The NiO-YSZ powder was then extruded into an anode sheet (0.7 mm thick, 65 mm wide) using a preparation procedure described elsewhere [27]. A button cell size sample (32 mm diameter) as an NiO-YSZ anode substrate was cut from the anode sheet and then presintered at 1240 °C for 2 h in air. A thin YSZ electrolyte layer was coated onto the NiO-YSZ anode substrate by screen-printing using a YSZ paste, prepared by mixing YSZ powder (TZ-8Y, Tosoh), α-terpineol (Kanto Chemical Co.), ethyl cellulose (45 cP, Kishida Chemical Co.), a dispersant, and a plasticizer. A dense YSZ and porous NiO-YSZ assembly was obtained by co-sintering at 1360 °C for 3 h in air. The cathode had a double layer structure, namely, a functional layer (electrolyte side) and a current collection layer (surface side). Cathode paste for the functional layer was prepared using the LSM-YSZ nano-composite powder synthesized by spray pyrolysis with the same admixtures as in the YSZ paste, and that for the current collection layer was prepared using LSM powder ($La_{0.8}Sr_{0.2}MnO_{3-\delta}$, 1.2 μm, AGC Seimi Chemical Co.). First the LSM-YSZ paste for the functional layer was painted on the electrolyte surface and then the LSM paste for the current collection layer was painted on the functional layer. This cathode was then sintered at 1200 °C for 3 h in air. The effective area of the cathode was 0.283 cm^2. The cathode current collection layer was approximately 30 μm thick, cathode functional layer was 20 μm, electrolyte was 5 μm, and anode substrate was 0.55 mm.

The synthesized LSM-YSZ nano-composite powder was characterized using X-ray diffraction (XRD, SmartLab, Rigaku, Cu Kα), laser diffraction particle size analysis (Microtrack HRA 9320-X100, Nikkiso Co.), and field emission scanning electron microscopy (FE-SEM, JSM-6330F, JEOL). The microstructure of the cathode was observed using FE-SEM and scanning transmission electron microscopy (STEM, JEM-2100F, JEOL). Energy dispersive X-ray spectroscopy (EDX, JED-2300T, JEOL) equipped with the STEM was used for analyzing distribution of Zr (Lα, 2.042 keV) and La (Lα, 4.650 keV). Electrochemical performance of the anode-supported SOFC was evaluated using 3% humidified H_2 supplied to the anode as fuel at a feed rate of 70 mL min^{-1} and ambient air supplied to the cathode as oxidant at a feed rate of 140 mL min^{-1}. Electrochemical evaluation was based on current-voltage (*I-V*) measurements, electrochemical impedance spectroscopy (EIS), and durability test carried out using a potentiostat/galvanostat with a frequency response analyzer (Autolab PGSTAT302, Metrohm).

3. Results and discussion

Fig. 1 shows the characterization results of the LSM-YSZ nano-composite powder synthesized by spray pyrolysis. FE-SEM images (Fig. 1a) show that the as-prepared particles had spherical morphology with uniform particle size. The particle size distribution measured by laser diffraction (Fig. 1b) also exhibited a very narrow distribution. The particle diameter at 10%, 50%, and 90% of cumulative less-than volume distribution, denoted as D_{10}, D_{50}, and D_{90}, was 0.58, 0.76, and 1.02 μm, respectively. Note that the particles observed here were secondary particles formed by crystalline and/or amorphous nano-size LSM and YSZ particles. In general, spray pyrolysis can yield submicron-size spherical particles with a narrow size distribution. Fig. 1a and b indicate that our powder preparation process successfully controlled the secondary particle structure. The XRD patterns for the as-prepared powder and sintered powder at 1200 °C for 3 h in air (Fig. 1c) show no apparent peaks for the as-prepared powder, although a broad peak appeared around 2θ of the main peaks for LSM (30.1°) and YSZ (32.6°), suggesting that LSM and YSZ were not fully crystallized and possibly existed as amorphous. After sintering at 1200 °C for 3 h (the same temperature used in the cathode fabrication), sharp peaks for LSM and YSZ were clearly identifiable. The estimated weight ratio of LSM:YSZ by Rietveld method was 47:53, which was almost the same as the targeted weight ratio (45:55). In the case of powder synthesis using precursors containing La, Sr, Mn, Y, and Zr, undesirable chemical compounds such as $SrZrO_3$ and $La_2Zr_2O_7$ are sometimes produced with LSM and YSZ. In Fig. 1c, no peaks for $SrZrO_3$ and $La_2Zr_2O_7$ were observed. These results suggest that a cathode can be fabricated using the LSM-YSZ nano-composite powder with no impurity phases.

Fig. 2 shows the cross-sectional images of the anode-supported SOFC with the cathode in which the functional layer was prepared using the LSM-YSZ nano-composite powder and the LSM current collection layer was on top of the functional layer. Note that the images shown here are the initial microstructure of the SOFC before electrochemical measurements (an identical sample was used for the electrochemical measurements). As shown in Fig. 2b, by using a relatively large grain LSM (D_{50} = 1.2 μm), the current collection layer was designed to achieve high porosity (approximately 50%)