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Preparation and characterization of one-dimensional nano-structured composite cathodes for solid oxide fuel cells

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ABSTRACT

$La_{0.8}Sr_{0.2}MnO_3/Zr_{0.92}Y_{0.08}O_2$ (LSM/YSZ) composite nanotubes of different diameters were co-synthesized by a pore-wetting technique as cathode materials for solid oxide fuel cells. A fast firing method was introduced to improve the contact between the LSM/YSZ composite cathode and the YSZ electrolyte, and to retain the original nanotube structure. The influence of heating and cooling rates, as well as the diameter of the nanotubes, on the microstructure and further on the electrochemical performance of the LSM/YSZ composite cathodes were studied. The microstructure study indicated that the LSM/YSZ composite cathodes, which underwent a 1100 °C heat treatment, exhibited nanotube and nanorod structures using heating and cooling rates of 200 and 100 °C min^{-1}. Area-specific resistance (ASR) of composite cathodes was characterized by electrochemical impedance spectroscopy. The nanotube-structured cathodes prepared using the heating and cooling rates of 200 °C min^{-1} exhibited lower ASR than the nanorod-structured cathodes. For the nanotube structured LSM/YSZ composite cathodes of different diameters, the cathode prepared using the 400 nm template exhibited the lowest ASR. At 700 °C, 750 °C, and 800 °C, the ASRs were 0.55, 0.40, and 0.26 Ω cm^2, respectively. The low ASR was mainly due to the small grain size, homogeneous particle distribution, and fine pore structure of the material.

1. Introduction

In recent years, considerable efforts have been devoted toward developing the intermediate temperature-solid oxide fuel cells (IT-SOFCs) [1–5]. Lowering the operating temperature to 500 °C-800 °C can suppress the degradation of the components, extend the range of acceptable materials, improve cell durability, and reduce system cost. However, reducing the operation temperature results in the decrease in electrode kinetics and the increase in polarization resistance, and these outcomes are the key problem that limits the development of IT-SOFCs. This effect is most pronounced for oxygen reduction at the cathode. To lower the polarization resistance of the cathode, favourable electronic and ionic conductivity and high catalytic activity for oxygen reduction must be maintained [6–9].

At present, tailoring the electrode microstructure is an effective approach to improving the electrochemical performance of cathodes. The nanostructure has been considered an optimal electrode structure because of its high catalytic activity and large triple-phase boundary (TPB). To date, one-dimensional nano-structured materials, including nanowires, nanorods, and nanotubes, have been used as SOFC cathodes, and they demonstrate superior electrochemical properties. Bellino et al. [10,11] prepared $La_{0.6}Sr_{0.4}CoO_3$ nanotubes that exhibit extremely low polarization resistance for SOFCs through the pore-injecting technique. Pinedo et al. [12] fabricated $Pr_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ nanotubes, and a final ordered three-dimensional (3D) nanostructure was formed. Nanostructured $Pr_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3/Ce_{0.8}Sm_{0.2}O_2$ (PSFC/SDC) composite cathodes [13] made of PSFC/SDC composite nanotubes were investigated, and they exhibited a smaller area-specific resistance (ASR) value than the conventional sample. A 3D fibrous $Sm_{0.5}Sr_{0.5}CoO_3/Ce_{0.8}Sm_{0.2}O_{1.9}$ cathode, which possesses high porosity and interconnectivity and low polarization resistance, was fabricated [14]. Zhao et al. [15] prepared $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_3$ nanotube/$Ce_{0.8}Gd_{0.2}O_{1.9}$ nanoparticle composite cathodes for SOFCs. The cathodes achieved ASRs of 4.70, 1.12, 0.27, and 0.07 Ω cm^2 at 500 °C, 550 °C, 600 °C, and 650 °C. Low ASR values are

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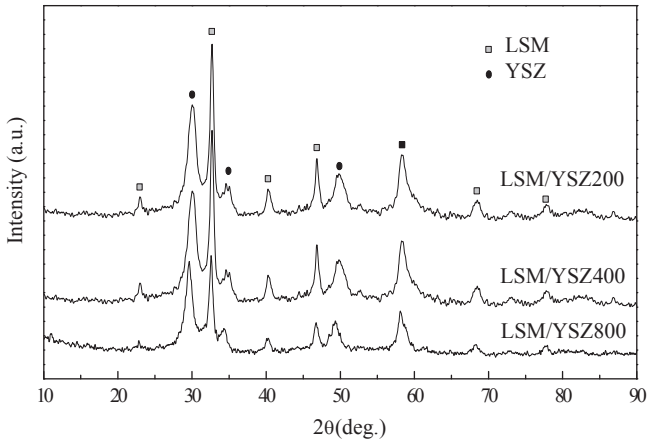

Fig. 1. XRD patterns of the L/Y200, L/Y400, and L/Y800 nanotubes.

mainly related to the optimal microstructure with larger TPBs and higher porosity.

Our group previously reported on the co-synthesis and characterization of $La_{0.8}Sr_{0.2}MnO_{3-\delta}/Zr_{0.92}Y_{0.08}O_2$ (LSM/YSZ) composite nanotubes as a cathode material for SOFCs [16]. The nanotube-structured cathodes reveal a low ASR value, which is attributed to the high specific surface area (SSA) and multi-scale porosity. In this study, further investigation on the nanotube LSM/YSZ composite cathodes was conducted. The influence of heating rates, cooling rates, and the nanotube diameter on the microstructure, and the electrochemical performance of the LSM/YSZ composite cathodes were studied. When used as cathode in SOFCs, the as-prepared nanostructured composites of LSM/YSZ exhibited high electrochemical performance.

2. Material and methods

2.1. Materials

Commercial polycarbonate (PC) membranes (Whatman, UK) with pore sizes of 200, 400, and 800 nm were used as templates. All raw materials were of analytical grade and used as-received without further purification. YSZ electrolytes were prepared from uniaxially pressing commercial YSZ powders (40 nm, Tosoh) at 300 MPa and sintering at 1500 °C for 6 h to yield 0.7 mm-thick disk-shaped pellets with a relative density of over 96% [17]. The Ni/YSZ anode-supported YSZ electrolyte was prepared by tape-casting for fuel cell tests, as introduced in our previous paper [18].

2.2. Preparation of LSM/YSZ nanotubes

The mixture (0.15 mol L^{-1}) of $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, $Mn(NO_3)_2 \cdot 4H_2O$, $Y(NO_3)_3 \cdot 6H_2O$, and $ZrO(NO_3)_2 \cdot 2H_2O$ in deionized water was stirred for 10 min to make the precursor solution of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ and $Zr_{0.92}Y_{0.08}O_2$ (weight ratio 1:1). Several drops of the precursor solution were spread on a glass slide and covered with PC membranes. The membranes would be filled with the solution because of capillary action. After storing at 30 °C in vacuum for 12 h, the filled PC membranes were calcined in a furnace at 800 °C for 10 min at the heating rate of 2 °C min^{-1} and cooled to room temperature naturally in the furnace. The resulting powder was a collection of LSM/YSZ composite nanotubes. For convenience, composite nanotubes prepared using PC templates of 200, 400, and

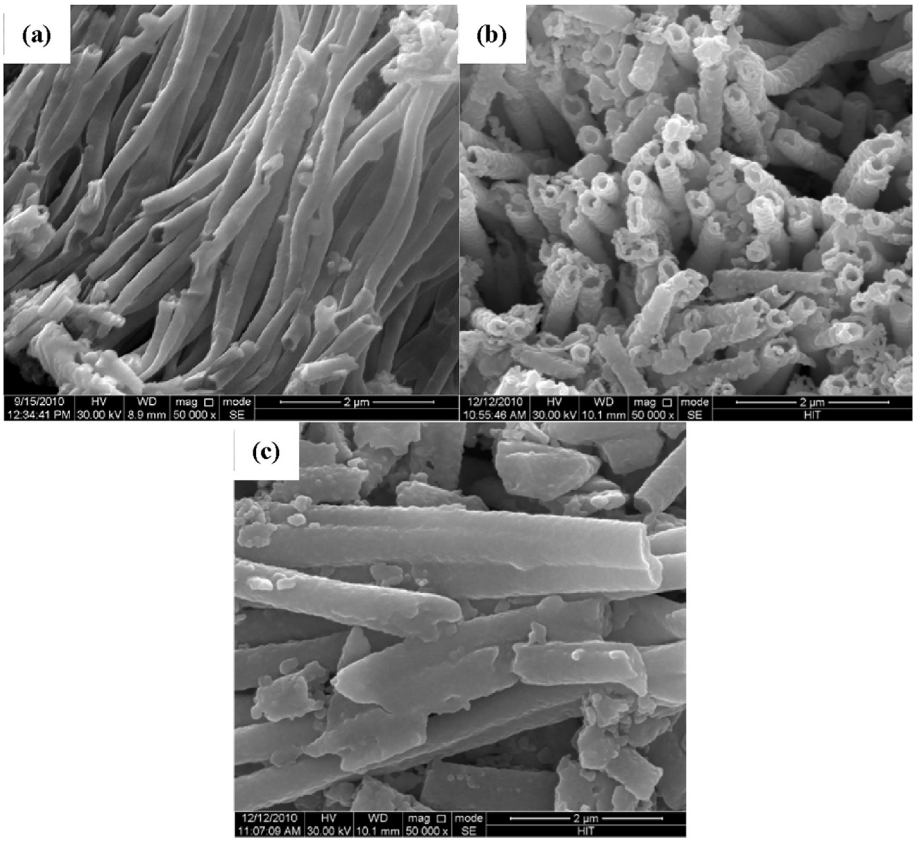

Fig. 2. SEM images of the (a) L/Y200, (b) L/Y400, and (c) L/Y800 nanotubes.