



Original Research Paper

Effect of starting solution concentration in spray pyrolysis on powder properties and electrochemical electrode performance



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ABSTRACT

Nano-composite powders consisting of Sr-doped SmCoO_3 (SSC) and Sm-doped CeO_2 (SDC) were synthesized by spray pyrolysis using different cation concentration solutions, and the effect of this cation concentration on the electrochemical performance of electrodes fabricated using the powders was investigated. Regardless of the cation concentration, spherical particles consisting of nano-order fine SSC and SDC crystallites were successfully obtained. Although the crystal size of all the synthesized powders was almost the same, the particle size increased with increasing cation concentration. The microstructure of the cathodes fabricated using the nano-composite powders clearly depended on the particle size of the starting powders; the microstructure became coarser with increasing particle size and the original particle shapes partially remained in the cathode network. Also, electrochemical measurements for solid oxide fuel cells with these cathodes revealed that the electrode performance was related to the microstructure. The electrode polarization resistance decreased with decreasing particle size, and a relatively fine microstructure cathode exhibited lower electrode polarization resistance, resulting in a high performance of 1.52 W cm^{-2} at 700°C . These results indicate that controlling the particle size, as well as controlling the nanostructure within the particles, is crucial to attain high performance electrodes.

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1. Introduction

High temperature type electrochemical ceramic cells such as fuel cells and electrolysis cells are devices expected to realize high efficiency energy conversion. Although the cell performance primarily depends on the intrinsic characteristics such as conductivity and catalytic activity of the materials used in the cell components, the optimization of cell structure is also essential to maximally utilize the characteristics of the materials. In particular, in the electrode structure in a cell, the electrochemically active region must be designed as large as possible to facilitate electronic, ionic, and gas pathways [1]. The electrode microstructure often dominates overall cell performance. A critical factor determining the electrode microstructure is the properties of the ceramic powder used as raw material for the electrode, for example, particle size distribution, specific surface area, morphology, crystallinity, and sinterability [2–5]. Thus, synthesis of ceramic powders that have superior properties for high performance electrodes has been extensively researched.

Spray pyrolysis is a powder preparation process that can control particle structure at the nano-order level [6–8]. In parallel with synthesizing nano-size crystallites, submicron-size secondary particles consisting of the crystallites have a narrow size distribution. Changing precursor type used for the atomized solution can also produce various particle morphologies such as hollow, porous, and solid dense structures [9]. In particular, spray pyrolysis can effectively prepare composite powders [10–12]. Simultaneous synthesis of several materials yields particles in which nano-size crystallites of synthesized materials are highly distributed among each other, namely, nano-composite powders. The unique structure of powders prepared by spray pyrolysis leads to fine electrode structure with high surface area and uniform networks, resulting in high performance electrodes in electrochemical ceramic cells [13–21]. Besides the unique structure of the powders, a simple powder preparation process in which a powder can be continually obtained includes only the following three steps: (i) atomization of droplets, (ii) transport of droplets and synthesis into particles in heaters, and (iii) capture of the synthesized powder [6–8]. However, spray pyrolysis is inferior to conventional solid-state synthesis processes and other wet synthesis processes in its powder production rate, defined as the amount of produced powder per specific time

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[6,14]. Although higher material concentration involved in an atomized solution in spray pyrolysis leads to higher production rate, it affects the properties of the prepared powders [6,8,22]. In particular, the particle size increases with increasing material concentration. In the case of powder materials used for electrodes, change in particle size often significantly influences the electrode performance, even if the change in size is slight. To achieve high production rate while maintaining powder quality in spray pyrolysis, the relationship between particle size and resulting electrode performance must be clarified.

The present study investigated the relationship between particle size of powders prepared by spray pyrolysis and the electrochemical performance of electrodes fabricated using the powders. In the spray pyrolysis used here, we used ultrasonic vibrators for atomizing droplets to produce fine droplets of uniform size (approximately 1–10 μm) [6,8,18,22,23], and synthesized nano-composite powders consisting of Sr-doped SmCoO_3 (SSC) and Sm-doped CeO_2 (SDC), which are well-known as high performance electrode materials for electrochemical ceramic cells [24–27]. The particle size was controlled by adjusting the cation concentration for SSC–SDC in the starting solution from 0.02 to 0.5 mol L^{-1} . Anode-supported solid oxide fuel cells (SOFCs) with SSC–SDC cathodes using the nano-composite powders were fabricated and then were evaluated in fuel cell operation using humidified hydrogen and air.

2. Experimental

2.1. Synthesis of nano-composite powders by spray pyrolysis

The targeted chemical composition of the nano-composite powders was $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC) and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) at a weight ratio of 70:30. Four SSC–SDC aqueous starting solutions with different cation concentration, C (mol L^{-1}), were prepared. First, an aqueous solution was prepared by dissolving 87.43 g of $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.95% purity, Kanto Chemical Co., Japan), 34.11 g of $\text{Sr}(\text{NO}_3)_2$ (98.0% purity, Kanto Chemical Co., Japan), 93.81 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98.0% purity, Kanto Chemical Co. Japan), and 61.72 g of $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98.5% purity, Kanto Chemical Co., Japan) in distilled water to make a total volume of 1000 mL. This solution contained 0.5 mol L^{-1} SSC–SDC in total cation concentration (0.322 mol L^{-1} of SSC and 0.178 mol L^{-1} of SDC), called here 0.5 mol L^{-1} starting solution. Then, part of 0.5 mol L^{-1} starting solution was diluted with distilled water at three different volume ratios of 1:24, 1:4, and 1:1.5 to prepare three different C solutions, namely, 0.02, 0.1, and 0.2 mol L^{-1} starting solutions, respectively.

Nano-composite powders were prepared by spray pyrolysis. As shown in Fig. 1, the spray pyrolysis apparatus consisted of an atomizing section, a heating section, and a capture section. The starting solutions were atomized by three ultrasonic vibrators (1.75 MHz, TDK, Japan) in the atomizing section. During atomization, the water level and temperature of the solutions were kept

at 30 mm and 30 $^\circ\text{C}$, respectively, because these parameters affect the size and production rate of atomized droplets [14,21]. The droplets were transported into the heating section through a quartz tube (1.1 m long and an inner diameter of 52 mm) using air as carrier gas at a flow rate of 3 L min^{-1} . The heating section consisted of three serial electric furnaces set at 300, 700, and 900 $^\circ\text{C}$ from inlet to outlet, respectively. The droplets were continuously dried, dehydrated, decomposed, reacted, and crystallized in the heating section. Finally, the synthesized SSC–SDC nano-composite powders were captured by a polytetrafluoroethylene (PTFE) membrane filter (0.1 μm pores) in the capture section. These synthesized powders using 0.02, 0.1, 0.2, and 0.5 mol L^{-1} starting solutions were denoted as SSC–SDC(0.02), SSC–SDC(0.1), SSC–SDC(0.2), and SSC–SDC(0.5), respectively.

2.2. Fabrication of SOFC samples

The SOFC samples were a planar anode-supported type using a NiO–YSZ porous substrate prepared by an extrusion process. The anode substrate was composed of NiO powder (Sumitomo Metal Mining Co., Japan) and YSZ powder (TZ-8YS, Tosoh, Japan) at a weight ratio of 60:40. The detailed fabrication procedure of the anode substrate has been presented elsewhere [28]. An electrolyte paste, prepared by mixing YSZ powder (TZ-8Y, Tosoh, Japan) in α -terpineol (Kanto Chemical Co., Japan) with ethyl cellulose (45 cP, Kishida Chemical Co., Japan), a dispersant, and a plasticizer, was screen-printed on the anode substrate, and then the electrolyte and anode substrate were co-sintered at 1350 $^\circ\text{C}$ for 3 h in air. For an interlayer between the electrolyte and cathode, a $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) paste was prepared by mixing GDC powder (Anan Kasei Co., Japan) and the same admixtures as in the electrolyte paste. The GDC interlayer paste was screen-printed on the electrolyte, and then sintered at 1300 $^\circ\text{C}$ for 1 h in air. Four cathode pastes were prepared using the SSC–SDC nano-composite powders synthesized by spray pyrolysis with the same admixtures as in the electrolyte paste. Each cathode paste was painted on the interlayer, and then sintered at 950 $^\circ\text{C}$ for 1 h in air. The designed area of the cathode was 0.283 cm^2 . For a current-collection layer, Au paste (<1 μm thick, Tanaka Kikinzo Kogyo Co., Japan) was painted on the surface of the cathode and anode.

2.3. Characterization and measurements

The crystal structure of the synthesized SSC–SDC nano-composite powders was determined using X-ray diffraction (XRD, SmartLab, Rigaku, Japan) at room temperature with $\text{Cu K}\alpha$ radiation. The 2θ range in XRD was 20–80 $^\circ$ and the step size was 0.01 $^\circ$. The crystal size of SSC and SDC was estimated by the Scherrer equation with a Scherrer constant of 0.9. The morphology of the powders and the SOFCs was observed using scanning electron microscopy (SEM, JSM-5600, JEOL, Japan). In particle size distribution measurements, each powder was dispersed in distilled water

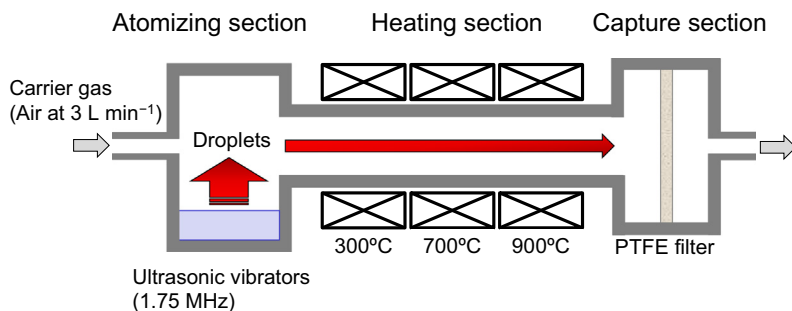


Fig. 1. Schematic of spray pyrolysis apparatus.

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