

## Improving the anode microstructure for SOFC with coprecipitated composite NiO/Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> powder

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Solid oxide fuel cell (SOFC) is an electrochemical energy conversion device with high efficiency and low pollution. There are two basic designs in SOFCs: electrolyte-supported and electrode-supported [1]. Conventional electrolyte-supported SOFCs with YSZ as electrolyte have to operate at high temperatures (900–1000 °C) as the ohmic resistance of YSZ membrane is too high at lower temperatures [2]. The high operating temperature leads to critical materials selection and degradation of the SOFC performance. Therefore, development of intermediate-temperature SOFCs that operate at 500–800 °C has been the recent trend. By reducing the thickness of YSZ electrolyte membrane, the operating temperature of electrode-supported SOFC can be reduced to 800 °C [3]. Furthermore, when alternative electrolyte material with higher ionic conductivity than YSZ, such as doped ceria, is used in electrode-supported SOFC, the operating temperature can be further reduced to 500–700 °C [4, 5]. In anode-supported SOFC, one major role of the anode is to give the proper reaction sites for electrochemical oxidation of the fuel, and the microstructure of anode is important to electrochemical performance of the SOFC [1, 6].

In this work, Ni/Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> (Ni/SDC) anode supported SOFCs with thin SDC electrolyte film and Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub>/SDC composite cathode have been prepared by tape casting, screen printing and co-sintering. The effect of anode microstructure to the power generating characteristics is discussed.

Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99.9%) and Sm<sub>2</sub>O<sub>3</sub> (99.9%) were used to synthesize Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> (SDC) powder. Samarium nitrate was prepared by adding nitric acid to samarium oxide. Mixed solution of cerium nitrate and samarium nitrate was dropped into ammonium oxalate solution under vigorous stirring and the pH value of the oxalate solution was controlled at 6.7 by dropping ammonium hydroxide. The precipitate was then washed three times with distilled water and three times with alcohol before drying at 50 °C. The dried precursor was calcined at 600 °C for 2 hr to prepare oxide powders.

This coprecipitation method was also used to prepare a composite NiO/Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> powder for anode substrate. Mixed solution consisted of cerium nitrate, samarium nitrate, and nickel nitrate was used to synthesize an oxalate precursor, and the precursor was calcined at 600 °C to prepare the composite NiO/SDC powder in which NiO had a weight percent of 60%.

Separate NiO powder was also prepared by heat decomposition of commercial analytically pure basic nickel carbonate at 600 °C. The NiO powder was mechanically mixed with SDC powder at a weight ratio of 60:40 to prepare the anode substrate.

The anode from the mechanically mixed NiO and SDC powder was labeled as MM, and the anode from the coprecipitated composite NiO/SDC powder was labeled as CC. The anode green tapes were fabricated by tape casting process, and thin SDC film was coated onto the anode green substrate by bi-layer tape casting which was described in a previous report [7]. The bi-layer green tapes were sintered at 1400 °C to densify Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> (SDC) layer. The cathode consisted of 70 wt% Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> and 30 wt% SDC was coated onto the electrolyte layer with screen printing and calcined at 1000 °C for 4 hr.

The V–I characteristics of single cells were tested at 500–700 °C by a fuel cell test system made in our laboratory. Moist hydrogen with flux of 30 ml min<sup>-1</sup> was the fuel gas, and stationary air was the oxidant. Microstructure of the cells was observed by scanning electron microscopy (SEM, X-650, Hitachi). The fracture surface of samples was coated a thin layer of gold for better conductivity before observation.

Fig. 1 shows the overview of the microstructure of anode supported electrolyte and cathode films. The thickness of the SDC layer is about 50 μm, and that of cathode layer is about 20 μm. The anode is 0.8 mm thick, and it shows a porous structure after being reduced in H<sub>2</sub> atmosphere.

Magnified SEM micrographs of the interface between Ni/Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> anode and SDC electrolyte are shown in Fig. 2. The dense electrolyte and porous anode exhibit

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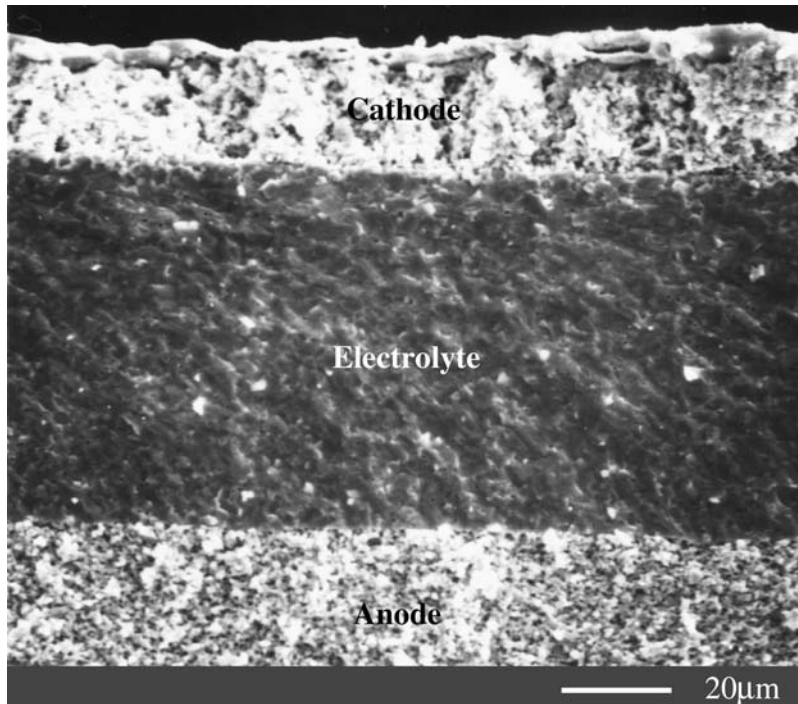


Figure 1 Overview of the microstructure of anode supported electrolyte and cathode films.

a good combination. It has been expected since anode and electrolyte layer have been attached together in green tapes. On the other hand, the two anodes exhibit different microstructure. As shown in Fig. 2a,  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$  in MM anode forms a skeleton and Ni particles fill in the holes. The holes in MM anode are some “ink bottle” shape. It indicates that the holes in MM anode may not have a proper connection for gas permeation [6]. In Fig. 2b, CC anode shows a homogeneous microstructure, the Ni and the  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$  particles are difficult to be distinguished from each other based on the micrograph. It indicates that the two phases, NiO and  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ ,

distribute very homogeneously in the coprecipitated composite  $\text{NiO}/\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$  powder for CC anode. It will enlarge the triple-phase boundary (TPB) region, where charge transfer reactions occur, and improve the performance of the cell [8].

The power generating performance of the two SOFCs is characterized at 500–700 °C, and the results are shown in Fig. 3. The open circuit voltage (OCV) at 500 °C reaches 0.97 V (see Fig. 3a). The OCV is as high as that of a SOFC supported by 1mm thick densified SDC layer [9]. It indicates that the thin SDC film supported by anode has been densified enough after co-sintering. At 500 °C, the

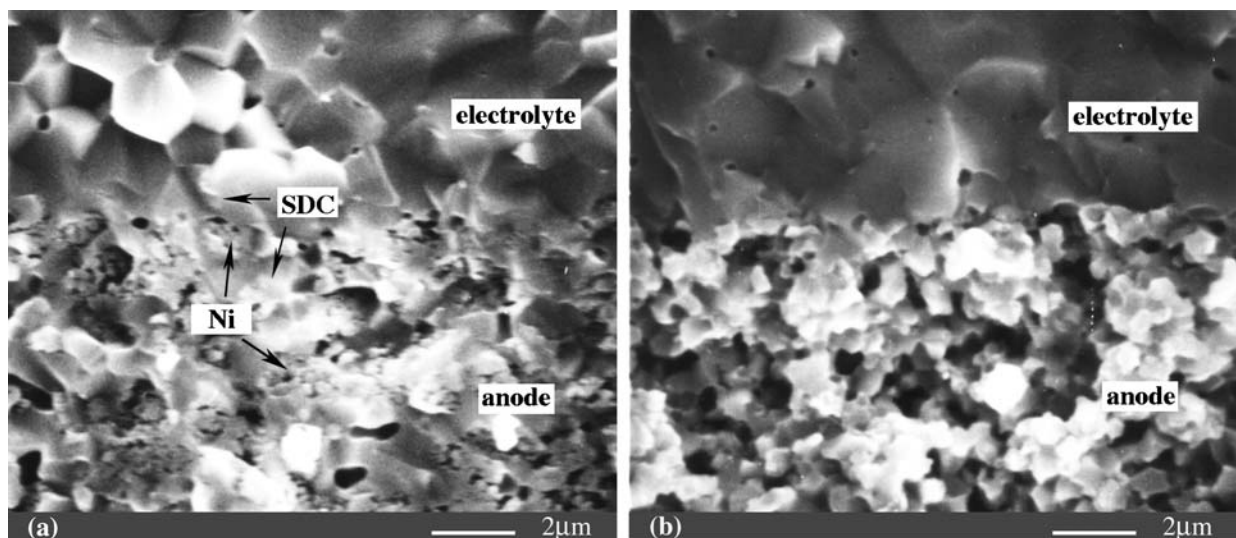


Figure 2 Microstructure of the interface between  $\text{Ni}/\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$  anode and SDC electrolyte: (a) MM anode (b) CC anode.

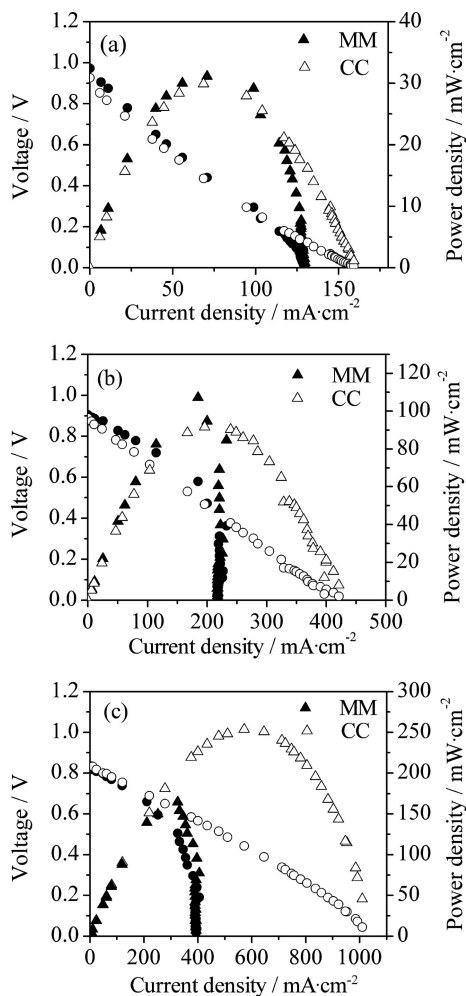


Figure 3 The power generating performance of SOFCs at (a) 500 °C, (b) 600 °C, (c) 700 °C.

power generating characteristics of the two cells are not influenced by different anode microstructure and exhibit similar performance with maximum power densities of about  $30 \text{ mW cm}^{-2}$ . The low conductivity of electrolyte and electrochemical ability of cathode may be critical factors at this low temperature [4, 10]. At 600 °C, however, different anode microstructure has caused different power generating characteristics (see Fig. 3b). Though the two cells exhibit similar maximum power densities of about  $100 \text{ mW cm}^{-2}$ , the power density and output voltage of MM cell drop down suddenly when the current density reaches about  $200 \text{ mA cm}^{-2}$ . It is a typical electrochemical phenomenon of concentration polarization [11]. Since the electrolyte and cathode layers of MM and CC cells are the same, the concentration polarization of MM cell is certainly resulted from its anode with “ink bottle” holes.

At 700 °C, as shown in Fig. 3c, the maximum power density of CC cell reaches  $260 \text{ mW cm}^{-2}$ , while that of MM cell only reaches  $170 \text{ mW cm}^{-2}$  because of serious concentration polarization. At 600 °C, the concentration polarization in MM anode occurs at about  $200 \text{ mW cm}^{-2}$ ; at 700 °C, however, it occurs at about  $300 \text{ mW cm}^{-2}$ . The reason is that the diffusion coefficient of anode gases increases with increasing temperature and the concentration polarization occurs at a higher current density.

In this work, bi-layer tape casting and co-sintering have been used to prepare anode supported thin  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$  film solid oxide fuel cells. The anode from oxalate coprecipitated composite  $\text{NiO/Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$  powder exhibits better electrochemical performance compared with that from mechanic-mixed  $\text{NiO/Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$  powder, and the power density reaches  $260 \text{ mW cm}^{-2}$  at 700 °C without concentration polarization.

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