FULL PAPER

Low-temperature fabrication of (Ba,Sr)(Co,Fe)O₃ cathode by the reactive sintering method

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In this study, we prepare Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3–δ} (BSCF) cathodes using the reactive sintering method. BSCF is known as a candidate for cathode material of intermediate temperature solid oxide fuel cell. This BSCF cathode is fabricated on the anode supported cells at a low-temperature of 700°C in order to overcome a crystal phase transition from cubic to hexagonal. Utilizing the reactive sintering, hexagonal BSCF cathode can be synthesized and sintered at 700°C by using the intermediate compound of BSCF. In addition, the reactive sintering can improve the sinterability of BSCF and decrease the ohmic and polarization resistances of the cells. The anode supported cell having hexagonal BSCF cathode shows a good power output, compared with the sample made from a commercial cubic BSCF powder. Its maximum power output reaches to ca. 1 W cm^{–2} at 700°C. It is considered that the reactive sintered BSCF cathode layer has a good interface with gadolinium doped ceria interlayer. It is found the hexagonal BSCF has good cathode properties if the cathode sintered well at low-temperature.

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1. Introduction

Solid oxide fuel cells (SOFCs) are efficient electricity generation systems by converting a chemical energy to an electrical energy. SOFCs can utilize the many kinds of fuel such as hydrogen, some hydrocarbon and alcohols because the it is operated at higher temperature around 700–1000°C, compared with other fuel cell systems.^{1),2)} Solid oxide electrolysis cells (SOECs), which are close to a reversibly operated SOFCs, can produce the hydrogen from water by using the surplus power such as renewable energies. Thus, it is known that SOFCs/SOECs can contribute to solve the energy and environmental problems. Recently, the intermediate temperature SOFCs (IT-SOFCs), which are operated at 400–600°C, are developed to overcome some difficulties.^{3),4)} One of the advantage to operate at intermediate temperature is the quick starting because the IT-SOFCs can be heated up to operation temperature in short time. Recently, the metal supported SOFCs, which have some advantages such as robustness and low material cost, are widely studied as next generation IT-SOFCs.^{5)–7)} The metal supported SOFCs are expected to endure the rapid start and stop cycle because its metal

substrate is much stronger than conventional ceramic base SOFCs.^{8)–11)} Besides, the metal supported SOFC is expected to be used as a power source for electric vehicle due to its durability.^{12),13)} Therefore, it is important to develop the novel process which can produce metal supported SOFCs at a low cost. We chose the Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3–δ} (BSCF) as a cathode material for IT-SOFCs which shows high activity at intermediate temperature.³⁾ We tried to overcome some challenges, in this study.

One problem is the phase transition of BSCF under intermediate temperature condition. It is known that BSCF has some crystal structures. Conventionally, the synthesis of BSCF powder and the fabrication of cathode layer are operated at higher than 850°C, and these are obtained with cubic phase BSCF.^{14)–16)} However, the phase transition from cubic to hexagonal phase occurs around 850°C when the temperature decreases.^{17),18)} This phase transition derives an abrupt volume change, and this change causes mechanical stress and the generation of microcracks.¹⁹⁾ Therefore, the cathode properties of hexagonal BSCF are unclear because it is difficult to fabricate the hexagonal BSCF cathode. Another challenge is the fabrication of BSCF cathode on stainless-steel base metal supported cells. The cathodes on the metal supported cells must be fabricated in the condition that metal substrate is never oxidized. However, it is difficult to fabricate the cathode in the reducing atmosphere because typical cathode materials of SOFCs are easily reductively decomposed. When the

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stainless-steel is used as a substrate, the cathode fabrication must be done at 700°C in air atmosphere. Therefore, it is important to develop the low-temperature process in air to fabricate the cathode at less than 700°C.

In this study, a low-temperature process for the fabrication of BSCF cathode was developed. In order to prevent the phase transition, the BSCF cathode is directly made with hexagonal phase by sintering at a low-temperature of 700°C. BSCF cathodes were prepared by two approaches. The first approach is using the hexagonal BSCF fine powder. As we previously reported in the literature, the BSCF hexagonal powder was prepared by the novel low-temperature solid-state reaction using the peroxides raw materials.²⁰⁾ This fine powder of hexagonal BSCF was used cathode material. Another approach is utilization of the reactive sintering method for fabrication of BSCF cathode. The reactive sintering carries out the synthesis of material and the sintering at the same time by using the raw materials of a target compound. In our previous report, it was found that sinterability and electrical conductivity of hexagonal BSCF was improved by using the reactive sintering method. Thus, we develop the hexagonal BSCF cathode on the conventional anode supported cell by utilizing the reactive sintering method at 700°C. Besides, the electrochemical properties of hexagonal BSCF cathodes were evaluated.

2. Experimental

2.1 Powder synthesis for cathode pastes

BSCF powders were prepared by low-temperature solid-state synthesis method which we developed.²⁰⁾ BaO₂, SrO₂, amorphous Co₃O₄·*n*H₂O, and Fe₂O₃·*n*H₂O were used as starting materials. Cobalt and iron base hydrous oxides were prepared by precipitation method. Weighing out 8.76 g of CoCl₂·6H₂O (Kojundo Chemical Laboratory Co., Ltd.) and 2.49 g of FeCl₃·6H₂O (Kojundo Chemical Laboratory Co., Ltd.), these were dissolved into 100 mL of distilled water at room temperature, respectively. This solution was stirred for 30 min. After adding 5 mol L⁻¹ of NaOH aq. solution at a volume required to reach pH 8, the precipitates were rinsed out with distilled water and filtered. BaO₂ and SrO₂ were also prepared by the solution method. Weighing out 7.40 g of Ba(OH)₂·8H₂O (Wako Pure Chemical Industries, Ltd.) and 6.24 g of Sr(OH)₂·8H₂O (Kojundo Chemical Laboratory Co., Ltd.), these were dissolved into 100 mL of distilled water, respectively. After adding 5 mL of a 30 wt % H₂O₂ solution little by little, the precipitates were retrieved by filtering and drying at 100°C for 3 h. These powders were mixed, and this mixture was heated at several temperatures for 1 h.

2.2 Fabrication of anode supported cells

Powders of NiO (Sumitomo Metal Mining Co.) and yttria stabilized zirconia (YSZ) (TZ-8YS, Tosoh) were mixed at a weight ratio of 60:40. Besides, pore former and binder were added to this powder mixture. The pore former was a graphite carbon and a binder was 10 wt % of polyvinyl alcohol water solution. A button cell size green

body (30 mm diameter) as an NiO-YSZ anode substrate was made by uni-axial-pressing at 10 MPa. These green body was calcinated at 1150°C for 2 h in air. The electrolyte layer of YSZ was fabricated on the NiO-YSZ anode substrate by spin-coating method. For spin-coating, the YSZ slurry was prepared by ball-milling YSZ powder (TZ-8Y, Tosoh) in ethanol and toluene mixture solvent with polyvinyl butyral binder, amine-based dispersant, and plasticizer for 48 h. A dense electrolyte layer was obtained by co-sintering with an anode substrate at 1360°C for 3 h in air. The gadolinium doped ceria (GDC) interlayer was fabricated on the YSZ electrolyte layer by the screen printing. The GDC paste for screen printing was prepared by mixing GDC powder (GCO90/10, Solvay Special Chem Japan), α -terpineol (Kanto Chemical Co.), ethyl cellulose (Kishida Chemical Co.), a dispersant, and a plasticizer. The GDC layer was heat-treated at 1300°C for 3 h in air. The cathode layer was fabricated on the GDC interlayer. The pastes for cathode were made by the same method as a GDC paste using three types of BSCF powders. Each cathode was then sintered at 700 or 750°C for 1 h in air.

2.3 Characterization

Synthesized powders for cathode pastes were characterized by an X-ray diffractometer (XRD; SmartLab, Rigaku) using Cu K α radiation (40 kV, 30 mA). Microstructures of the cathodes were observed by a field emission scanning electron microscopy (FE-SEM; JSM-6335FM, JEOL) at an accelerating voltage of 15 kV. Electrochemical performance of the anode-supported SOFCs were evaluated at several temperatures with flowing 3% humidified H₂ to the anode as fuel at a feed rate of 100 mL min⁻¹ and synthetic air (N₂:O₂ = 79:21) to the cathode as oxidant at a feed rate of 100 mL min⁻¹, using a potentio-galvanostat with a frequency response analyzer (VSP, BioLogic).

3. Results and discussions

Figure 1 shows the XRD patterns of powder obtained by the heating the starting material powder mixture at several temperatures. The XRD pattern of the product heat-treated at 300°C cannot be identified as BSCF base compounds. It was considered that this product was obtained as an intermediate compound. When the sample was heat-treated at 400°C, the product showed the pattern corresponding to the crystal structure of hexagonal phase barium strontium cobaltite. The intensity of peaks in XRD patterns became sharp by heat-treatment at 700°C. The improvement of crystallinity and the grain growth occurred by high temperature heat-treatment. In our previous report, it was found that the sinterability of the hexagonal BSCF powder prepared at 400°C is better than that of the powders prepared at higher temperatures.²⁰⁾ Thus, using the powders of the intermediated compound obtained at 300°C and the hexagonal BSCF powder prepared at 400°C, the pastes for cathode was made. The anode-supported cells were made from these pastes. The sample names and fabrication conditions are listed in **Table 1**.

Fig. 1. XRD patterns of the intermediate compound and BSCF powders obtained by heat-treating the starting material mixture at (a) 300°C, (b) 400°C and (c) 700°C for 1 h.

Table 1. Conditions for fabrication of anode supported cells

Sample	Heat-treatment Temperature/°C	
	Powder calcination	Cathode fabrication
RS-3070	300	700
RS-3075	300	750
RS-4070	400	700
RS-4075	400	750
Com-70	—	700

Fig. 2. Impedance spectra of anode-supported SOFC with BSCF cathodes sintered at 700°C under OCV condition using 3% humidified H₂ and synthetic air.

Figure 2 shows impedance spectra of samples, measured at 700°C under open circuit voltage (OCV) condition. Besides, ohmic resistances R_{ohm} and polarization resistances R_p of samples are indicated in Fig. 3. R_{ohm} was determined from the intercept at the real axis at the higher frequency side of the impedance spectra, and R_p was determined from the difference between the two intercepts at the lower and higher frequency sides, shown in Fig. 2. Comparing RS-4070 and RS-4075 which were fabricated from the hexagonal BSCF powder calcinated at 400°C, RS-4075 had a smaller polarization resistance. Particularly, the polarization resistance of RS-4075 around low

Fig. 3. Area-specific resistances of anode-supported SOFCs with BSCF cathodes shown in Fig. 2.

frequency area (ca. 10^2 Hz), corresponding to oxygen exchange process on the surface of the cathode,²¹⁾ was reduced comparing that of RS-4070. The oxygen exchange process on the surface of the cathode is affected by many factors such as surface area and crystallinity of cathode material. Considering that the polarization resistance was improved by higher temperature heat-treatment, it was speculated to correspond to improvement of the crystallinity. The RS-3070 and RS-3075, which were fabricated from the intermediate compound powder, showed lower resistances compared with RS-4070 and RS-4075. Focusing on the ohmic resistance shown in Fig. 3, it is considered that RS-3070 and RS-3075 had good interface between GDC interlayer and cathode layer. Moreover, the polarization resistances R_p became smaller. It was considered that the ion diffusion process in the cathode was also improved.²¹⁾ Thus, it was confirmed that the resistance of cathode can be reduced by the reactive sintering using the intermediate compound calcinated at 300°C as a material for the cathode paste. Comparing RS-3070 and RS-3075, these ohmic resistances were similar value. In contrast, the polarization resistance R_p of RS-3075 was slightly larger than that of RS-3070. It was considered that it was due to the reduction of surface area in cathode because of grain growth during the cathode fabrication at 750°C. From these results, the fine structure of cathode can be made at 700°C by using the reactive sintering method. Figure 4 shows cross-sectional SEM images of cathodes in RS-3070 and RS-4070. Both cathodes consisted of small BSCF particles which was about 100 nm. However, the large distance and space were observed at the interface between cathode and GDC interlayer in RS-4070. As mentioned above, the sinterability of BSCF is improved by using the intermediate compound due to the reactive sintering. Each metal ion can diffuse easily because the synthesis reaction and sintering occur at the same time.^{22)–24)} The better interface among hexagonal BSCF particles in

Fig. 4. Cross sectional SEM images of BSCF cathodes prepared at 700°C made from (a) intermediate compound heated at 300°C (RS-3070) and (b) hexagonal BSCF powder heated at 400°C (RS-4070).

Fig. 5. I - V characteristics and power densities for anode-supported SOFCs of (a) RS-3070 and (b) Com-70, measured by using 3% humidified H₂ and synthetic air.

Fig. 6. Impedance spectra of anode-supported SOFCs of (a) RS-3070 and (b) Com-70, measured at 700°C under OCV condition using 3% humidified H₂ and synthetic air.

cathode can be obtained. In addition, the good connection between the BSCF cathode layer and the GDC interlayer was also obtained by using the reactive sintering method. Thus, the ohmic resistance of RS-3070 was smaller than that of RS-4070 as shown in Fig. 3.

For the comparison, the anode supported cell, having the cathode fabricated at 700°C using the commercial BSCF powder, was prepared. This sample was named as Com-70, as shown in Table 1. The commercial BSCF powder had the cubic phase structure, which is confirmed

by XRD measurement (data not shown). The cubic BSCF is known as a good cathode material which has a high electrical conductivity, compared with the hexagonal BSCF.^{20),25)–27)} Figure 5 shows I - V characteristics and power densities for anode-supported SOFCs of RS-3070 and Com-70. Besides, the impedance spectra of RS-3070 and Com-70 at several temperatures under OCV condition are shown in Fig. 6. As shown in Fig. 5, the maximum power output of RS-3070 was higher than that of Com-70 in all temperature conditions, and it reached to

Fig. 7. Area-specific resistances for anode-supported SOFCs of RS-3070 and Com-70.

Fig. 8. Cross sectional SEM image of the cathode of Com-70, which was sintered at 700°C, derived from commercial cubic BSCF powder.

about 1 W cm^{-2} at 700°C. **Figure 7** shows the temperature dependences of ohmic resistances R_{ohm} and polarization resistances R_p , obtained from the results in Fig. 6. It was found that the polarization resistances R_p of both samples were almost same. Thus, it was considered that the performance including a catalytic activity of hexagonal BSCF cathode was comparable that of cubic phase BSCF. In contrast, it was found that the ohmic resistance R_{ohm} of RS-3070 was smaller than that of Com-70. This difference is according to resistance at the interface between cathode and GDC interlayer. The better interface can be obtained by the reactive sintering using the intermediate compound. **Figure 8** shows the cross-sectional SEM image of cathode in Com-70. The cathode of Com-70 also consisted of small BSCF particles. Besides it had the good interface between cathode and GDC interlayer, and it was comparable with that of RS-3070 shown in Fig. 4(a). It was considered that the difference of the ohmic resistance was depended on the local structure at the interfaces. From these results, it was

considered that the hexagonal BSCF had the good cathode performance and it was comparable with cubic BSCF when the cathode structure had an ideal interface and small particles. Using the reactive sintering method to improve the sinterability of hexagonal BSCF, the cathode performance can be improved in spite of a low-temperature fabrication at 700°C. The high performance hexagonal BSCF cathode was successfully developed.

4. Conclusion

In this study, the low-temperature sintering of $(\text{Ba,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$ cathode by utilizing the reactive sintering method was conducted.

Using the peroxides of Ba and Sr, the intermediate compound and the hexagonal phase BSCF were obtained by heat-treating at 300 and 400°C, respectively. These powders of intermediate compound and hexagonal BSCF were used as the raw materials to fabricate the cathode on anode supported cells. When the hexagonal BSCF powder was used as cathode powder, the cell had large ohmic and polarization resistances, R_{ohm} and R_p . In contrast, the cell having the cathode prepared from the intermediate compound had lower resistances. It was considered that the reactive sintering method using the intermediate compound can improve the sinterability of cathode material. Thus, the fine interface between the cathode and the GDC interlayer can be obtained. Moreover, the ohmic resistance of the cathode prepared by reactive sintering method was lower than that of the sample prepared by using the commercial BSCF powder. The cell having hexagonal BSCF cathode prepared by reactive sintering method showed a good power output about 1 W cm^{-2} at 700°C although the cathode was made at 700°C. Hexagonal phase BSCF can perform good electrochemical performance by improving the sinterability utilizing the reactive sintering method.

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