Electrochemical Performance and Cr Tolerance in a $\text{La}_{1-x}\text{Ba}_x\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ ($x = 0.3, 0.4$ and 0.5) Cathode for Solid Oxide Fuel Cells

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ABSTRACT

The electrochemical performance and Cr poisoning behavior of $\text{La}_{1-x}\text{Ba}_x\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ (LBCF, $x = 0.3, 0.4, 0.5$) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) cathodes were investigated for solid oxide fuel cells (SOFCs). The polarization resistance of the LBCF/GDC/LBCF symmetrical cell was found to decrease with increasing Ba content (x value). This phenomenon might be associated with the high oxygen vacancy concentration in the LBCF sample, with $x = 0.5$. In addition, there was no chromium poisoning in the LBCF cathode. On the other hand, the polarization resistance of the LSCF cathode was found to significantly increase after exposure to gaseous chromium species; it appears that this result stemmed from the formation of SrCrO_4 phase. Therefore, it can be expected that LBCF can be a durable potential cathode material for intermediate-temperature solid oxide fuel cells (IT-SOFC).

Key words : Solid oxide fuel cells, Cathode, Perovskite, $\text{La}_{1-x}\text{Ba}_x\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$, Cr poisoning

1. Introduction

A solid oxide fuel cell (SOFC) is an electrochemical device that converts chemical energy from hydrogen-rich fuels into electricity and useful high-quality heat. Since SOFCs operate at high temperatures above 800°C , higher efficiencies than those of other types of fuel cells may be expected. In addition, SOFCs do not require expensive platinum-based catalysts, and fuel flexibility and invulnerability to carbon monoxide poisoning are other advantages over fuel cells that operate at low temperatures.¹⁾ However, high-temperature operation at 800 to 1000°C causes several problems, such as performance degradation due to the reaction between component materials, vulnerability to high-temperature thermal cycles, etc.²⁾ Recently, many studies have concentrated on the development of an intermediate temperature SOFC (IT-SOFC) with operation temperatures lowered to 650 - 850°C . In particular, many studies have been conducted on cathode materials that exhibit rapid oxygen reduction characteristics even at temperatures below 700°C .^{1,3)}

As cathode materials for IT-SOFCs, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) of perovskite series are used most frequently, while $(\text{La},\text{Sr})\text{MnO}_3$ (LSM)-based composites with YSZ are used in some areas.⁴⁻⁶⁾ While the above cathode materials have a mixed ionic and electronic conductivity so as to have high catalytic activity at low operation temperatures and the advantage of their thermal expansion coefficients being sim-

ilar to those of electrolyte materials,³⁾ they suffer from performance degradation due to chromium vapor produced in ferrite stainless steels used as a connection material. It has been reported that Sr in LSCF and Mn in LSM reacts with gaseous chromium species to increase polarization resistance.⁷⁾ Ferrite stainless steels are used as a connecting material for SOFCs because they have high thermal conductivity and electrical conductivity with very low ionic conductivity, and they are inexpensive.⁸⁾ Although oxidation protecting films may be coated to suppress the formation of gaseous chromium species, strategic studies for the development of cathode materials that would be stable against chromium poisoning were recently proposed.⁹⁾ There has been a gradually increasing demand for the development of new cathode materials, not including Sr or Mn, which do not chemically react with gaseous chromium species.⁷⁾

$(\text{La},\text{Ba})(\text{Co},\text{Fe})\text{O}_3$ (LBCF) is a perovskite-type oxide in which Sr of the LSCF is replaced by Ba. Since LBCF is known to show good catalytic activity even in the presence of an Fe-Cr alloy, it is expected to have potential as a cathode material for IT-SOFC.^{8,10)} In the present study, the electrochemical performance of $\text{La}_{1-x}\text{Ba}_x\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ ($x = 0.3, 0.4, 0.5$) perovskite oxide was evaluated as a function of Ba substitution concentrations, and its stability against chromium was evaluated by analyzing changes in the polarization resistance before and after exposure to Cr vapor, and these results were compared with those for the LSCF cathode.

2. Experimental Procedure

$\text{La}_{1-x}\text{Ba}_x\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ (LBCF) powder was synthesized by using a glycine-nitrate process (GNP). The powder synthesis process using GNP is schematically shown in Fig. 1. (a).

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$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich, USA), $\text{Ba}(\text{NO}_3)_2$ (99.0%, Sigma-Aldrich, USA), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98.0%, Sigma-Aldrich, USA), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.5%, Sigma-Aldrich, USA) and glycine (99.0%, Junsei, Japan) were used as the starting materials. The mole ratio of metal ions to glycine was 0.25. The metal nitrates and glycine were dissolved in distilled water. The pH value of the solution was approximately 3. To make a homogeneous precursor, the solution was stirred and heated on a hot plate at 100°C for 2 h. It was then heated to enable the water to evaporate, causing the solution to become dry. Once the combustion reaction started, it was completed in less than 5 min. The exact time depends on the amount of starting materials used. The obtained ash was calcined in a furnace at 1000°C for 5 h.

To evaluate the electrochemical performance of the cathode, an electrolyte-supported symmetric cell consisting of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ (GDC) electrolyte and LBCF electrodes, LBCF/GDC/LBCF was prepared. The GDC powder (AnanKasei, Japan) was pressed uniaxially into disks in a WC-Co alloy mold (25 mm in diameter), which was followed by cold isostatic pressing (CIP) at 200 MPa using a rubber mold with a stainless steel cylinder placed in the center. After CIP, the pressed pellets were fired at 1450°C for 5 h. The thickness of the GDC electrolyte was 300 μm after grinding and polish-

ing. The LBCF electrodes were coated on both sides of the GDC electrolyte by screen printing. The LBCF/GDC/LBCF symmetrical cells were finally heat-treated at 1000°C for 2 h. For comparison, LSCF/GDC/LSCF symmetric cells were prepared in the same way using commercial LSCF6428 (Fuel Cell Materials, USA) powder.

To evaluate cathode poisoning behavior under gaseous chromium species, the following experiments were carried out. First, a porous chromium oxide (Cr_2O_3) sample (20 mm in diameter and 5 mm in thickness) was prepared from commercially available Cr_2O_3 powder (99%, Junsei, Japan). The Cr_2O_3 powder was uniaxially pressed into a disk and the powder compact was subsequently heat-treated at 1000°C for 1 h. The LBCF/GDC/LBCF and LSCF/GDC/LSCF cells were heat-treated at 800°C for 100 h with the Cr_2O_3 disks, as shown in Fig. 1. (b). The Cr_2O_3 disks were placed on the upper and the lower sides of LBCF/GDC/LBCF and LSCF/GDC/LSCF symmetric cells. To avoid direct contact between the electrode surfaces and the Cr_2O_3 disks, Pt meshes were inserted between each Cr_2O_3 disk and the cells. To exclude thermal degradation effect from the chromium poisoning of the cathode, the same cell was also heat-treated at 800°C for 100 h in air atmosphere with no Cr_2O_3 disk.

For characterization of the crystalline phase, X-ray dif-

Fig. 1. Schematic diagram of the process used in synthesizing LBCF powders (a) and the Cr poisoning experimental setup (b).

fraction (XRD, DMAX-2500, Rigaku Co., Ltd., Japan) was performed using Ni-filtered CuK α radiation. The microstructure was observed by field emission scanning electron microscopy (FE-SEM, S-3200, Philips).

The AC impedance spectra were obtained under air atmosphere with an excitation potential of 20 mV over the frequency range of 1 MHz to 0.01 Hz by an impedance analyzer (IM6e, Zahner). The two Pt wires from the electrodes were connected to the working and counter terminals of the impedance analyzer, respectively.

3. Results and Discussion

The XRD patterns of $\text{La}_{1-x}\text{Ba}_x\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ ($x = 0.3, 0.4, 0.5$) powder are shown in Fig. 2. In the present study, the atomic ratio of Co:Fe of the LBCF powder was 0.9:0.1, while three samples with different Ba to La ratios were prepared. In the case of $x = 0.3$, LBCF having a single phase of perovskite could be obtained when the powder sample was calcined at 1000°C for 5 h. On the other hand, a secondary phase, barium cobalt oxide ($\text{Ba}_8\text{Co}_7\text{O}_{21}$) was detected in the $x = 0.4$ and 0.5 samples, and the peak intensity of the secondary phase slightly increased with increasing x value. This result suggests that the large amount of Ba substitution for La resulted in the formation of the secondary phase.

Figure 3 shows the temperature dependence of the polarization resistance values of each electrode calculated from the impedance spectrum results for $\text{La}_{1-x}\text{Ba}_x\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ ($x = 0.3, 0.4, 0.5$) symmetric cells. As compared with the composition of $x = 0.3$, the LBCF with the compositions of $x = 0.4$ and 0.5 exhibited low polarization resistance values, and the lowest polarization resistance value could be obtained from the LBCF with the composition of $x = 0.5$. In the case of B-site substitution, the binding force of Fe-O is stronger than that of Co-O, and the catalytic activity of LBCF has been reported to be reduced as the lattice oxygen content (3- δ) was increased when the Fe content was high.¹⁰⁾ When the Ba^{2+} substitution for La^{3+} at the A-site of the perovskite structure is increased, the oxygen vacancy ($\text{V}_\text{O}^{\bullet\bullet}$) concentration increases, affecting the oxygen content (3- δ) due to electric charge compensation (+3/+2). Here, δ is the concentration of oxygen vacancy ($\text{V}_\text{O}^{\bullet\bullet}$), and it is considered that the catalyst activity for oxygen reduction reaction is the best when $x = 0.5$, since the concentration of $\text{V}_\text{O}^{\bullet\bullet}$ is the highest and the lattice oxygen vacancy content (3- δ) is the lowest.

To evaluate the durability of the LBCF cathode against chromium poisoning, the impedance spectra before and after chromium poisoning were measured and compared. Chromium poisoning experiments were conducted for the LBCF5591/GDC/LBCF cell, which had the lowest polarization resistance, and the LSCF. The chromium poisoning experiments were conducted for the cell with an LSCF electrode by the same method. Figures 4 and 5 show the ac impedance spectra obtained from the LBCF5591/GDC/LBCF5591 and LSCF/GDC/LSCF symmetric cells before

Fig. 2. XRD patterns of the synthesized LBCF ($x = 0.3, 0.4, 0.5$) powders by glycine-nitrate process.

Fig. 3. Polarization resistances of LBCF ($x = 0.3, 0.4, 0.5$) cathodes as a function of temperature.

and after chromium poisoning, and the polarization resistance values of each electrode calculated from Figs. 4 and 5 are given in Table 1.

Because the LBCF had lower polarization resistance values than the LSCF in all temperature regions before chromium poisoning, the LBCF was demonstrated to be an electrode with very high catalytic activity as an SOFC cathode. As shown in Fig. 4 and Table 1, the polarization resistance of the LSCF cathode was greatly increased by exposure to Cr vapor (100 hours). For example, the polarization resistance was $0.22 \text{ } \Omega\text{cm}^2$ at 700°C before chromium poisoning, while it was increased to $1.02 \text{ } \Omega\text{cm}^2$ by almost 5 times. This result indicates that LSCF is very vulnerable to Cr vapor exposure and that the performance deterioration due to Cr poisoning is quite serious. On the other hand, LBCF showed almost no change in polarization resistance values under the same condition, and ohmic resistance values were decreased somewhat so that the total resistance values could be seen to have decreased.

Fig. 4. AC impedance spectra of the LBCF5591 cathode at various temperatures before and after Cr poisoning.

Fig. 5. AC impedance spectra of the LBCF5591 cathode at various temperatures before and after Cr poisoning.

Table 1. Polarization Resistances of LBCF and LSCF Cathodes Measured at Various Temperatures

Operation Temperature (°C)	LBCF5591		LSCF6428	
	Before Cr poisoning R_p (Ωcm^2)	After Cr poisoning R_p (Ωcm^2)	Before Cr poisoning R_p (Ωcm^2)	After Cr poisoning R_p (Ωcm^2)
600	0.51	0.50	1.78	9.38
650	0.27	0.24	0.58	2.91
700	0.13	0.12	0.22	1.02
750	0.07	0.07	0.10	0.40
800	0.03	0.04	0.05	0.16

Fig. 6. XRD patterns of the LBCF5591 cathode before and after Cr poisoning.

Fig. 7. Cross-sectional SEM images of the LBCF5591 cathode.

Although Ba and Sr are alkaline earth metals, dissolution enthalpy when Ba^{2+} ions are substituted in the La^{3+} -based perovskite has been reported to have a more negative value than that observed when Sr^{2+} ions are substituted.¹¹⁾ This means that substitution with Ba^{2+} ions instead of La^{3+} ions in a perovskite crystal structure is energetically more favorable than Sr^{2+} . Therefore, in comparison with LBCF, LSCF may react with chromium more easily when exposed to Cr vapor phase. In the present study, the fact that strontium chromite formed in the LSCF, whereas unwanted phases such as barium chromite were not detected in the case of LBCF, is attributable to the fact that the phase stability of LBCF is higher than that of LSCF.

These results suggest that LBCF has great potential for use as a cathode material with excellent long-term stability since it shows excellent catalytic activity for oxygen reduction reaction at the cathode and low reactivity with not only Cr vapor but also electrolyte and other SOFC components. Although a previous study reported that the thermal expansion coefficient of LBCF is higher than that of LSCF, this problem can be overcome through blending with electrolyte

Fig. 8. Cross-sectional SEM images of the LSCF/GDC/Ni-YSZ cell (a), LSCF cathode (b), and LSCF cathode after Cr poisoning (c).

materials like GDC and YSZ.^{5,10)} Although LBCF reportedly reacts with Cr vapor in some composition (LBCF6428) to produce barium chromite, there was no reaction with Cr vapor in an LBCF5591 sample, and the electrochemical characteristics were also excellent in the present study.^{10,12)}

Figure 6 shows the XRD patterns of the LBCF electrode before and after chromium poisoning. It appears that there was no change in the crystal phases before and after chromium poisoning. This result implies that LBCF is very robust against chromium poisoning and that no reaction occurs between Cr vapor and LBCF even upon exposure to Cr vapor.

Figure 7 shows cross-sectional SEM images of an LBCF/GDC/LBCF symmetrical cell. As is evident in Fig. 7, the thickness of the LBCF electrode was estimated to be approximately 20 μm and the porous LBCF cathode adhered well to the GDC electrolyte. There was no defect such as delamination in the sample. Figures 8 (b), (c) show SEM images that reveal the microstructure of the LSCF cathode before and after chromium poisoning. Comparing Figs. 8 (b) and (c) reveals that changes in the surface shapes had occurred, which was presumably caused by the production of strontium chromite phase on some particle surfaces of the LSCF electrode.^{8,12)}

Figure 9 presents the simulation result for the equivalent circuit model of the impedance spectra for the LBCF and LSCF cathodes. Each polarization resistance element was analyzed, and the results are shown in Table 2. In the equivalent circuit model, L_0 is the inductance value from the cable connected with the apparatus, R_0 is the ohmic resistance produced by contact with the GDC electrolyte. Here, $R_H Q_H$ and $R_L Q_L$ denote the high-frequency and low-frequency regions, respectively, while Q is an element considered as a non-ideal capacitor, which has been reported to

Fig. 9. AC impedance spectra and equivalent circuit models of LBCF (a) and LSCF (b) cathodes at 750°C; symbols and solid lines indicate measured and fitted ac impedance spectra, respectively.

be similar to an actual capacitor.¹⁰⁾ Impedance spectra consist of at least two semi-circles for the high-frequency region (HF) ($> 10^2\text{Hz}$) and the low-frequency region (LF) ($< 10^2\text{Hz}$). According to Adler et al., the polarization resistance in the high-frequency region (R_H) is related to oxygen ion conduction, while the polarization resistance in the low-frequency region (R_L) is an effect of mass transfer, such as diffusion, etc. of oxygen gas.¹³⁾ As seen in Fig. 9, the impedance spectra of LBCF consist of two semi-circles: a large semi-circle at high frequency and a small one at low frequency, while it seems that the LSCF cathode has one large semi-circle.

According to Table 2, both R_H and R_L values of LSCF increased after chromium poisoning; R_H increased by 20 times, indicating a higher ratio of increase. The increased R_H in LSCF after chromium poisoning might be due to the strontium chromite phase, which hinders oxygen ion diffusion and conduction. In addition, the microstructure change due to the formation of strontium chromite phase on the LSCF particle surfaces may be responsible for the increased R_L value. On the other hand, the LBCF showed no change in R_H or R_L before and after chromium poisoning. One interesting feature observed in the impedance spectra of LBCF is

Table 2. R_H , R_L , and R_p Values of LBCF and LSCF Cathodes Measured from Fig. 9 (a) and (b)

$R(\Omega\text{cm}^2)$	LBCF5591		LSCF6428	
	Before Cr poisoning	After Cr poisoning	Before Cr poisoning	After Cr poisoning
R_H	0.067	0.068	0.01	0.25
R_L	0.02	0.02	0.10	0.16
R_p	0.07	0.07	0.10	0.40

that the semi-circle at high frequency was larger than that at low frequency. This indicates that the high frequency contribution to the total polarization resistance was great in LBCF. For example, the R_H value of LBCF before chromium poisoning was $0.067\Omega\text{cm}^2$, while the R_L value of LBCF was $0.02\Omega\text{cm}^2$. Therefore, the polarization resistance of the LBCF cathode could be further reduced through the optimization of electrode microstructure and composition.

4. Conclusions

$\text{La}_{1-x}\text{Ba}_x\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ (LBCF, $x = 0.3, 0.4, 0.5$) has been proposed as a cathode material for solid oxide fuel cells (SOFCs), and the chromium poisoning phenomenon of LBCF and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) has been investigated. As the x values (i.e., substitution amounts of Ba) increased, polarization resistance decreased, and the polarization resistance of the LBCF ($x = 0.5$) cathode was lower than that of the LSCF cathode. In addition, no change in polarization resistance was observed before and after chromium poisoning. Meanwhile, the chromium poisoning phenomenon was observed in the LSCF, and the polarization resistance had greatly increased after exposure to Cr vapor. This result is attributable to the SrCrO_4 phase produced by the reaction between Cr vapor and the LSCF. The fact that no chromium poisoning was observed in the LBCF cathode suggests that Ba exists in a more stable manner in the La-based perovskite crystal structure than Sr. If the problems with a high thermal expansion coefficient can be solved in the future through blending with electrolyte, etc., then LBCF could be promising as a highly durable cathode material to replace LSCF.

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