— Article —

Optimization of Segmented-in-series Tubular SOFCs using an $\text{La}_{0.5}\text{Sr}_{0.5-x}\text{Ca}_x\text{MnO}_3$ System Cathode and the Generation Characteristics Under Pressurization

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In this research, we studied the optimization of a segmented-in-series tubular solid oxide fuel cell using $\text{La}_{0.5}\text{Sr}_{0.5-x}\text{Ca}_x\text{MnO}_3$ system materials for the cathode. $\text{La}_{0.5}\text{Sr}_{0.25}\text{Ca}_{0.25}\text{MnO}_3$ (LSCM25) was chosen for the cathode to obtain high electric conductivity and prevent the formation of highly resistive second phases with Y_2O_3 -stabilized ZrO_2 (YSZ) electrolyte as a result of X-ray diffraction. To obtain lower resistance at the cathode/electrolyte interface, we studied the optimization of the cathode interlayer by changing the LSCM25-YSZ volume ratio and YSZ particle sizes. As a result, the lowest resistance was obtained at 50 vol. % LSCM25 (particle size: 3 μm) + 50 vol. % YSZ (2 μm). The area-specific resistance of a tubular cell stack using the LSCM25 cathode and the LSCM25-YSZ interlayer decreased by 17% compared to a stack using only an LSCM25 cathode. We also conducted power-generation tests under pressurization to measure the cell stack performance integrated with micro gas turbines. Judging from the I - V characteristics, an increase of test pressure brought about not only an increase of open circuit voltage but also a decrease of internal resistances. According to our analysis of the internal resistances using the current interruption method, the electrode polarizations decreased as the operating pressure rose.

Key Words : Solid Oxide Fuel Cells, Cathode, Lanthanum Manganese Oxide, Pressurized Performance

1 Introduction

The solid oxide fuel cell (SOFC) is a high-temperature electrochemical device which converts chemical energy from fuels such as hydrogen, natural gas, and coal gasification gas into DC electricity. A pressurized SOFC hybrid power system integrated with a gas turbine (GT) can achieve an extremely high electric generation efficiency of 70%, based on the lower heating value (LHV) of natural gas.¹⁾ To realize the pressurized SOFC-GT combined cycle system, it is important to understand power-generation characteristics of SOFC under pressurization. The performance of SOFC is known to improve with an increase in operating pressure.^{2,3)}

Figure 1 shows the structure of the segmented-in-series tubular SOFC. The tubular type SOFC consists of cells arranged on a substrate tube and connected in series with an interconnector. Fuel is fed inside the substrate tube, while oxidant air is supplied to the external side and generated H_2O and CO_2 are discharged from the inner side.

In this study we sought to realize a SOFC/micro-GT combined cycle system by measuring the power-generation characteristics of a tubular type SOFC in the range of 0.1 - 0.4 MPa and analyzing the performance improvement by pressurization. The cell stacks for the test were

made up of high-temperature SOFC (1173-1273 K) using a 10 mol% Y_2O_3 stabilized ZrO_2 (10YSZ) electrolyte, NiO-YSZ anode, and $\text{La}_{0.5}\text{Sr}_{0.5-x}\text{Ca}_x\text{MnO}_3$ (LSCM) cathode. Table 1 shows development subjects for applying LSCM to the tubular type SOFC.

(La, Sr) MnO_3 (LSM) and (La, Ca) MnO_3 (LCM) are widely used cathode material with YSZ electrolyte, because of its high electric conductivity, chemical compatibility with YSZ, and thermal stability at operating conditions. Much of the work was reported electric conductivity and reactivity with YSZ as a function of stron-

Fig. 1 Cross section of segmented-in-series tubular type SOFC.

Table 1 Development subjects for applying LSCM to the tubular type SOFC.

Item	Requirements	Experimental contents
Composition	<ul style="list-style-type: none"> • High electric conductivity • Prevention of the formation of highly resistive second phases such as $\text{La}_2\text{Zr}_2\text{O}_7$, SrZrO_3, CaZrO_3 	Optimization of Ca substitution amount by measuring the electric conductivity of the changed x specimens and analyzing the reactivity with YSZ
CCCL	High electric conductivity within the crack-free shrinkage rate during cathode sintering	Optimization of the LSCM particle size distribution by measuring the relative density, shrinkage rate and electric conductivity
CIL	Decrease of the interface resistance	(1) Optimization of LSCM-YSZ volume ratio (2) Optimization of YSZ particle size while keeping the LSCM-YSZ volume ratio

tium substitution amount of LSM.⁴⁻²⁰⁾ If the formation of high resistive second phase can be prevented, $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (LSM50) offers promise as a cathode material having high electric conductivity (300 S cm^{-1} or above in dense pellet).⁴⁻⁶⁾ The thermodynamic analysis by Yokokawa *et al.* predicted that it would be easier to form SrZrO_3 than CaZrO_3 .²¹⁾ Then, we studied the Ca substitution amount of x necessary to confer high electric conductivity and prevent the formation of highly resistive zirconates with YSZ.

Second, we studied the LSCM for cathode current collection layer (CCCL). In our tubular type SOFC, the cathodes are printed and fired after co-sintering of the substrate tube, anode, electrolyte, and interconnector. The cathode firing temperature is kept lower than the co-sintering temperature, in order to prevent the formation of highly resistive zirconates. For this reason, cracking will be induced if there is high rate of shrinkage of a printed LSCM film during the cathode sintering. Thus, we studied how well the electric conductivity could be improved within the crack-free shrinkage rate by controlling the particle size distribution of LSCM.

Third, we studied the cathode interlayer (CIL) in LSCM-YSZ in an effort to decrease the interface resistance between the cathode and electrolyte. The considerable affects of the CIL characteristics on the SOFC generation performance have prompted studies on many aspects of LSM-YSZ CIL.^{16,22-34)} In the present research, we studied the optimization of LSCM-YSZ mixed powders.

We compared the electrical performance of tubular type cell stacks with or without the LSCM-YSZ CIL in atmospheric pressure to verify the effect of LSCM-YSZ CIL. Next, we tested the cell stack with the CIL under pressurized conditions up to 0.4 MPa to measure the generation performance of the integrated system with micro gas turbines. Further, we measured the change in the internal resistance of the cell by the current interruption method, in order to analyze the improvement of electrical performance with the increase of pressure.

2 Experimental

2.1 Sample Preparation

LSCM powders were synthesized by solid state reactions from La_2O_3 , SrCO_3 , CaCO_3 , and MnO_2 . The calcium

substitution amounts x were 0, 0.15, 0.2, 0.25, 0.5. The prepared powders were mixed together by ball milling for 20 h and calcined at 1473 K for 10 h. The single phase of perovskite structure was confirmed by powder X-ray diffraction (XRD) for every LSCM composition.

The synthesized powders were molded by uniaxial pressing and calcined in air at 1623-1723 K for 2 h to form a square rod with a relative density of more than 95%. The electric conductivity was measured by the 4-point DC method in air at 1273 K.

YSZ powder was pressed and fired in air at 1673 K for 2 h to form pellets with a 28 mm diameter, 1 mm thickness and relative density of more than 95%. To investigate the reactivity of LSCM and YSZ, each LSCM slurry was printed on a YSZ pellet and sintered in air at 1573 K for 2 h. The slurry was prepared by kneading the oxide powder with organic binder and a dispersant using a three-roll mill. The LSCM films baked on the YSZ pellets were thinly shaved with a knife and the film surfaces were then analyzed by XRD to detect the formation of secondary phases.

Coarse (particle size : 53 μm) and fine (3 μm) powders of LSCM were mixed at the volume ratio of 90/10 to 0/100 vol.% by a V-blender to study the particle size distribution of LSCM for CCCL. All particle sizes were measured by laser diffraction particle size analyzer in this study. Each mixed powder was pressed into square rods and baked in air at 1573 K for 2 h. The relative density, shrinkage rate, and electric conductivity of each sample after baking were measured. The shrinkage rate was calculated on the basis of green length and width.

LSCM (particle size : 3 μm) and YSZ (0.5 μm) powders were mixed with ethanol solvent for 45 h by ball milling to measure the interface resistance between LSCM-YSZ CIL and YSZ electrolyte. The ratio of LSCM-YSZ was 100-0 to 60-40 vol.%. The volume ratio of LSCM-YSZ was maintained at the composition shown later, and powders of the same LSCM and YSZ having various sizes were mixed. The sizes of YSZ powders were 0.5, 2, 8, 20 μm . All mixed powders were kneaded with an organic binder and dispersant by the three-roll mill. The prepared slurries were printed on the dense sintered YSZ pellets and calcined in air at 1573 K for 2 h. Pt paste was printed on the other side of the pellet as the counter electrode and baked in air at 1173 K for 1 h. The prepared half-cells

had an effective generation area of 0.79 cm^2 . Pt mesh with Pt lead wire was attached onto the oxide and Pt electrodes with Pt paste to provide current collection. In addition, a Pt wire with Pt paste was bound around the radial surface of the pellet as a reference electrode.

Electrochemical measurements were conducted in an alumina tube placed inside the furnace by the three-terminal method using a frequency analyzer (NF Circuit Design Block Company Limited, type 5000) and a potentiostat (Toho Technology Company, Limited, Type 2000). The impedance spectra of half-cells were measured under open circuit using a signal amplitude of 10 mV over a frequency range of $0.01 \sim 10^5 \text{ Hz}$. The measurements were carried out in air at 1173 K. The microstructure was characterized by scanning electron microscopy (SEM).

2.2 Cell stack fabrication

A segmented-in-series tubular type SOFC consisted of a substrate tube, anodes, anode interlayers, electrolytes, interconnectors, CILs, and CCCLs. Calcium-stabilized ZrO_2 (CSZ) powder was mixed with a binder and distilled water and kneaded. The CSZ substrate tubes were uniaxially extruded through dies with outside diameters of 22 and 28 mm (thickness of 3 mm) after sintering.

Powders of NiO-YSZ anode and NiO-YSZ anode interlayer were mixed in ethanol solvent for 24 and 15 h by ball-milling, respectively. $\text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_3$ and 10YSZ were used for the interconnector and electrolyte, respectively. The slurries for screen-printing were prepared by the oxide powders with an organic binder and a dispersant using the three-roll mill.

Each slurry was screen-printed in the order of the anodes, the anode interlayers, the electrolytes, and the interconnectors on the substrate tubes and co-sintered in air at 1673–1733 K for 4 h. The CIL and CCCL was screen-printed after the co-sintering and baked in air at 1573–1638 K for 2 h. Tubular type cell stacks with or without CIL were fabricated to validate the effect of LSCM-YSZ CIL at a diameter of 22 mm. The thicknesses of the anode, anode interlayer, electrolyte, interconnector, CIL, and CCCL were 150, 20, 90, 20, 10 and 1000 μm , respectively. Table 2 shows the specification of the fabricated cell stacks.

2.3 Performance test of cell stack

A schematic diagram of the electrical performance test apparatus is shown in Fig. 2. Fuel was supplied to the cell stack through the inner side of the fuel injection tube from the top of the apparatus. Fuel was turned up at the bottom and supplied to the cell stack, and the unreacted fuel was discharged from the upper part of

the apparatus. Air, meanwhile, was supplied from bottom of the cell stack and turned down in the upper part, and the exhaust air was discharged from the bottom of the apparatus. A schematic diagram and photograph of the type 2-2 cell stack are shown in Fig. 3. This stack was composed of 34 cells. The performance test was conducted on 33 cells using the cells at both ends as current collectors. The performance tests on type 1 and type 2-1, with 15 cells, were conducted on 14 cells in the same way. Pt mesh welded Pt lead wire was attached to the edge of cathode in the No. 1 and No. 34 cells with Pt paste to provide current collection. Pt wires with Pt paste were bound around the cathode surfaces to measure the voltages. The cell stack voltage (Vs), downstream No. 1 (V1), and upstream No. 33 (V33) were measured in type 2-2.

The cell stacks were heated from room temperature up to 1173 K at a constant rate of 100 K h^{-1} while feeding distilled H_2 (1 Nl min^{-1} , $\text{H}_2/\text{N}_2 = 5/95\%$) and air (6.55 Nl min^{-1}) in the anode and cathode, respectively. In the type 1 and type 2-1, the current-voltage (I - V) characteristics were measured at 1173 K using $0.786 \text{ Nl min}^{-1}$ of diluted H_2 ($\text{H}_2/\text{N}_2 = 70/30\%$) and 6.55 Nl min^{-1} of air for the fuel and oxidant, respectively. These flow rates corresponded to 70% of fuel utilization and 14% of air utilization at 280 mA cm^{-2} , respectively. The type 2-2 cell stack was tested using synthesis fuel ($\text{H}_2/\text{CO}/\text{CO}_2/\text{CH}_4/$

Fig. 2 Schematic diagram of experimental apparatus for a segmented-in-series tubular type cell stack.

Table 2 Specification for the fabricated tubular type cell stack.

	Outer diameter (mm)	Length (mm)	The number of in-series cells	Cathode interlayer
Type 1	22	550	15	-
Type 2-1	22	550	15	LSCM-YSZ
Type 2-2	28	1500	34	LSCM-YSZ

Fig. 3 A schematic diagram and photograph of the type 2-2 cell stack. The schematic diagram shows the voltage measurement cells and lead wire of the current collector for the generation performance test. V1 is the No. 1 cell voltage, V33 is the No. 33 cell voltage, and Vs is the stack voltage.

H₂O = 14/2/30/10/43%) of reformed methane with steam at a steam/carbon ratio (S/C) of 4 under 0.1–0.4 MPa. The test apparatus was installed in a pressure vessel and the total pressure was regulated by a control valve in the air exhaust line. Positive pressure of 0.5 kPa was provided from the fuel side by adjusting the differential pressure of the fuel and air with a control valve prepared in the fuel exhaust line. The gas flow rates were regulated by mass flow controllers. The electrochemical characteristics under pressurization were measured by the current interruption method using a current pulse generator (Hokuto Denko Corp., HC-114) and an oscilloscope (Yokogawa Electric Corp., DL750P).

3 Results and Discussion

3.1 Ca substitution amount x of LSCM

In order to determine the amount of Ca substitution x , we measured the electric conductivity of the specimens and analyzed the reactivity with YSZ by XRD.

The electric conductivity of LSCM square rods was measured as a function of the calcium substitution amount x in air at 1273 K. The conductivity is highest at approximately 370 S cm⁻¹ in La_{0.5}Sr_{0.5}MnO₃ of $x = 0$ and decreases with the addition of calcium, as shown in Fig. 4. Even if the x values changed to 0.15–0.25, the electric conductivity is held at approximately 340 S cm⁻¹.

Figure 5 shows the results of XRD of the surfaces with thinly shaved LSCM films sintered at 1573 K on the YSZ pellets. No secondary phases are observed in $x = 0.2, 0.25$, but SrZrO₃ phase is detected at x values of 0.1 or less. The present result is in agreement with prior reports, in which highly resistive SrZrO₃ formed at a strontium substitution amount of 0.3–0.4 in LSM system cathode materials.^{11,20)}

For the above reasons, we decided to adopt La_{0.5}Sr_{0.25}Ca_{0.25}MnO₃ (LSCM25) as the cathode material. LSCM25 provides equivalent amounts of Sr and Ca because of its high electric conductivity and its effect in

Fig. 4 Variation of electric conductivity with the amount of calcium substitution for La_{0.5}Sr_{0.5-x}Ca_xMnO₃ in air at 1273 K.

Fig. 5 XRD patterns of YSZ pellet surfaces in contact with La_{0.5}Sr_{0.5-x}Ca_xMnO₃.

preventing the formation of secondary phases with YSZ electrolyte.

3.2 Optimization of LSCM particle size distribution

The co-sintered tube doesn't shrink while the CCCL is baked, as the cathode-sintering temperature is kept lower than the co-sintering temperature in order to prevent the formation of highly resistive zirconates. For this reason, a crack will form in the CCCL if the shrinkage rate of a printed LSCM25 film is large during sintering. That is, the CCCL needs to increase the electric conductivity with decreasing the shrinkage rate. When Mizusaki *et al.* examined the relation between the electric conductivity and shrinkage rate of a porous electrode, they found that a decrease of the shrinkage rate reduced the neck region of particles and decreased the electric conductivity.³⁵⁾ On the other hand, in order to increase the electric conductivity of the CCCL, it is effective to increase the relative density after sintering. As one method of controlling the shrinkage rate and increasing the relative density after calcination, there is improvement in the packing density before sintering. That is, an effective way to increase the electric conductivity and control the shrinkage rate is to raise the packing density before sintering. With this in mind, we decided to study the improvement of the electric conductivity within the crack-free shrinkage rate by controlling the particle size distribution of LSCM25.

We measured the changes of the shrinkage rate by sintering and packing density before calcination as functions of the addition of coarse LSCM25 powder, in order to optimize the volume ratio of coarse/fine powders in CCCL. The shrinkage rate decreases as coarse LSCM25 powder was added, as shown in Fig. 6. The packing density before calcination increases with the addition of powder up to a maximum packing density at 70%, then decreases thereafter. The packing density before sintering can be expressed by the following equation (1)³⁶⁾

$$\rho_G = \rho_s \left(1 - \frac{\Delta L}{L_0} \right)^3 \quad (1)$$

where ρ_G is the packing density before sintering, ρ_s is the relative density after sintering, L_0 is a sample length before sintering, and ΔL is a shrinkage length.

Figure 7 shows the relation between the electric conductivity and relative density after sintering as a function of the shrinkage rate. Even when the shrinkage rate rises from 4 to 8%, these values remain almost constant. The coarse/fine powders were mixed in such a way that would encourage the packing density before baking to increase in the domain where the shrinkage rate was low (see Fig. 6). As a consequence, we assumed that the decrease of the relative density after baking was also suppressed. Our results demonstrated that the electric conductivity of CCCL could be improved by changing the relative density after calcination via control of the shrinkage rate.

A tubular type cell stack was fabricated coarse/fine mixed powders of 60/40 vol. % with an electric conductivity of about 120 S cm⁻¹. As the result, the fine control of the particle size distribution of the cathode materials leads to a crack-free delaminated tubular type cell stack.

3.3 Optimization of CIL

Next, we measured the interface resistance while changing the LSCM25-YSZ volume ratio from 100-0 to 40-60% using powders of LSCM25 (particle size : 3 μ m) and YSZ (0.5 μ m). The lowest interface resistance is obtained at 50 vol.% of YSZ, as shown in Fig. 8. Applying the LSCM25 powder having particle size of 3 μ m and the composition of YSZ 50 vol. %, we measured the interface resistance while changing the YSZ particle sizes in the range of 0.5-20 μ m to optimize the CIL. The optimum is obtained at the YSZ particle size of 2 μ m, as shown in Fig. 9.

Figure 10 shows the polished cross sections between

Fig. 6 Changes of the shrinkage rate and packing density before firing for the volume ratio of coarse powder.

Fig. 7 Changes of the LSCM25 electric conductivity and the relative density after sintering as a function of the shrinkage rate.

Fig. 8 Variation of the interface resistance as a function of YSZ volume ratio.

Fig. 9 Change of the interface resistance as a function of YSZ particle size.

the CIL and YSZ interface. In Fig. 9, the interface resistance is the lowest with the YSZ particle size of 2 μm (A) and highest with the YSZ particle size of 20 μm (B). As observed in Fig. 10, the microstructure of (A) is finer than that of (B), and particles of (A) continuously contacted each other with thicker necking than that observed in (B). The contact length of CIL/YSZ is longer in (A) than in (B), the latter having big pores along the interface.

Kenjo *et al.* reported that the polarization resistance of the La_yMnO_3 -YSZ composite cathode depends on the La_yMnO_3 -YSZ weight ratio and is lowest at 50-50 wt.% (approximately 48-52 vol. %) when the particle sizes of the two components are similar¹⁶. Tsai *et al.* investigated two different types of LSM, *i.e.*, $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ and $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.9}\text{MnO}_3$, mixed with YSZ. The optimum interface resistances in their experiments were obtained at 40-60 vol.% of LSM-YSZ for $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ and at 50-50 vol.% for $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.9}\text{MnO}_3$.²⁵ The optimum interface resistance in the present study was obtained at 50-50 vol. % of LSCM25-YSZ, a volume ratio comparable to those obtained in the reports described above, whereas the LSM composition differed. According to prior reports,

Fig. 10 SEM images of the LSCM25-YSZ interlayer using fine- and coarse-YSZ powder (LSCM25 particle size = 3 μm , LSCM25-YSZ = 50-50 vol.%). The YSZ particle sizes were 2 μm and 20 μm in (A) and (B), respectively. The white lines on CIL/electrolyte interface show contact length.

electrochemical reactions occur only at the triple phase boundary (TPB) of cathode/electrolyte interface between pure LSM electrodes and YSZ.^{16,24,25} When the LSM is replaced with an LSM-YSZ mixture, an additional TPB length within the LSM-YSZ but near the YSZ electrolyte can contribute to the reactions and decrease interface resistance. The maximum effective length of TPB while the cathode material, electrolyte material, and gas are all in contact with each other is thought to be obtained at LSCM25-YSZ = 50-50 vol.%, with a LSCM25 particle size of 3 μm and YSZ of 2 μm .

3.4 Electrical Performance of cell stack

3.4.1 Effect of LSCM-YSZ CIL In the next experiments we sought to evaluate the electrical performance of the LSCM25 CCCL and the CIL of LSCM25-YSZ (50 vol. % LSCM25 (particle size : 3 μm) + 50 vol.% YSZ (2 μm)) by fabricating cell stacks of type 1 and type 2-1 with 15 cells (22 mm in diameter and 550 mm in length). We carried out the performance test at 1173 K in atmospheric pressure using hydrogen as fuel and air as oxidant. Figure 11 shows the average voltage of 14 cells. The performance of type 2-1 applied for LSCM25-YSZ CIL is higher than that of type 1. The area-specific resistances (ASRs) derived from *I-V* characteristics are 1.7 and 1.4 Ωcm^2 for type 1 and type 2-1, respectively, and the cell stack resistance decreases by 17% with the use of LSCM25-YSZ CIL. The ASR represents the mean value of the overall cell stack resistance, including the

interconnector.

3.4.2 Performance test under a pressurized condition

Figure 12 shows the I - V characteristics of type 2-2 averaged by 33 cells. The type 2-2 cell stack obtains approximately 86 W/tube at an average voltage of 0.65 V, 240 mA cm⁻² (fuel utilization of 60%, air utilization of 21%), 1173 K, and 0.1 MPa using hydrogen as fuel. The performance test was conducted under internal reforming conditions using the synthesis gas of reformed CH₄ with steam (S/C = 4) under the pressures of 0.1, 0.2, and 0.4 MPa. The OCV increases and the slopes of the I - V characteristics decreases as the test pressure rises.

Figure 13 shows the change of the ASR derived from I - V characteristics as a function of the test pressure. The ASR represents the mean value of the overall cell stack resistance, including the interconnector. The effect of

Fig. 11 I - V characteristics of the tubular-type SOFC with effective generation cell number of 14 at 1173 K.

Fig. 12 I - V characteristics of the tubular-type SOFC with effective generation cell number of 33 using an LSCM25-YSZ interlayer at 1173 K. The fuel was composed of H₂/N₂ = 70/30% and a synthesis gas of reformed CH₄ with steam (S/C = 4). The oxidant was air.

ASR reduction decreases as the test pressure rises. Figure 14 shows the improvements of OCV and operating voltage (300 mA cm⁻², fuel utilization of 75%, air utilization of 27%) by pressurization. The voltage differences of pressurization (0.2, 0.4 MPa) and atmospheric pressure are shown at the mean cell stack value in Fig.14. The OCV increases by about 10 mV and 30 mV at 0.2 MPa and 0.4 MPa, respectively. The improvement of OCV by pressurization agreed well with the calculation value of Nernst equation. On the other hand, the operating voltage at 300 mA cm⁻² increases by about 40 mV and 70 mV at 0.2 MPa and 0.4 MPa, respectively. Thus, the pressurization brings about a much greater improvement in the operating voltage than it did in the OCV. From this result, we assumed that the pressurization decreases the internal resistance of the cell stack, as shown in Fig. 13.

Next, we measured the internal resistance of the cell stack by the current interruption method in order to analyze the improvement of the operating voltage by pressurization. We conducted the measurement at the inlet (No. 33) and outlet (No. 1) cells of the fuel flow. The steady voltage E of a cell is shown in equation (2)

$$E = E_{rev} - IR - \eta \quad (2)$$

Fig. 13 Change of ASR as a function of test pressure.

Fig. 14 Differences of measurement voltage between pressurization (0.2, 0.4 MPa) and atmospheric pressure.

where IR is ohmic polarizations, η is electrode polarizations, and E_{rev} is equilibrium potential.

Figure 15 shows changes of the respective resistances as a function of test pressure analyzed at 300 mA cm^{-2} . The resistances under pressurization were normalized at the resistance of 0.1 MPa. The ohmic polarizations are almost constant with increasing operating pressure, but the electrode polarizations decreases. These results indicate that the improvement in the operating voltage brought about by pressurization can be attributed to the increase of the OCV and decrease of the electrode polarizations accompanying mass transport losses such as activation- and concentration-polarizations.

Matsui *et al.* measured the electrode polarization behavior under pressurized atmospheres using the two types of tubular cells, as follows.³⁾

$\text{H}_2\text{-H}_2\text{O}$ (0.1-0.3 MPa), Ni-YSZ | YSZ | LSM, air (0.1 MPa) (a)

O_2 or $\text{O}_2\text{-N}_2$ (0.1-0.3 MPa), LSM | YSZ | LSM, air (0.1 MPa) (b)

Anodes and cathodes may be simultaneously pressurized like our experiments to prevent a damage of cell

Fig. 15 Changes of ohmic polarizations (IR) and electrode polarizations (η) as a function of test pressure. Resistances under pressurization were normalized to those of 0.1 MPa.

stack and seal part in an actual SOFC module. However, in the experiment of Matsui *et al.*, only the inner side electrode was pressurized in a total range of 0.1-0.3 MPa while keeping an outer-side pressure of 0.1 MPa using (a) and (b) cells, in order to investigate the electrode polarization behavior of cathode and anode by pressurization, respectively.³⁾ As the result, it was shown that the activation polarizations of both electrodes were decreased mainly.³⁾

Both electrodes were pressurized simultaneously in our experiments, hence the power-generation tests on cells (a) and (b) were carried out concurrently. Given that the fundamental composition of the cathode and anode materials is similar, we can assume that the mechanism of electrochemical reaction at the electrodes is similar, as well. It is presumed that the decrease of electrode polarizations in Fig. 15 is mainly based on the decrease of the activation polarizations of both electrodes.

4 Conclusions

This research was conducted to study the optimization of segmented-in-series tubular SOFC using LSCM for the cathode material and the improvement of the power-generation performance under pressurization.

The electric conductivity of LSCM decreased via the substitution of calcium, but it remained constant at about 340 S cm^{-1} in the range of x values from 0.15 to 0.25. Further, no secondary phases with YSZ were observed with values of $x = 0.2$ and 0.25. Based on the above results, we decided to adopt LSCM25 as the cathode material to take advantage of its high electric conductivity and effect in preventing the formation of highly resistive secondary phases with YSZ.

We finely controlled the particle size distribution with coarse and fine powders using LSCM25 for CCCL. By increasing the packing density of the LSCM25 film before the cathode sintering and controlling the ratio of coarse/fine powders, we managed to prevent the shrinkage-generated cracking during the calcinations and obtained an electric conductivity of 120 S cm^{-1} .

We optimized the interlayer of LSCM25 and YSZ mixed material to decrease the interface resistance between the cathode and the electrolyte. The lowest interface resistance was obtained at 50 vol.% LSCM25 (particle size : $3 \mu\text{m}$) + 50 vol. % YSZ ($2 \mu\text{m}$).

The use of the LSCM25-YSZ interlayer increased the generation performance of the segmented-in-series tubular SOFC by about 17%. We analyzed the internal resistances under the generation conditions using internal reformed synthesis gas in pressurization. Our results demonstrated that the improvement in operating voltage obtained by pressurization was attributable to the increase of OCV and the decrease of the electrode polarizations.

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