Structural Modification of Segmented-in-series Tubular SOFCs Using Performance Simulation and the Effect of (Sm, Ce)O₂ Cathode Interlayer on the Generation Characteristics under Pressurization

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To improve the segmented-in-series tubular SOFC performance operating at 1173 K, we studied cathode interlayer (CIL) and a structural modification of the cell stack using a performance simulation. As the result of changing CIL into (Ce_{0.8}Sm_{0.2})O₂ (SDC20) (type 2) from La_{0.7}Sr_{0.3}MnO₃-YSZ (type 1), ohmic polarization (η_{IR}) and activation/concentration polarizations ($\eta_A + \eta_C$) of type 2 decreased 16% and 47% than those of type 1, respectively. Next, based on the simulation results of η_{IR} , a tubular SOFC (type 4) with structural modification in the length ratio of the effective generation part (EGP) and interconnector part (ICP) was fabricated by applying SDC20 to CIL. Ohmic polarization of type 4 decreased 52% than that of type 2, while $\eta_A + \eta_C$ increased 63%. However, the generation performance of type 4 improved than that of type 2, since η_{IR} decreased more than the increase of $\eta_A + \eta_C$. In a pressurized test of type 4, an increase of pressure resulted in a decrease of the area specific resistance calculated from the inclination of *I-V* characteristics including EGP and ICP resistances. In a durability test of type 4 conducted for 7000 h in atmospheric pressure, a degradation rate of 0.73% 1000 h⁻¹ was obtained.

Key Words : Solid Oxide Fuel Cells (SOFCs), Performance Simulation, (Sm, Ce)O₂ Cathode Interlayer, Pressurized Performance

1 Introduction

Solid oxide fuel cells (SOFCs) can be combined with gas turbines (GTs) to form large (several hundred kW to multi-MW) pressurized hybrid power generation systems. SOFC/GT combined cycle systems using natural gas as fuel can attain an extremely high efficiency of over 70% on lower heating value (LHV) in multi-hundred megawatt class plant. And because SOFCs can also use coal gasification gas, a resource with ample reserves as fuel, they can be expected as a technology for the high-efficiency utilization of fossil fuels.¹⁾ Our ultimate target is a hybrid system of an SOFC-GT-steam turbine (ST) using coal gasification gas as fuel, but many technical issues must be solved before such a system can be realized. As first step towards the realization of a high-efficiency power-generation system using SOFCs, we are developing a pressurized SOFC system integrated with a micro-GT (MGT).

The segmented-in-series tubular SOFC is suitable for a GT combined system accompanied by a dynamic fluctuation for the robust structure. The tubular type SOFC is composed of an effective generation part (EGP), an interconnector part (ICP). EGP is an anode/electrolyte/cathode and ICP is an anode/interconnector/cathode. Nagata

et al. studied maximum power using a simulation model of ohmic polarizations of segmented-in-series SOFCs. As the result, they showed that the maximum value of the power exists as a function of number of series-cells determined from the lengths of EGP (L_e) and ICP (L_{ic}) even in a cell of the same materials when the total length is constant.²⁾ In this study, we applied the simulation model to our tubular SOFC and studied how the modified cell stack structure changed the electrical performance. The tubular cell stacks were made up of high-temperature SOFC (1173-1273 K) using a 10 mol% Y₂O₃ stabilized ZrO₂ (10YSZ) electrolyte, NiO/YSZ anode and La_{0.5}Sr_{0.25}Ca_{0.25}MnO₃ (LSCM) cathode current collection layer (CCCL).

(La, Sr) MnO₃ (LSM) is the most commonly used cathode material with YSZ electrolyte operating at high temperatures (1173-1273 K). The chief advantages that have led to its widespread adoption are high electric conductivity, high chemical compatibility with YSZ, and thermal stability at operating conditions. The drawback of LSM is a negligible oxygen ion conductivity. A common method to improve the activity of LSM is to add ionic conducting phases such as YSZ, scandia stabilized zirconia (ScSZ), and rare-earth doped ceria.³⁻¹⁶⁾ The addi-

tion of ionic conductivity significantly improves the performance of LSM cathode interlayer (CIL). This improvement is generally attributed to the extension of the three phase boundary (TPB) length at the cathode/electrolyte interface.⁴⁻¹⁶ In attempts to decrease the cathode/electrolyte interface resistance, various groups are developing manufacturing techniques which control the fine structure of the TPB region. The main approaches in these attempts are ion impregnation, spray pyrolysis, sol-gel process, and mechanochemical processing.^{10,12,16-22}

(La, Sr)CoO₃ (LSCO) and (La, Sr)FeO₃ (LSF) with electronic and ionic conductivity have been studied as cathode materials whose catalytic activity for the oxygen reduction reaction (ORR) exceeds that of La_{1-x}Sr_xMnO₃ (LSM) to realize the low-temperature operation (873-1073 K) of the SOFC.²³ LSCO and LSF, however, have severe problems in compatibility with YSZ electrolyte. The formation of high-resistivity secondary phases such as La₂Zr₂O₇ and SrZrO₃ degrades the electrode performance.²⁴⁻²⁷ Rare-earth doped ceria (such as (Gd, Ce)O_{2-x} (GDC), (Sm, Ce)O_{2-x} (SDC), or (La, Ce)O_{2-x} (LDC)) is widely adopted in intermediate-temperature SOFCs as a CIL to prevent the formation of high-resistivity secondary phases.²⁸⁻³³ Previous works have demonstrated reductions of cathodic polarization through the adoption of rare-earth doped ceria to LSM cathode materials such as LSCO and LSF, while durability test results have hardly been reported.^{14,34-35}

This paper focuses on the modification of the cell stack structure and the application of rare-earth doped ceria to the CIL for the LSCM CCCL. To improve the performance of the segmented-in-series tubular SOFC, we studied the cell stack structure using the simulation model developed by Nagata *et al.* First, to study the power change per tube by the modification of cell stack structure, we calculated the power as a function of L_c/L_{ic} . Second, in order to study the electrical performance of rare-earth doped ceria as the CIL, we compared (Sm_{0.2}Ce_{0.8})O₂ (SDC20) with mixed powders of LSM-YSZ using cell stacks with a conventional structure. Third, we fabricated a cell stack with a modified structure based on a performance simulation using SDC20 to the CIL, then measured the generation performance at atmospheric pressure. Fourth, we tested the improved

Fig. 1 Cross section of segmented-in-series tubular type SOFC. L_c is the effective generation part (EGP), L_{ic} is the interconnector part (ICP).

cell stack under pressurized conditions up to 0.6 MPa to measure the generation performance of the integrated system with an MGT. Lastly, we conducted durability tests on the improved cell stack at atmospheric pressure and higher pressures.

2 Performance simulation

The steady voltage E of SOFC is shown in equation [1],

$$E = E_{rev} - \eta_{IR} - \eta_A - \eta_C \quad [1]$$

where E_{rev} is equilibrium potential, η_{IR} is ohmic polarization, η_A is activation polarization, and η_C is concentration polarization. In this research, we studied the optimization of stack structure using the η_{IR} simulation model without including the η_A and η_C variables from the model of Nagata *et al.* As both electrodes/electrolyte, interconnector interfaces are assumed to have good adherence, we can simulate the total η_{IR} considered on the current distribution in this model.²⁾

The equilibrium potential E_{rev} of each cell is shown by the Nernst equation as follows:

$$E_{rev} = \frac{RT}{4F} \ln \frac{P_{O_2}(c)}{P_{O_2}(a)} \quad [2]$$

where R is the ideal gas constant, F is the Farady constant, T is temperature, and $P_{O_2}(c)$ and $P_{O_2}(a)$ are the oxygen partial pressure of the cathode and anode, respectively.

When the load current I flows into a cell on the substrate tube with diameter D from one end of the anode (as shown in Fig. 2) and then flows out of the other end of the cathode, the current density $J_c(x)$ in distance x is given by the following equation from a corner point:²⁾

$$J_c(x) = \frac{I}{\rho_c \delta_c} [A \sinh(\alpha x) + B \cosh(\alpha x)] \quad [3]$$

$$\alpha = \sqrt{\frac{1}{\rho_c \delta_c} \left(\frac{\rho_a}{\delta_a} + \frac{\rho_f}{\delta_f} \right)} \quad [4]$$

$$A = -\frac{1}{\alpha \pi D} \frac{\rho_f}{\delta_f} \quad [5]$$

Fig. 2 Performance simulation model of the EGP. D is the diameter of the substrate tube, I is the load current, x is the distance from one end of the cell.

$$B = \frac{1}{\alpha\pi D} \frac{\frac{\rho_a}{\delta_a} + \frac{\rho_f}{\delta_f} \cosh(\alpha L_c)}{\sinh(\alpha L_c)} \quad [6]$$

where ρ_a , ρ_f and ρ_c are the cathode, anode, and electrolyte resistivity, respectively; δ_a , δ_f and δ_c are the cathode, anode, and electrolyte thickness, respectively; and I is the load current.

The equivalent internal resistance R_c of the cell observed at the both ends of the EGP is given by the following equation:²⁾

$$R_c = \frac{\frac{\rho_a}{\delta_a} \frac{\rho_f}{\delta_f} [2 + \alpha L_c \sinh(\alpha L_c)] + \left[\left(\frac{\rho_a}{\delta_a} \right)^2 + \left(\frac{\rho_f}{\delta_f} \right)^2 \right] \cosh(\alpha L_c)}{\alpha\pi D \left[\frac{\rho_a}{\delta_a} + \frac{\rho_f}{\delta_f} \right] \sinh(\alpha L_c)} \quad [7]$$

Similarly, the internal resistance R_i of the ICP is given as:²⁾

$$R_i = \frac{\frac{\rho_a}{\delta_a} \frac{\rho_f}{\delta_f} [2 + \beta L_{ic} \sinh(\beta L_{ic})] + \left[\left(\frac{\rho_a}{\delta_a} \right)^2 + \left(\frac{\rho_f}{\delta_f} \right)^2 \right] \cosh(\beta L_{ic})}{\beta\pi D \left[\frac{\rho_a}{\delta_a} + \frac{\rho_f}{\delta_f} \right] \sinh(\beta L_{ic})} \quad [8]$$

$$\beta = \sqrt{\frac{1}{\rho_{ic} \delta_{ic}} \left(\frac{\rho_a}{\delta_a} + \frac{\rho_f}{\delta_f} \right)} \quad [9]$$

where ρ_{ic} is the interconnector resistivity and δ_{ic} is the interconnector thickness.

Equations [3] to [9] indicate that the ohmic polarization characteristics of the electrolyte and interconnector are influenced by $\rho_c \delta_c$ and $\rho_{ic} \delta_{ic}$, and those of the electrodes are influenced by ρ_f / δ_f and ρ_a / δ_a .

The load current of the segmented-in-series tubular SOFC flows in the long direction in the cathode and anode, and in the thickness direction in the electrolyte. When the ρ_f / δ_f of anode is small than the ρ_a / δ_a of cathode, the load current flows in the long direction in the anode with high electric conductivity, then flows out intensively to the cathode at the end of electrolyte. The current concentration is emphasized with the extension of EGP length, while it will be relaxed, if the difference of ρ_f / δ_f and ρ_a / δ_a is small and the $\rho_c \delta_c$ is large. Therefore, the compatibility of the ρ_f / δ_f , ρ_a / δ_a , $\rho_c \delta_c$ and the length of EGP is important for the reduction of the current concentration. Nagata et al. showed that maximum power of one cell changes by the ρ_f / δ_f , ρ_a / δ_a , $\rho_c \delta_c$ and the length of EGP.²⁾

On the other hand, if the EGP is shortened and the number of series-cells is increased, the cathodic and anodic η_{IR} of one cell will decrease, while the number of interconnectors without contribution of power generation also increases. Thus, the number of series-cells determined from the lengths of EGP and ICP also influences the power of one tube when the total length is constant. Furthermore, the increase of EGP area of one tube, *i.e.*, lengthening EGP and shortening ICP, can be considered to be effective for the improvement of the power.

In this research, the power of one tube was studied as

functions of L_c , L_{ic} and the number of series-cells (n) when the electric conductivity of the electrolyte, anode, CCCL and interconnector and thicknesses of them, *i.e.*, $\rho_c \delta_c$, ρ_f / δ_f , ρ_a / δ_a and $\rho_{ic} \delta_{ic}$, are constant. In order to investigate the relation between L_c , L_{ic} , n , and an power, L_c / L_{ic} was used to the parameter. As L_c / L_{ic} increases, EGP of one cell lengthens and the number of series-cells decreases. On the other hand, as L_c / L_{ic} decreases, EGP of one cell is shortened and the number of series-cells decreases. The power of each stack structure was calculated as a function of L_c / L_{ic} at 0.65V of the mean voltage when the ICP length is 7, 10 and 13 mm. Here, the maximum number of series-cells n within 1000 mm of the total length was determined by adding L_c and L_{ic} . The equilibrium potential of each stack was calculated when the fuel and air utilization rates were 60% ($H_2/N_2/H_2O = 70/29.7/0.3\%$) and 20%, respectively.

The 10YSZ electrolyte, LSCM CCCL, Ni-YSZ anode and (Sr, La)TiO₃ interconnector had electric conductivities of 0.1, 150, 1000, and 0.05 S cm⁻¹, and thicknesses of 90, 1000, 150, 20 μ m, respectively. Hence, the $\rho_c \delta_c$, ρ_a / δ_a , ρ_f / δ_f , and $\rho_{ic} \delta_{ic}$, were 0.09, 0.067, 0.067 and 0.04, respectively. The load current concentration can be considered to be relatively low, since the ρ_a / δ_a and ρ_f / δ_f are equal.

3 Experimental

3.1 Cell stack fabrication

The segmented-in-series tubular type SOFC consisted of a substrate tube, anodes, anode interlayers (AILs), electrolytes, interconnectors, CILs, and CCCLs. The substrate tube, anodes, AILs, electrolytes, interconnectors and CCCLs were composed of calcium-stabilized ZrO₂ (CSZ), Ni-YSZ, Ni-YSZ, 10YSZ, (Sr, La)TiO₃ and LSCM, respectively. The CIL for comparison with SDC20 used mixed powders of (La_{0.7}Sr_{0.3})MnO₃-YSZ = 60-40 wt. % (LSM70-YSZ). All composition materials were made from commercial powders, and the crystal structures were confirmed to be suitable by powder x-ray diffraction (XRD). LSM70 and YSZ powders were weighed by pre-determined composition and mixed in ethanol solvent for 45 h by ball-milling. Similarly, powders of NiO-YSZ anode and NiO-YSZ AIL were respectively mixed in ethanol solvent for 24 and 15 h by the same method.

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. The slurries for screen-printing were prepared from the oxide powders with an organic binder and a dispersant using a three-roll mill.

Each slurry was screen-printed to fabricate the anodes, AILs, electrolytes, and interconnectors on the substrate tubes, in that order, and co-sintered in air at 1673-1733 K for 4 h. The CILs and CCCLs were screen-printed after the co-sintering and baked in air at 1573-1638 K for 2 h. The thicknesses of the anode, AIL, electrolyte, interconnector, CIL, and CCCL were 150, 20, 90, 20, 10, and 1000 μ m, respectively.

Table 1 shows the specifications of the fabricated cell stack. To compare the performance of the CIL, type 1

Table 1 Specification of tubular type cell stacks.

	Type1	Type2	Type3	Type4
Dimensions	OD28mm × L1500mm	OD28mm × L1500mm	OD22mm × L550mm	OD28mm × L1500mm
L_c/L_{ic}	2	2	1	1
Number of Cells	34	34	22	48
Cathode Interlayer	LSM70-YSZ	SDC	SDC	SDC

and type 2 were fabricated from LSM70-YSZ and SDC20, respectively. The combination effect, *i.e.*, the SDC CIL and modification of the stack structure in the performance simulation, was studied using a type 3 short stack. Finally, a type 4 cell stack for modules scaled up to a type 3 was fabricated. The length of L_c and L_{ic} summed together was about 1000 mm for type 1, type 2, and type 4.

3.2 Electrochemical characterization

Figure 3 shows a schematic diagram of the electrochemical performance test apparatus. Fuel was supplied to the cell stack through the inside of the fuel injection tube from the top of the apparatus. The fuel was redirected upwards from the bottom and supplied to the cell stack, and the unreacted fuel was exhausted from the upper part of the apparatus. Air, meanwhile, was supplied from the bottom of the cell stack and redirected downwards from the upper part, and the exhaust air was discharged from the bottom. A schematic diagram of the type 4 cell stack is shown in Fig. 4. This stack was composed of 48 cells, and 47 of them were tested using the cells at the two ends as current collectors. The per-

formance characteristics of types 1 and 2 with 34 cells and type 3 with 22 cells were tested by the same method (by testing 33 cells and 21 cells, respectively). Pt mesh welded Pt lead wire was attached to the edge of cathode in the No. 1 and No. 48 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 (V_s) and downstream No. 1 (V_1) were measured in the type 4.

The cell stacks were heated from room temperature up to 1173 K at a constant rate of 100 K h⁻¹, while distilled H₂ (1 Nl min⁻¹, H₂/N₂ = 5/95%) was fed into the anode and air (6.55 Nl min⁻¹) was fed into the cathode. The *I*-*V* characteristics were measured at 1173 K using diluted H₂ (H₂/N₂ = 70/30%) as the fuel and air as the oxidant. At each current density, fuel and air were adjusted to the flow rate at which the fuel and air utilization rates became constant at 60% and 20%, respectively. The load current was controlled by an electronic load regulating resistor (Takasago Ltd., FK-200L), and fuel and air were supplied by mass flow controllers (Tokyo Keiso Co., Ltd.). The electrochemical characteristics of types 1, 2, and 4 were measured by the current interruption method with a current pulse generator (Hokuto Denko Corp., HC-114) and oscilloscope (Yokogawa Electric Corp., DL750P). To investigate the performance of the improvement cell stack combined with an MGT under pressurization, the type 3 cell stack was tested using synthesis fuel (H₂/CO/CO₂/CH₄/H₂O = 14/2/30/10/43%) of reformed methane with steam at a steam/carbon ratio (S/C) of 4 under pressures of 0.1–0.6 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 applied from the fuel side by adjusting the differential pressure of the fuel and air with a control valve prepared in the fuel exhaust line.

Long-term durability tests of the types 3 and 4 were carried out. The type 4 was tested for about 7000 h under the following conditions using diluted H₂ (H₂/N₂ =

Fig. 3 Schematic diagram of experimental apparatus for a segmented-in-series tubular type cell stack.

Fig. 4 A schematic view of voltage measurement cell and lead wires of the current collector for the generation performance test. V_1 is the No. 1 cell voltage and V_s is the cell stack voltage.

70/30%) and air as the fuel and oxidant, respectively: 1173 K, 0.1 MPa, current density of 380 mA cm^{-2} , fuel utilization rate of 60%, air utilization rate of 20%. To study the pressurized durability combined with an MGT, the type 3 was tested for approximately 1400 h under the conditions using a synthesis fuel ($\text{H}_2/\text{CO}/\text{CO}_2/\text{CH}_4/\text{H}_2\text{O} = 14/2/30/10/43\%$) of reformed methane with steam at a steam/carbon ratio (S/C) of 4: 1173 K, 0.4 MPa, current density of 500 mA cm^{-2} , fuel utilization rate of 60%, air utilization rate of 20%.

4 Results and discussion

4.1 Performance simulation

Figure 5 shows the changes of power of one tube, EGP area, the number of series-cells and the load current as a function of L_c/L_{ic} at $L_{ic} = 7, 10$, and 13 mm . The simulation model of Nagata *et al.* is taking into consideration of only the ohmic polarizations calculated from the electric conductivity of the composition materials, thus, it differs from the actual performance. For this reason, the power, EGP area and the load current are normalized at the values of $L_{ic} = 7 \text{ mm}$ and $L_c/L_{ic} = 12.9$.

From Fig. 5(A), when $L_{ic} = 7, 10$, or 13 mm , we see that the power peaks in the L_c/L_{ic} range of 0.5 to 1, and increases as L_{ic} shortens. From Fig. 5(B), the EGP area of one cell (EGPAC) increases linearly to L_c/L_{ic} . The EGP area of one tube (EGPAS) increases rapidly until about 3 of L_c/L_{ic} , while it increases slightly in more than 3. The number of series-cells decreases with the increase of L_c/L_{ic} , while the load current shows the maximum value when L_c/L_{ic} is about 1 from Fig. 5(C). The load current can be estimated to increase as the EGP of one cell (EGPC) lengthens, but then to decrease, because the η_{IR} of one cell increases caused by the current concentration when the L_c/L_{ic} exceeds 1.

Figure 6 shows the changes of area specific resistances (ASRs) of the EGP, ICP and EGP + ICP as a function of L_c/L_{ic} at $L_{ic} = 7, 10$, and 13 mm . The ASRs are also normalized at the values (ASR_0) of $L_{ic} = 7 \text{ mm}$ and $L_c/L_{ic} = 12.9$. Figure 6 shows the ASR changes of one cell and one tube, respectively. The ASR/ASR_0 of EGPC increases exponentially in spite of the decrease of load current in the range of more than 1.5 of L_c/L_{ic} as shown in Fig. 6(A). The uniform distributivity of the load current can be considered to decrease with the increase of the L_c/L_{ic} , *i.e.*, the increase of EGPC length. The ASR/ASR_0 of EGP of one tube (EGPS) can be considered to be the minimum value at between 0.5 and 2 of L_c/L_{ic} from the influence of the number of series-cells as shown in Fig. 6(A).

The ASR/ASR_0 of ICP of one cell (ICPC) increases linearly for L_c/L_{ic} as shown in Fig. 6(B). The ASR of ICPC multiplied the η_{IR} by the EGPAC. For this reason, the ASR of ICPC increases as the EGPC lengthens. On the other hand, as shown in Fig. 7, the η_{IR} of ICP of one tube (ICPS) decreases with the increase of L_c/L_{ic} , *i.e.*, the decrease of the number of interconnector. The ASR/ASR_0 of ICPC agrees roughly even if L_{ic} is changed to 7, 10, 13 mm, but the ASR/ASR_0 and η_{IR}/η_{IR0} of ICPS rise in order to increase the number of interconnector as

Fig. 5 Variations of (A) power, (B) area of effective generation part (EGPA) and (C) number of series-cells and load current at 0.65V of mean voltage as a function of L_c/L_{ic} . The power, EGPA and load current are normalized at the values of $L_{ic} = 7 \text{ mm}$ and $L_c/L_{ic} = 12.9$. P is power, EGPAC is EGPA of one cell, EGPAS is EGPA of one tube and I is load current.

L_{ic} shortens.

The ASR/ASR_0 of EGPC + ICPC increases exponentially as a function of L_c/L_{ic} like that of EGPC, while the ASR/ASR_0 of EGPS + ICPS increases monotonously as shown in Fig. 6(C). The load current value rises with the increase of L_c/L_{ic} . However, if the threshold of L_c/L_{ic} is exceeded, η_{IR} of EGPC increases with the decrease of the current distributivity, and then the load current decreases. The power of one tube can be considered to decrease at about 1 of L_c/L_{ic} , because the load current value decreases when the working voltage is constant. The power of one tube is also influenced by the number of interconnectors without contribution to power generation. As mentioned above, it is suggested that the tubular type SOFC has the optimal stack structure where the maximum power is obtained from the relationships of cell stack structure, load current value and number of series-cells.

In the type 1 conventional stack structure, L_{ic} and

L_c/L_{ic} are 10mm and 2, respectively. A performance improvement can be expected by shortening L_{ic} , but the change of power may be small. A technical issue of position accuracy in screen printing may also occur from both modifications of L_{ic} and L_c/L_{ic} . For this reason, we studied the change of power with the decrease of L_c/L_{ic} at $L_{ic} = 10$ mm in this research. Specifically, we fabricated types 3 and 4 by changing the L_c/L_{ic} of the cell stacks from 2 to 1 as shown in Table 1, and then tested the per-

formances.

4.2 Performance of the cell stacks

To verify the effect of using SDC20 for the CIL and the modification of L_c/L_{ic} from 2 to 1, we measured types 1 to 4 electrochemically. Figure 8 shows the I - V characteristics of types 1 to 4. The mean voltage of each cell stack including η_{IR} of the interconnector is shown in Fig. 8. The electrochemical measurements were conducted at 1173 K, 0.1 MPa using diluted H_2 ($H_2/N_2 = 70/30\%$) and air as the fuel and oxidant, respectively. The flow rates of fuel and air were adjusted to fix the utilization rates of fuel and air at 60% and 20%, respectively, at each current density. The area specific resistance (ASR) of type 1 with the CIL made from LSM70-YSZ was $0.95 \Omega \text{ cm}^2$, while that of type 2 made from SDC20 decreased to $0.81 \Omega \text{ cm}^2$. The ASR is derived from I - V characteristics, hence it represents the mean value of the overall cell stack resistance, including the interconnector. The I - V characteristics are similar for types 3 and 4, the stacks in which L_c/L_{ic} is modified from 2 to 1 based on the results of the performance simulation. As a result, we find that the performance of the scaled-up cell stack can be predicted roughly by the short stack performance. The ASRs of types 3 and 4 are 0.51 and $0.44 \Omega \text{ cm}^2$, respectively.

In comparing types 1 and 2, the ASR decreases by 15% when we change the CIL from LSM70-YSZ to SDC20. Furthermore, the ASR decreases by 46% when we modify the stack structure, even if the cell stacks are fabricated using the same materials for types 2 and 4. Since the ASR of η_{IR} was also expected to decrease 47% by modifying L_c/L_{ic} from 2 to 1 in the performance simulation, the measurement value is in good agreement with the simulation value. However, the ASR calculated from the slope of I - V characteristics is $\eta_{IR} + \eta_A + \eta_C$, thus, it differs from the η_{IR} of the simulation. For this reason, the η_{IR} and electrode polarizations of types 1, 2, and 4 were

Fig. 6 Normalized ASR changes of ohmic polarizations at $L_{ic} = 7$ mm and $L_c/L_{ic} = 12.9$ as a function of L_c/L_{ic} . (A) is the EGP, (B) is the ICP, and (C) is the EGP + ICP. EGPC and ICPC show the EGP and ICP of one cell, respectively. EGPS and IGPS show the EGP and ICP of one tube, respectively.

Fig. 7 Changes of normalized ohmic polarizations of ICPS at $L_{ic} = 7$ mm and $L_c/L_{ic} = 12.9$ as a function of L_c/L_{ic} .

Fig. 8 I - V characteristics of the type 1-4 cell stacks under atmospheric pressure.

analyzed by the current interruption method shown later.

Figure 9 and 10 respectively show changes of power-density and power as functions of current density. In Fig. 9, the power density improves in the following order: type 1 (LSM70-YSZ), type 2 (SDC20), types 3 and 4 with the modified stack structure. For the short stack in Fig. 10, the power of type 3 is lower than that of the other cell stacks. The power and power-density of types 1, 2, and 4 improve to 100, 124, and 168 W, and 0.18, 0.22, and 0.41 W cm⁻² at the steady working voltage of 0.65 V in our module, respectively.

4.3 Electrochemical measurement

Electrochemical measurements were taken for types 1, 2, 4 to analyze the performance improvement factors of

Fig. 9 Power density changes of the type 1-4 cell stacks as a function of current density under atmospheric pressure.

Fig. 10 Power variations of the type 1-4 cell stacks as a function of current density under atmospheric pressure.

the cell stacks by the current interruption method. The measurements were conducted at the furthest downstream cell in which the fuel and air utilization rates were the same, as the number of in-series cells of type 4 differed from those of types 1 and 2. The experimental conditions were current density of 280 mA cm⁻² with fuel and air utilization rates of 60% and 20%, respectively. Figure 11 shows the results of electrochemical measurement. The ASRs differ from the values calculated from *I-V* characteristics of mean voltage for the furthest downstream cell of fuel and air. From Fig. 11, we see that by changing the CIL from LSM70-YSZ (type 1) to SDC20 (type 2), η_{IR} and $\eta_A + \eta_C$ decrease by 16% and 47%, respectively.

ORR on the cathode occurs at the triple phase boundary (TPB) of (LSM70-YSZ)/YSZ in type 1.³⁶⁻³⁸⁾ Leng *et al.* measured the activation energies of a pure LSM cathode and LSM-GDC composite cathode using electrolyte to YSZ and GDC. The activation energies of (LSM-GDC)/YSZ and (LSM-GDC)/GDC were 190 from 173 kJ mol⁻¹, and thus were in almost good agreement with the 175 kJ mol⁻¹ of (LSM-YSZ)/YSZ. On this basis, Leng *et al.* estimated that the LSM-GDC composite cathode has the same ORR mechanism as pure LSM.¹³⁾ This result suggests that, as in the case with GDC, the ORR region of type 2 is comparable to the TPB of LSM/SDC20.

SDC20 is thought to function as an oxygen ion conductor under an oxygen partial pressure in cathode atmosphere. On this basis, the η_{IR} of SDC20 can be predicted to increase compared with LSM70-YSZ, a material with electronic- and ionic-conductivity. Yet as it turns out, η_{IR} and $\eta_A + \eta_C$ actually decrease. The $\eta_{IR} + \eta_A + \eta_C$ can be considered to decrease, since the adhesion of LSM/SDC20 interface improves compared with (LSM70-YSZ)/YSZ and then the TPB increases by the improved adhesion. High-resistivity second phases such as the La₂Zr₂O₇ and SrZrO₃ formed in the (LSM70-YSZ)/YSZ interface of type 1 are also thought to contribute to the low performance in type 1.

When the ASRs of types 2 and 4 is compared, the η_{IR}

Fig. 11 Electrochemical measurement results of the types 1, 2, and 4 cell stacks by the current interruption method at a current density of 280 mA cm⁻² and temperature of 1173K. The utilization rates of fuel and air are 60% and 20%, respectively.

of type 4 decreases 52% than that of type 2, while the $\eta_A + \eta_C$ increase 63%. The experimental value is in roughly agreement with the simulation value, since the ASR of η_{IR} of type 4 was also expected to decrease 47% than that of type 2 in the performance simulation. The η_{IR} of type 4 is thought to decrease by shortening the load current path of one cell.

Activation polarization η_A is expressed by Butler-Volmer equation as follows:

$$I = I_0 \left[\exp \left(\frac{\alpha n F \eta_A}{RT} \right) - \exp \left(\frac{-(1-\alpha) n F \eta_A}{RT} \right) \right] \quad [10]$$

$$\eta_A = \frac{2RT}{\alpha n F} \sinh^{-1} \left(\frac{I}{I_0} \right) \quad [11]$$

where I_0 is exchange current density, α is symmetry coefficient.

Concentration polarization η_C is shown by using Fick's first law of diffusion and Nernst equation as follows:

$$\eta_C = \frac{RT}{nF} \ln \frac{C_s}{C_B} \quad [12]$$

where C_B is bulk concentration of gaseous species and C_s is its surface concentration at the interface of electrode and electrolyte.

Exchange current density I_0 depends on the TPB length and the partial pressure of gaseous species at the TPB. The C_s of η_C depends on the thickness of the gas diffusion layer, the effective diffusion coefficient of gaseous species, the porosities of electrodes and substrate tube, the tortuosity and the bulk concentration of gas phase. For this reason, η_A and η_C can be considered to depend on the microstructure of the TPB and the gas diffusivity. Hence, current concentration can be considered as an increase factor of $\eta_A + \eta_C$. Since type 4 uses the same material of type 2 and shortens the EGP, the load current of type 4 can be presumed to be distributed uniformly than that of type 2. In addition, since current density, fuel and air utilization rates and measurement temperature are also the same, $\eta_A + \eta_C$ of type 4 can be considered not to increase than that of type 2. However, $\eta_A + \eta_C$ of type 4 increased compared with type 2. In an analysis with a high-energy x-ray from beam line BL24XUC1 of the Spring-8 synchrotron, Yamaguchi *et al.* detected an unknown phase of what was presumed to be a $\text{ZrO}_2\text{-Sc}_2\text{O}_3\text{-CeO}_2\text{-Gd}_2\text{O}_3$ solid solution in the interface of an ScSZ-GDC interlayer.¹¹⁾ A similar high-resistivity phase may also be formed in our tubular type SOFC. Given that the quantity of the second phase formation varies in each stack, $\eta_A + \eta_C$ of type 4 can be considered to increase in comparison with that of type 2. The modification of cell stack structure may also lead to the increase of $\eta_A + \eta_C$ by changing the microstructure of TPB or increasing the cross leak of fuel and air, since the optimization of preparation conditions of type 4 was insufficient. Further work is now underway to investigate the increase of $\eta_A + \eta_C$.

The SOFC modules are generally operated in the range of current density where the I - V characteristics have a straight line relation. Further, η_{IR} is the dominant

factor of voltage drop ($E_{rev} - E$) in the segmented-in-series tubular SOFC having the long current path. For this reason, the cell stack is thought to be modified to a roughly suitable structure by applying the simulation model of Nagata *et al.* We may be able to develop a still more optimal structure by including activation- and concentration-polarizations in the simulation model, and thereby improving accuracy. For the above reasons, the further performance improvement of the tubular SOFC can be expected by the development of simulation model including electrode polarizations and the optimization of preparation conditions.

The previous reports showed that cathode/electrolyte interface resistance decreased by changing the CIL from a pure doped ceria to a composite material of doped ceria-LSM.^{11,14)} For this reason, we may be able to decrease the interface resistance of cathode/electrolyte in our tubular SOFC by fabricating the CIL from a mixed powder of LSM-SDC20 with electronic and ionic conductivity.

4. 4 Performance test under pressurized conditions

The power generation test of type 3 was carried out under pressurization to measure the cell stack performance integrated with an MGT. The test was conducted under internal reforming conditions using a synthesis gas of reformed CH_4 with steam ($S/C = 4$) at 1173K. The test pressures were 0.1, 0.2, 0.4, and 0.6 MPa. The utilization rates of fuel and air were fixed at 60% and 20%, respectively. Figure 12 shows I - V characteristics of mean voltage including η_{IR} of interconnector. At 0.1 MPa, the output voltage using synthesis gas as fuel is decreased than that of hydrogen fuel, while both ASRs derived from the slope of the I - V characteristics are $0.62 \Omega \text{ cm}^2$. When the synthesis gas is used as fuel, the partial pressures of CO and H_2O rise above the levels with hydrogen fuel. Because the anode concentration polarization

Fig. 12 I - V characteristics of the type 3 cell stack using a synthesis fuel of reformed methane with steam ($S/C = 4$) under pressurization.

increases as the diffusion coefficient of the fuel gas decreases, we predicted that the ASR increases concurrently. Yet because the ASRs are the same in this research, we presumed that the gas permeability of the substrate tube and anodes is sufficient with a fuel utilization rate of 60%, and is not influenced by the fuel species. Thus, the difference of output voltage at 0.1 MPa can presumably be attributed to the decrease of the equilibrium potential brought about by the use of steam for fuel gas reform.

Figure 13 shows current-power density characteristics including η_{IR} of the interconnector. The mean voltage and power density increase as the test pressure rises, in comparison with the results with synthesis fuel from Fig. 12 and 13. The power density of type 3 reaches 0.36 W cm^{-2} (mean voltage = 0.65 V) at 0.6 MPa , 600 mA cm^{-2} .

Figure 14 shows the change of 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 ASR decreases as the test pressure rises. This result indicates that the cell stack performance under pressurization improves not only via the increase of the equilibrium potential, but also via the decrease of internal resistance. This effect of pressurization reducing the ASR weakens as the test pressure increases. Internal resistances with CIL of LSCM-YSZ were analyzed in our previous study.³⁹⁾ As the result, it was presumed that the decrease of internal resistance was attributable to the decrease of η_A at both electrodes. Since the fundamental composition of the cathode and anode is similar, the decrease of internal resistance of type 4 obtained by pressurization can be considered the decrease of η_A of both electrodes.

Fig. 13 Power density changes of type 3 as a function of current density using a synthesis fuel of reformed methane with steam ($S/C = 4$) under pressurization.

4.5 Long-term behavior

Next, we tested type 3 (short stack) and type 4 (scaled-up stack) under pressurization and atmospheric pressure, respectively, in order to verify the cell stack durability with the modified stack structure and SDC20 for the CIL. The durability test for type 3 was carried out with a synthesis fuel of reformed methane with steam under the following conditions: current density of 500 mA cm^{-2} , fuel utilization of 60%, air utilization of 20%, temperature of 1173 K , and pressure of 0.4 MPa . Figure 15 shows the mean voltage behavior in the durability test. The mean voltage changes stably, and no degradation is observed for 1400 h. No decreases of mean voltage were observed before and after three thermal cycles carried out during the durability test.

Fig. 14 ASR change of type 3 as a function of test pressure.

Fig. 15 Long-term behavior of the type 3 mean voltage using a synthesis fuel of reformed methane with steam ($S/C = 4$) under pressurization. The current density is 500 mA cm^{-2} , the fuel utilization rate is 60%, the air utilization rate is 20%, the temperature is 1173 K , and the pressure is 0.4 MPa .

Fig. 16 Long-term behavior of the type 4 mean voltage using a diluted hydrogen fuel at 380 mA cm^{-2} , 1173 K and atmospheric pressure. The utilization rates of fuel and air are 60% and 20%, respectively.

The durability test of type 4 was conducted with a fuel of diluted hydrogen ($\text{H}_2/\text{N}_2 = 70/30$) under the following conditions: current density of 380 mA cm^{-2} , fuel utilization of 60%, air utilization of 20%, temperature of 1173 K, and pressure of 0.1 MPa. The mean voltage behavior in the durability test is shown in Fig. 16. The behavior of the mean voltage changes stably for 7000 h without large degradation, and the degradation rate calculated from the regression line is $0.73\% \text{ } 1000 \text{ h}^{-1}$. Thermal cycle tests were executed at 60, 870, 4800, and 5300 h, and no remarkable performance degradation is observed before and after the thermal cycles of any of the tests. As mentioned above, we verified that the cell stack with the modified stack structure and the CIL of SDC20 has a durability of over 7000 h at atmospheric pressure. Further studies are now underway to investigate the degradation factor and mechanisms for durability improvement.

5 Conclusions

In this study we sought to improve the generation performance of segmented-in-series tubular SOFCs by investigating a modified cell stack structure in performance simulations and the application of SDC20 to the CIL.

In calculations of the power changes as a function of L_c/L_{ic} at $L_{ic} = 7, 10$, and 13 mm , the power peaked at 0.5–1 of L_c/L_{ic} in every case.

The ASR of the cell stack with the CIL made from SDC20 (type 2) derived from I - V characteristics was 15% lower than the ASR of the cell stack with LSM70-YSZ (type 1) in the structure $L_c/L_{ic} = 2$. Moreover, the ASR of the cell stack with the CIL of SDC20 and an L_c/L_{ic} structural modification from 2 to 1 via performance simulation (type 4) decreased by 46% compared to the SDC20 cell stack without the structural modification (type 2).

In our electrochemical measurements, η_{IR} and $\eta_A + \eta_C$ both decreased when the CIL was changed from LSM70-YSZ (type 1) to SDC20 (type 2). For this reason, we considered that the adherence of the LSCM/SDC20 (type 2)

interface was superior to that of (LSM70-YSZ)/YSZ (type 1), and further, that the adhesion improvement also improved the TPB. The decrease of η_{IR} of a structural modification of L_c/L_{ic} from 2 (type 2) to 1 (type 4) was in roughly agreement with the performance simulation value, while the $\eta_A + \eta_C$ increased. However, the generation performance of type 4 improved than that of type 2, since the η_{IR} decreased more than the increase of $\eta_A + \eta_C$.

We carried out a performance test of type 3 using a synthesis fuel of reformed methane with steam under pressurization, in order to verify the performance of the cell stack integrated with an MGT. In this test, the ASR decreased as the operating pressure rose. The result demonstrated that the improvement in the operating voltage obtained by pressurization was attributable to the increase of equilibrium potential and the decrease of the electrode polarizations.

The mean voltage of the improved cell stack (type3) was stable for 1400 h in the durability test using the synthesis fuel of reformed methane at the pressure of 0.4 MPa. In the durability test of type 4 using diluted hydrogen at atmospheric pressure, the mean voltage remained stable for 7000 h and the degradation rate was $0.73\% \text{ } 1000 \text{ h}^{-1}$. No degradation was observed in any of the four thermal cycles carried out during the durability test. Further work to improve the durability remains to be done.

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