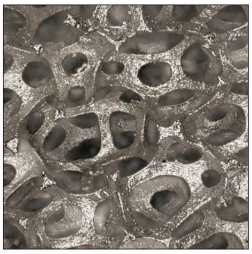

Performance of Solid Oxide Fuel Cell with Porous Metal as a Current Collector

Koma NUMATA*, Kazuki OKUNO, Akihisa HOSOE, Kengo TSUKAMOTO, Masatoshi MAJIMA, and Hitoshi TSUCHIDA

Sumitomo Electric Toyama Co. Ltd. is aiming to apply Celmet, a porous metal product, as a current collector for solid oxide fuel cells (SOFC). NiCo Celmet is particularly suitable for cathode current collectors as it forms conductive oxides in a high-temperature and high-oxidant atmosphere. We reported that fuel cells using the NiCo Celmet exhibit high power density even without gas flow channels in the interconnector because of its high gas diffusivity. In this study, to elucidate the mechanism of high power density, we investigated the influence on DC resistance by applying Celmet as a current collector. We clarified that the contactability between the cell and Celmet is improved by shaping Celmet along the warp of the cell. Moreover, we found that NiCo Celmet can maintain good contactability as its oxidation expansion applies pressure from the inside of the stack.

Keywords: solid oxide fuel cell, porous material, current collector, NiCo alloy, conductive oxide

1. Introduction

Recently, the SDGs*1 have been promoted with the aim of realizing a sustainable society. One of the activities of the SDGs is to make energy cleaner. Present energy demand is predominantly met by fossil fuels,(1) which produce carbon-derived greenhouse gases. Against such a background, there are expectations for the realization of a carbon-neutral society. One of the proposed solutions, the realization of a "hydrogen society," is attracting attention. H_2 produced from renewable energy sources such as solar power and offshore wind power can be transported via pipelines or tanker trucks to high-energy-demand areas. Electricity generated from H_2 can create a clean energy network.(2) Technologies for the production, transportation, and utilization (electricity generation) of H_2 are indispensable for the realization of a carbon-neutral society. In this paper, the authors focus on the development of electricity generation technology. Electricity can be produced from H_2 either by using the thermal energy of H_2 combustion or by converting H_2 directly into electrical energy. In particular, the latter, called a "fuel cell," is attracting attention due to its high energy conversion efficiency.(3) Solid oxide fuel cells (SOFCs) are expected to be widely used in the future because they exhibit higher energy efficiency than other fuel cells such as polymer electrolyte fuel cells, and also do not require the use of expensive precious metal catalysts such as platinum. However, SOFCs have not yet been widely adopted due to the need for further performance improvement and cost reduction.

Figure 1 shows the structure of a typical SOFC stack.*2 An SOFC consists mainly of a cell, current collectors, and interconnectors (ICs)*3. The cell, made of power-generation ceramics, is a lamination of a cathode, an electrolyte, and an anode. Due to differences in the coefficient of thermal expansion (CTE) between the three layers, the cell becomes warped while being sintered at a high temperature, which can reduce the contactability between the IC and the cell. To improve the contactability, a current collector such as a mesh coated with LSC,*4 Ag, Pt, or other conductive paste is inserted between the IC and the cell as needed. We confirmed in our previous study that using a porous metal with a three-dimensional mesh structure (hereafter, "Celmet") as a current collector improves gas diffusion and increases the power output without the need for grooving the IC.(4) This paper reports the mechanism of stack performance improvement we have newly elucidated in terms of the effect of Celmet on contact resistance.

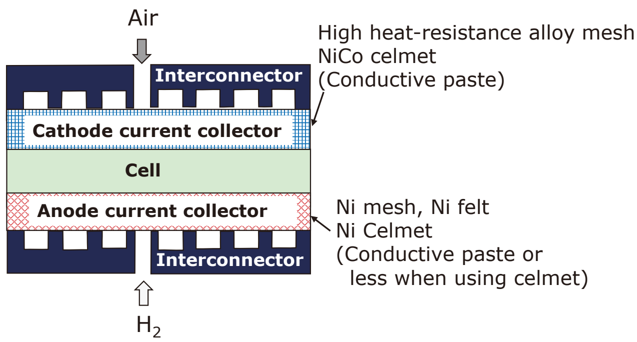

Fig. 1. Structure of SOFC

2. Experiment Method

2-1 Preparation of NiCo Celmet

The NiCo Celmet to be used as the cathode current collector of the SOFC was manufactured by the following processes: (1) conductive treatment of the surface of resin with a three-dimensional network structure; (2) the deposition of predetermined amounts of Ni and Co on the resin's surface by electroplating; and (3) the burning off of resin by heat-treatment and reduction. The thickness of all the Celmet specimens with a pore diameter*5 of approximately 850 μm used in this study was adjusted by roll-pressing samples to the predetermined thickness.

2-2 Evaluating the contactability

The contactability between the IC and the cell or between the cell and Celmet was evaluated as shown in Fig. 2. A commercially available φ100 mm YSZ*[6] cell manufactured by Elcogen AS was used as the cell. The pressure sensor used was an “I-SCAN75” manufactured by Nitta Corporation. The load was applied to the specimen using a mechanical strength tester (AGX-V) manufactured by Shimadzu Corporation. The cell used for evaluation was convexly warped in the center on the cathode side by approximately 1 mm.

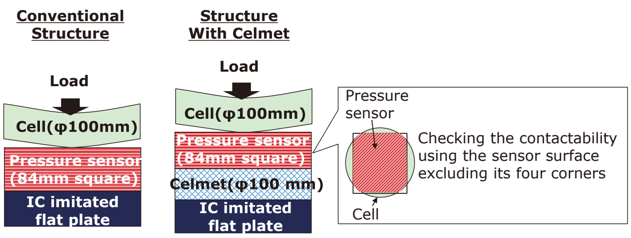

Fig. 2. Schematic Illustration of Evaluation of the contactability

2-3 Measuring the expansion coefficient of Celmet

An SOFC, which is made by laminating various kinds of components at room temperature (R.T.), operates when its temperature is raised. This means that knowing the CTE of Celmet is important to ensure an adequate contactability between the Celmet and the cell or between the Celmet and the IC. However, due to the high porosity of Celmet and the relatively thin specimen thickness of 0.5 mm in anticipation of its use for SOFC current collectors, it was difficult to measure the CTE using the widely used TMA method*[7] due to low expansion detection accuracy. Alternatively, NiCo Celmet which thickness had been adjusted to 0.5 mm, or NiCo oxide Celmet made by completely oxidizing NiCo Celmet by heat treatment at 800°C for 200 hours in the air, was fixed to a jig, as shown in Fig. 3.

Then the temperature of the above specimen was raised while obtaining its cross-sectional images using X-ray radiography technique with synchrotron radiation. The thickness was measured from the images to calculate the CTE. In the experiment, SPring-8 BL16B2 (Sunbeam BM) was used. The wavelength of the X-ray was 0.04133 nm (30 keV). An Xsight micron LC manufactured by Rigaku Innovative Technologies Europe s.r.o. was used as the detector. Images were captured through a 10x optical lens at 0.65 µm per pixel. A DHS1100 manufactured by Anton Paar GmbH was used as the hot stage.

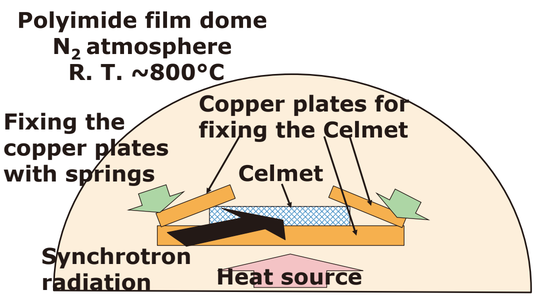

Fig. 3. Schematic Illustration of CTE measurement

Since NiCo Celmet is oxidized at temperatures of 600°C or higher, the expansion of this material must also be considered. In this experiment, NiCo oxide Celmet was made by completely oxidizing NiCo Celmet by heat treatment at 800°C for 200 hours in the air as shown in Fig. 4. The thickness of the NiCo oxide Celmet was measured at R.T. The oxidation expansion coefficient of NiCo Celmet was determined from the change in thickness before and after the oxidation treatment.

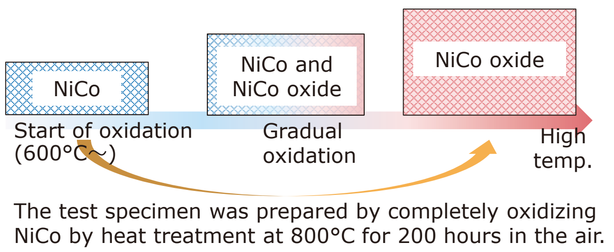

Fig. 4. Schematic Illustration of Oxidation Expansion Coefficient Measurement

2-4 Measurement of the power output of an SOFC comprising Celmet

We have made an SOFC comprising a commercially available φ100 mm YSZ cell. Ni felt was used as the anode current collector, and an FeCr alloy mesh or NiCo Celmet was used as the cathode current collector. In addition, an FeCr alloy plate with a 0.4 mm-deep groove gas passage or an FeCr alloy plate without a groove was used as the IC. LSC was used as the conductive paste on the cathode side, and Ag was applied to the anode. For an SOFC in which Celmet was used as the current collector on the cathode side, the power output was also evaluated without conductive paste on the cathode side to check the effect of Celmet on improving the contact. The gas flow rates were set to 0.9 L/min for air and 0.3 L/min for H_2, and the evaluation temperature was set to 750°C.

2-5 Heat cycle test and evaluation methods

For the heat cycle test, a commercially available φ120 mm YSZ cell was used. A Ni mesh was used for the anode current collector. An FeCr alloy mesh or NiCo Celmet was used for the cathode current collector, and LSC was used as a conductive paste. For the IC, an FeCr alloy plate with a 0.4 mm-deep groove was used. The stack was kept at 750°C for 100 hours while preliminarily supplying H_2 to the anode and air to the cathode, to completely oxidize the NiCo Celmet used as the cathode. After the above procedures, a heat cycle between 750°C and 100°C was repeated. The temperature was raised and lowered at a rate of 2°C/min, and N_2 was supplied to both electrodes during this procedure. Further, H_2 was supplied at a rate of 0.35 L/min and air at a rate of 0.95 L/min and the impedance was measured while 20 A was applied to the stack to check the DC resistance for each heat cycle.

3. Experimental Results

3-1 Evaluation of the contactability

The evaluation results for the contactability are shown in Fig. 5.

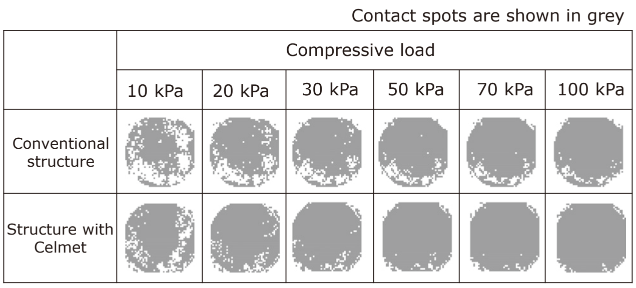

Fig. 5. Results for evaluation of the contactability

For the conventional structure, the contactability between the cell and a flat plate imitating the IC was evaluated. The results showed that there were many non-contact points when the load was small, but the contactability improved gradually as the load was increased. On the other hand, inserting Celmet between the cell and the plate imitating the IC was found to increase the number of contact points in comparison to the conventional structure. The image of the cause of improvement in the contactability is shown in Fig. 6. When the cell warps in the conventional structure, a non-contact area is created between the cell and the IC. However, when Celmet is used, it deforms and fills the non-contact area between the cell and the IC and reduces the number of non-contact points.

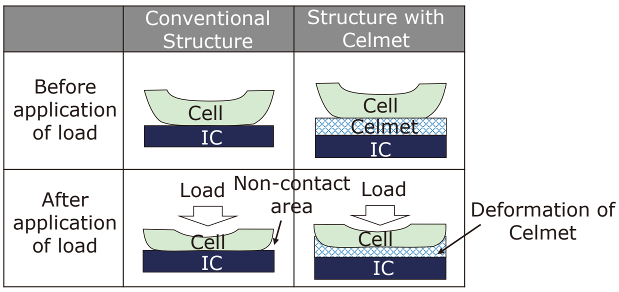

Fig. 6. Schematic Illustration of the contactability

Figure 7 shows the contact ratios calculated from the appearance frequencies of contact and non-contact points. Compared to the SOFC with a conventional structure, the SOFC comprising Celmet exhibited higher contact ratios throughout the entire load range. This result indicates that incorporating Celmet into SOFC stacks can reduce DC resistance by improving the contactability.

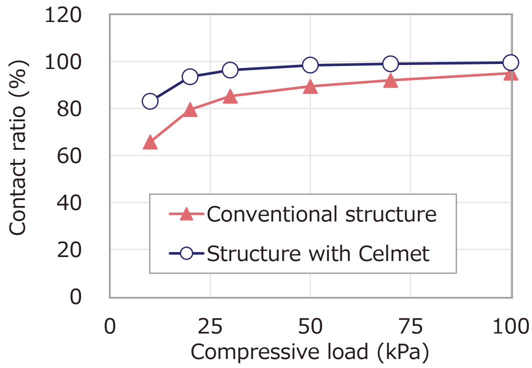

Fig. 7. Comparison of Contact Ratio at Each Load

3-2 Measurement of CTE

Figure 8 shows the images of NiCo Celmet and NiCo oxide obtained by X-ray radiography technique with synchrotron radiation.

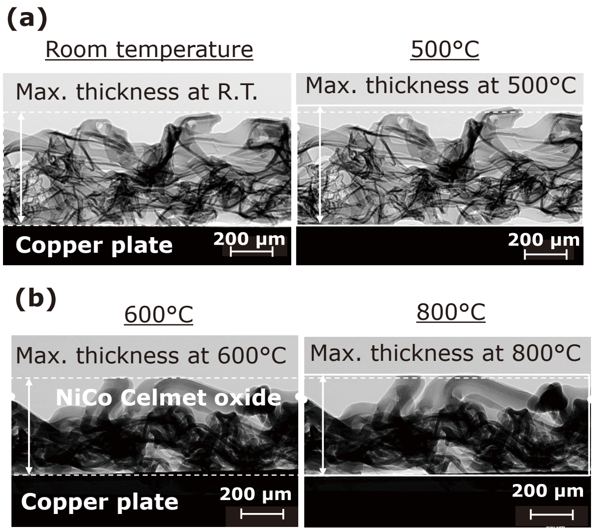

Fig. 8. X-ray radiography technique
(a) NiCo Celmet (b) NiCo oxide Celmet

It was confirmed from these images that Celmet increases in thickness as its temperature increases. As shown in Table 1, the CTE of NiCo Celmet calculated from its images was 16 × 10^{-6}/°C, while that of NiCo oxide

Table 1. List of CTE

	CTE /°C
NiCo Celmet	16×10^{-6}
NiCo oxide Celmet	7×10^{-6}
Ref. Ni	13.4×10^{-6}
Ref. Co	13.0×10^{-6}
Ref. $MgAl_2O_4$	7.45×10^{-6}
Ref. Mica	$30\text{~}60\times10^{-6}$

Celmet was 7 × 10^{-6}/°C.

As a reference, Table 1 also shows the CTE of a few substances that have been disclosed. It was confirmed that the CTE of NiCo Celmet is comparable to that[5] of metallic Ni and Co. Although we could not confirm whether or not the data on NiCo oxide Celmet had been published, its CTE was comparable to that of $MgAl_2O_4$ with the same crystal structure.[6] Furthermore, the thickness expansion of NiCo Celmet due to oxidation was calculated from its thicknesses before and after oxidation. As a result, a thickness increase of 5% was determined. Figure 9 shows a graph of the change in thickness of Celmet in air, including descriptions of the abovementioned thermal and oxidation expansions.

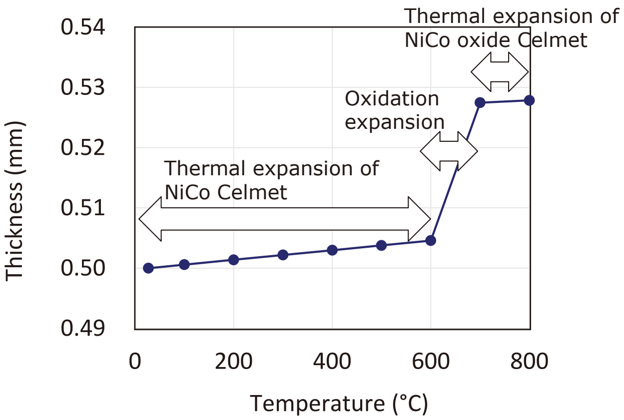

Fig. 9. Change in the Thickness of NiCo Celmet

In widely used SOFCs, an insulating spacer such as a mica*8 sheet is occasionally used around the periphery of the current collectors. If the expansion of the Celmet is smaller than the thermal expansion of the mica sheet in the above structure, the contactability of the Celmet with the neighboring cell and the IC may decrease (Fig. 10). In this study, the thickness expansion coefficients of individual materials were compared. As a result, the thickness expansion ratio of NiCo Celmet, which was approximately 5.6% when measured by raising its temperature from R.T. to 800°C, was found to be higher than the expansion coefficient of a mica sheet, which was 2.3 to 4.6% when calculated from the expansion coefficient of the mica sheet.[7] When the temperature of NiCo Celmet was raised to 800°C for its oxidation and then lowered to R.T., the oxidized NiCo Celmet shrank in thickness according to its CTE, thereby maintaining the increase in thickness due to oxidation expansion. This means that pressure can be applied from inside even when the SOFC stack is heated, and enough contactability can be maintained.

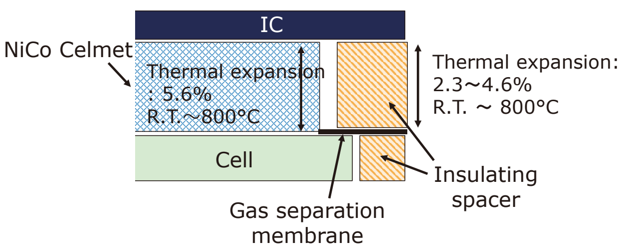

Fig. 10. Arrangement of Components in Stack

3-3 Evaluation of a single cell stack

Table 2 summarizes the results of evaluating a single cell stack under various conditions. For a comparative cell stack comprising an FeCr alloy mesh with conductive paste and one comprising only conductive paste, the evaluation was conducted in combination with a grooved IC. For a cell stack comprising NiCo Celmet, combination with a non-grooved IC was also evaluated. When measured with a 10 kHz high-frequency resistance meter, the DC resistance of the cell stack comprising the FeCr alloy mesh with conductive paste was 5 mΩ, while that of the cell stack comprising only conductive paste was 6 mΩ. On the other hand, the cell stack comprising Celmet reduced the DC resistance to approximately 2 to 3 mΩ. As above, the DC resistance of the cell stack comprising Celmet with no conductive paste was lower than that of the cell stacks with the comparative structures.

Table 2. SOFC Performance Evaluation Results

		Mesh	Without Current collector	Structure with Celmet ①	Structure with Celmet ②	Structure with Celmet ③
Structure	Current collector	FeCr alloy mesh	Non-use	NiCo Celmet	NiCo Celmet	NiCo Celmet
Structure	Conductive paste	LSC	LSC	LSC	Non-use	Non-use
Structure	Groove in IC	Use	Use	Use	Use	Non-use
Result	DC resistance (mΩ)	5	6	2	3	3
Result	Gas utilization (%)	43	33	>54	>54	>54
Result	Max. power density (mW/cm²)	333	281	433	376	412

These results were considered to derive from the use of Celmet and the resulting improvement in the contactability of Celmet with the IC and the cell, as described in the previous sections. Figure 11 also shows the power output

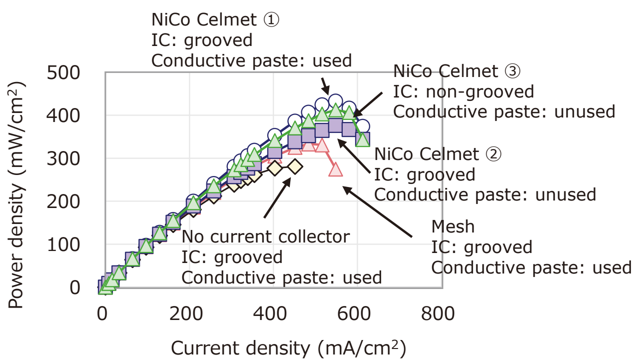

Fig. 11. Evaluation of Power Output

characteristics of the cell stack with each structure.

Since these characteristics include the effect of improved gas diffusivity achieved by using Celmet, their comparison does not reflect the effect of only reduced DC resistance. However, since it has been confirmed that high power output characteristics can be obtained by using Celmet for the current collector and this result will not differ even for a structure with no conductive paste, the use of Celmet is effective for increasing the power output of SOFC. Furthermore, in our previous study, we had reported that the high gas diffusivity of Celmet can eliminate the need for grooving ICs.[4] This time, we evaluated a cell stack with a non-grooved IC and no conductive paste on the cathode side. As a result, the power output of this stack was higher than that of stacks with comparative structures. It was also confirmed that the cost of cell stacks can be reduced.

3-4 Heat cycle evaluation of a single cell stack

To evaluate the current collection performance of Celmet, the power output of a single cell stack in each heat cycle was evaluated. The maximum power outputs obtained are plotted in Fig. 12.

It was confirmed that cell stacks comprising NiCo Celmet exhibit a higher power output retention ratio when compared with cell stacks comprising FeCr alloy mesh. To clarify the cause of the above result, we compared AC impedance between the first and the 15th cycles. As a result, the resistance increase ratio was smaller when NiCo Celmet was used than when the mesh material was used (Fig. 13). This increase in resistance is assumed to be caused not only by the contact resistance between the Celmet and the adjacent components, but also by an increase in the resistance of the cell and the IC themselves. However, when compared with the mesh material, the above result suggests that NiCo Celmet contributes to the maintenance of enough contactability during the heat cycle.

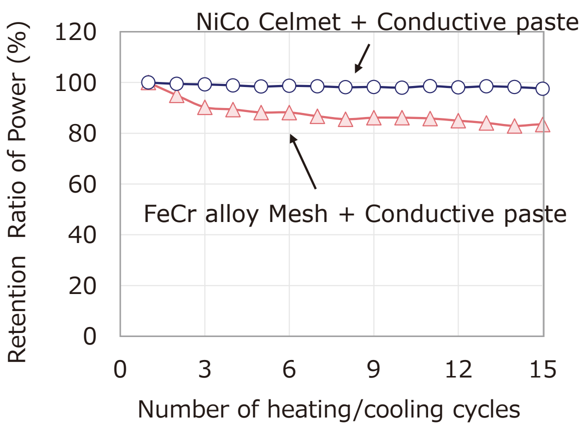

Fig. 12. Power Output Retention Ratio during Heat Cycles

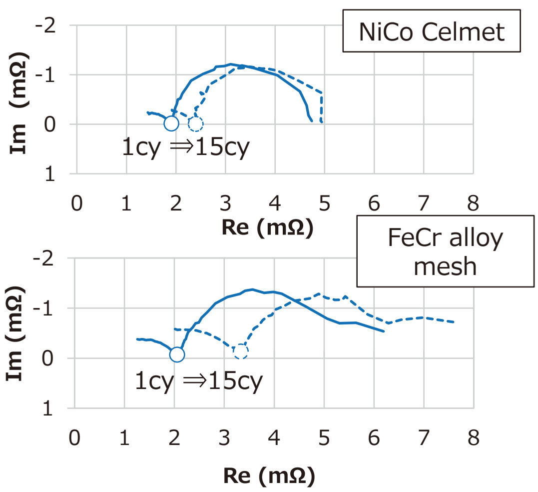

Fig. 13. Impedance before and after the Heat Cycle

4. Conclusions

To investigate the effect of NiCo Celmet on DC resistance, the contactability with a warped cell and the expansion coefficient were examined. The evaluation of the contactability revealed that Celmet deforms flexibly and ensures a good contactability. In addition, the expansion coefficient of NiCo Celmet was examined to understand its expansion behavior in the stack. Concerning the CTE, it was found that thickness expansion during temperature increase can be visualized using X-ray radiography. Furthermore, the thermal and oxidation expansion behaviors of NiCo Celmet inside the stack were clarified by calculating the oxidation expansion of this material from the thickness change before and after oxidation. NiCo Celmet was also compared with a mica sheet, a peripheral member of the current collector. The results revealed that NiCo Celmet expands more than the mica sheet, suggesting that NiCo Celmet allows the application of pressure from inside the stack and thus maintains enough contactability. Finally, a cell stack comprising NiCo Celmet was subjected to power output and heat cycle tests to check the effect of NiCo Celmet on DC resistance. In these tests, NiCo Celmet reduced DC resistance without the use of conductive paste, and tended to increase the power output compared to the conventional structure. In addition, NiCo Celmet can suppress the increase of DC resistance during the heat cycle, and is expected to improve the performance of cell stacks in terms of durability.

5. Acknowledgment

The X-ray radiography experiment at SPring-8 was conducted under proposal No. 2021B5331. We would like to express our gratitude to all persons involved in this experiment.

Technical Terms

∗1 SDGs: An abbreviation for Sustainable Development Goals, the international goals adopted in 2015 by the United Nations General Assembly for the sustainable development of human beings.

∗2 Stack: A structure in which a cell, which is an electricity generation component, is sandwiched between current collectors and interconnectors. A typical SOFC comprises laminated stacks. A stack made using a single cell to evaluate the basic performance is called a "single cell stack."

∗3 Interconnector: A wall used as a fuel cell component to prevent the hydrogen and air supplied to the fuel cell from mixing with each other. The interconnector is usually grooved to evenly diffuse the hydrogen and oxygen.

∗4 LSC: An abbreviation for lanthanum strontium cobalt oxide, a conductive oxide that can be used as the conductive paste powder for SOFCs.

∗5 Pore diameter: The mean distance between Celmet frames. The larger the pore diameter, the rougher the opening.

∗6 YSZ: An abbreviation for yttria-stabilized zirconia, a material used for the solid electrolyte of SOFCs.

∗7 TMA method: An analysis method for determining the CTE of a sample by measuring its dimensional change though a probe while varying the temperature of the sample.

∗8 Mica: A type of mineral. Due to its excellent insulating performance and heat resistance, mica can be used as an insulating material for SOFCs.

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