

Application of Ni Porous Metal to Solid Oxide Fuel Cells

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High thermal oxidation resistance and gas diffusion performance are required for the current collectors of solid oxide fuel cells (SOFCs). The authors have developed a Ni-Sn porous metal that has a high thermal oxidation resistance and gas diffusibility. In this work, the authors have evaluated the applicability of the Ni-Sn porous metal as the cathode collector of an SOFC in terms of the long-term durability, area-specific resistance, and power density. The Ni-10wt% Sn porous metal showed a weight increase of 0.14 mg/cm² and an area-specific resistance of 0.017 Ωcm² after withstanding a temperature of 600 °C for 3,000 hours. Thus, it is concluded that the Ni-Sn porous metal can be applied as the cathode collector for SOFCs operating in an intermediate temperature range. The authors have also tested the applicability of the Ni-Sn porous metal and the conventional Ni porous metal as an anode collector. Both the Ni-Sn and the Ni porous metals exhibited favorable compression characteristics and high power densities, equivalent to a Pt mesh, indicating that these metals are ideal as anode collectors, particularly at 800°C.

Keywords: solid oxide fuel cell (SOFC), porous metal, current collector, high corrosion resistance, power improvement

1. Introduction

With their high efficiency in converting chemical energy into electrical energy, solid oxide fuel cells (SOFCs) are expected to play a significant role as next-generation power generation devices.^{(1),(2)} In recent years, efforts have been directed towards lowering the operating temperature of the SOFCs for reduced costs and improved durability. These efforts include extensive studies on the use of relatively low-cost metals instead of the conventional ceramics as the cathode current collector*¹ and the anode current collector.

The cathode current collector needs to be made of an oxidation-resistant material for use in a high-temperature oxidative environment. Materials of interest have included iron-chromium (Fe-Cr) alloys.⁽³⁾⁻⁽⁸⁾ However, cathodes in the SOFCs are known to be subject to performance degradations owing to Cr poisoning.^{(9),(10)} Consequently, a Cr-free material is desirable for the current collector.

In contrast, the anode is placed in a reductive environment. Hence, nickel (Ni) is used for constructing the anode current collectors. However, the increasingly high fuel utilization during the operation of the SOFCs owing to demand for higher operating efficiencies has led to a lean hydrogen and a resultant non-negligible oxidation because of the water produced at the electrodes during the power generation. Therefore, the demand for oxidation-resistant anode current collectors is gradually increasing.

Meanwhile, a porous metal with a three-dimensionally arranged structure that rapidly warms the introduced gas, ensures a reduced pressure loss, and provides efficient gas dispersion has emerged as a promising current collector structure.^{(11),(12)}

dimensional structure and have identified the favorable properties of the material.⁽¹³⁾ As a next step, this paper discusses the applicability of the Ni porous metal and the Ni-Sn porous metals as current collectors for the SOFCs. The authors evaluated the metals in terms of the long-term oxidation resistance and electrical conductivity within the SOFC operating temperature ranges. In addition, the prototype SOFCs were tested with cathode and anode current collectors physically incorporating the porous metal. Figure 1 shows the SOFC structure. Table 1 shows the intended products and development targets based on the performances and properties^{(3)-(8),(14)} of the current SOFCs and the existing interconnectors.

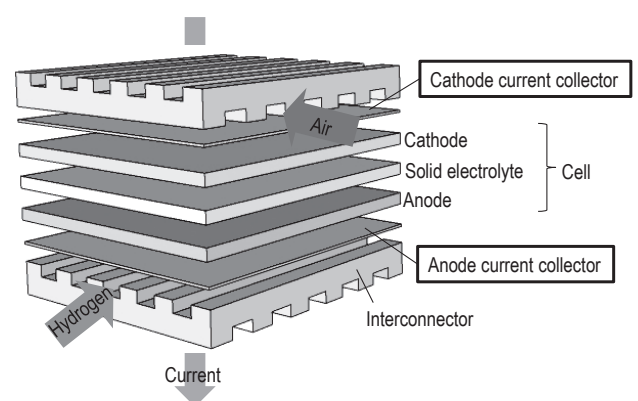


Fig. 1. SOFC structure

2. Development Targets

The authors have evaluated the fundamental oxidation resistance of an Ni-Sn porous metal formed into a three-

Table 1. Intended products and development targets

Intended product	Property	Target
Cathode current collector	Oxidation resistance	Max. weight increase: 1 mg/cm ² after 1000 h No exfoliation or unusual oxidation
	Electrical resistance	Max. high-temp. area-specific resistance: 0.1 Ωcm ²
	Applicability to cells	Comparable to Pt meshes in power generation, when used in a prototype SOFC (single-cell)
Anode current collector	Compression characteristic	Min. squeeze at 200 kPa or less: 0.1 mm
	Applicability to cell stacks*2	Comparable to an Ni porous metal in power generation, when used in a prototype SOFC (single-cell) Successful application to prototype SOFCs (short stack*3)

3. Experimental Method

3-1 Preparation of Ni and Ni-Sn porous metals

A polyurethane foam with interconnected cells was treated to become electrically conductive. This was followed by the application of a predetermined amount of nickel via electroplating. The base material, or plastic foam, was removed through heat treatment at 800°C. The remaining nickel was processed in a reducing gas at approximately 1000°C to generate a nickel porous metal.⁽¹⁵⁾

Next, the Ni porous metal was coated with a predetermined amount of Sn by electroplating. Additionally, this was heat-treated in a reducing gas at approximately 1000°C to obtain an Ni-Sn porous metal by Sn diffusion into Ni. Figure 2 shows an SEM*4 image of the surface of the Ni-Sn porous metal. The typical properties of this porous metal are shown in Table 2.⁽¹³⁾

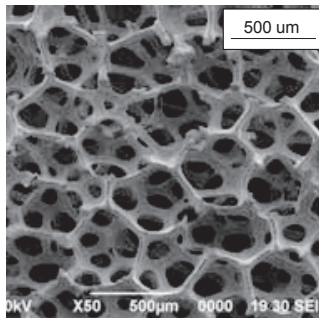


Fig. 2. SEM image of an Ni-Sn porous metal surface

Table 2. Typical properties of an Ni-Sn porous metal⁽¹³⁾

Property	Value
Weight per unit area of metal (g/m ²)	700
Thickness (mm)	1.4
Average pore size (μm)	500
Porosity (%)	94 max.

3-2 Property evaluation tailored for cathode current collectors

3-2-1 Oxidation resistance evaluation

A cathode current collector needs to be resistant to oxidation because it is placed in a high-temperature oxidizing atmosphere. To ascertain the relationship between the Sn content and the high-temperature oxidation resistance, the Ni-Sn porous metal was heat-treated in the air at 800°C for 1000 hours and at 600°C for 3000 hours, followed by weight increase measurements. Sample pieces were cut into 50 × 50 × 1.4 mm. The Ni-Sn porous metal with a 10 wt% Sn content (hereafter, the Ni-10Sn porous metal) was subjected to weight increase measurements every certain periods of time to check the oxidation characteristics of the samples.

3-2-2 Evaluation of the area-specific resistance

The output power of the SOFC depends on the sum of the resistance of each of its components. Consequently, the current collector, a key part of the SOFC, is required to be highly conductive. Therefore, using the DC four terminal method, the area-specific resistance of the Ni-Sn porous metal was measured. As SOFCs generally use a spring to apply force on the cells, a 3 kgf (11.8 kPa) weight was placed on the samples during the area-specific resistance evaluation to simulate the operating environment and represent the actual SOFC operating conditions to the greatest extent possible.

The measurement was conducted in the air at 600°C for 1000 hours. The sample size was the same as in the oxidation resistance evaluation, i.e., 5 cm² and 1.4 mm in thickness. The evaluation was conducted for the Ni-10Sn and the Ni-14Sn porous metals. An Ni porous metal was used as a sample for comparison purposes.

3-2-3 Prototype SOFC (single-cell) incorporating the porous metal as the cathode current collector and the power generation evaluation

Prototype SOFCs with yttria-stabilized zirconia (YSZ)*5 solid electrolytes were constructed using the Ni-10Sn porous metal or a Pt mesh (0.08 mm in diameter, 80 mesh) as the cathode current collectors for comparison purposes. Figure 3 shows a schematic diagram of the prototype SOFCs. A ferrite Fe-Cr alloy was used as the material for the upper and lower plates as well as for the voltage plates. In addition, mica was used as the material for insulating the plates and for sealing.

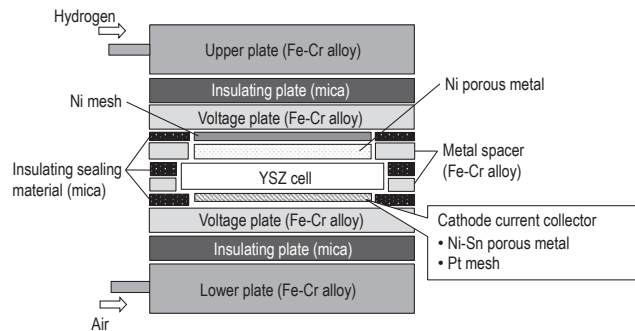


Fig. 3. Schematic diagram of the prototype SOFCs

The operating temperature was set to 600°C, considering the oxidation of the Ni-Sn porous metal. The anode was placed in a 100% hydrogen atmosphere; the cathode was in a 20% oxygen and 80% nitrogen atmosphere, both without humidification controls. The flow rates were set to 1 L/min for both the anode and the cathode. When the open circuit voltage (OCV)^{*6} had stabilized, the current versus voltage (IV) characteristics were measured.

3-3 Characteristic evaluation tailored for anode current collectors

3-3-1 Compression test

To reduce the contact resistance and ensure the sealing performances of the SOFCs, a force is applied to the SOFC stacks. Hence, the compression characteristics of the Ni porous metal were evaluated in argon (Ar) gas at typical SOFC operating temperatures of 600°C and 800°C, respectively. The 20-mm diameter samples were subjected to increasing temperatures at a rate of 20°C/min and measured at a compression rate of 0.5 mm/min.

3-3-2 Prototype SOFC (single-cell) and short stack incorporating the porous metal as the anode current collector and the power generation evaluation

Another prototype SOFCs (single-cell) were constructed, using the Ni porous metal or the Ni-10Sn porous metal as the anode current collectors, as in the case of the cathode current collector. These prototype SOFCs were tested and evaluated in terms of the power generation. The anode differs from the cathode in that it is in a reductive atmosphere and is therefore, free from the oxidation considerations. Accordingly, the operating temperature was set to 800°C. The other conditions were similar to those for the power generation evaluation of the cathode current collector.

Moreover, to study the applicability of the porous metal for the SOFC stacks, a prototype short stack comprising of five stacked cells was constructed and subjected to a power generation evaluation. Incidentally, the Ni porous metal was used as the anode current collector material.

4. Results and Discussion

4-1 Application as a cathode current collector

4-1-1 Oxidation resistance evaluation

For Ni-Sn porous metals with various Sn contents, Fig. 4 shows the increases in the weights pre- and post- the heat treatments performed in the air at 800°C for 1000 hours and at 600°C for 3,000 hours, respectively. In the case of the heat treatment at 800°C for 1,000 hours, Ni-Sn porous metals increased in weight after the heat treatment irrespective of their Sn content, with a weight increase exceeding 1.7 mg/cm², revealing a noticeable level of oxidation. In contrast, after heat treatment at 600°C for 3,000 hours, the weight increases were 1.3 mg/cm² for the Ni-3Sn porous metal, 0.25 mg/cm² for the Ni-5Sn porous metal, 0.13 mg/cm² for the Ni-8Sn porous metal, and 0.14 mg/cm² for the Ni-10Sn porous metal. For Ni-Sn porous metals with an Sn content of 5 wt% or more, the oxidation was noticeably retarded in spite of a long-term heat treatment for 3,000 hours. The weight increases of these porous metals were below the set target of 1 mg/cm².

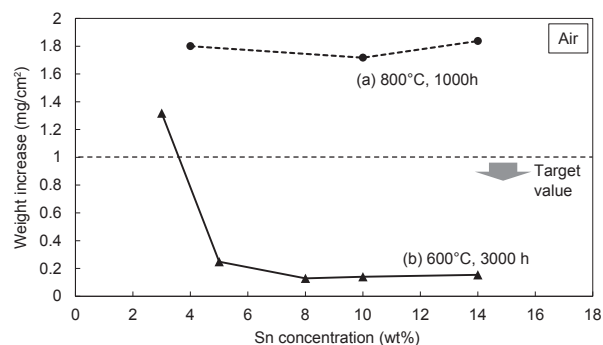


Fig. 4. Sn concentration vs. the weight increase at 600 °C/800 °C

Next, Fig. 5 shows the changes in the weight increase over time for the Ni-10Sn porous metal at 600°C, one of the samples with a favorable oxidation resistance.

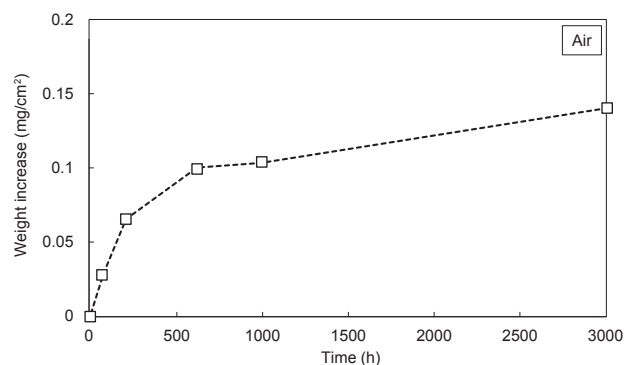


Fig. 5. Changes in the weight increase over time for the Ni-10Sn porous metal

A significant increase in weight owing to oxidation was observed in the early phase. However, the increase became slower with time. As the weight increase followed a parabolic rule representing the general oxidation characteristics in which the diffusion of ions in the oxide films is rate-determining, it is inferred that an exfoliation of the oxide films or an unusual oxidation did not occur. In the oxidation of a material that follows the parabolic rule, the oxidation rate constant (K_p)^{*7} is an index of the oxidation characteristic of the material. The constant, K_p , is expressed by the following equation:

$$\left(\frac{\Delta m}{S}\right)^2 = K_p t \quad \dots\dots\dots (1)$$

where, Δm is the weight increase; t is the elapsed time; and S is the surface area. For the Ni-10Sn porous metal evaluated in this study, K_p was $1.3 \times 10^{-15} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$ in the case with the heat treatment at 600°C for 3,000 hours. The constant, K_p , is typically $1\text{--}2 \times 10^{-14} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$ at the operating temperatures of the SOFC interconnector materials. Hence, Ni-Sn porous metals are believed to be sufficiently resistant to oxidation at 600°C.

4-1-2 Area-specific resistance evaluation

Figure 6 shows the area-specific resistance measurement results for the case with the heat treatment at 600°C for 1,000 hours.

The resistance of the Ni porous metal increased substantially following the low-resistance phase, immediately after the beginning of the evaluation. In comparison, the Ni-10Sn porous metal exhibited a higher area-specific resistance than the Ni porous metal at room temperature and in the initial phase owing to the addition of Sn. However, after a period of 1,000 hours, the resistance of the Ni-10Sn porous metal was stable and considerably low at 0.017 Ωcm^2 . The Ni-10Sn porous metal appears to be successful in terms of the electrical conductivity at 600°C because the area-specific resistance of the general-purpose interconnector material for the SOFCs is between 0.015 and 0.030 Ωcm^2 ; in addition, the area-specific resistance widely accepted as permissible is 0.1 Ωcm^2 or less.⁽¹⁶⁾ Incidentally, the Ni-10Sn porous metal exhibited a slightly low area-specific resistance during the initial several hundred hours. One possible reason for this is that it involves a process, wherein, a thermodynamically stable phase of Ni_3Sn at 600°C is formed, following the initial state in which Sn is a solid solution in Ni.

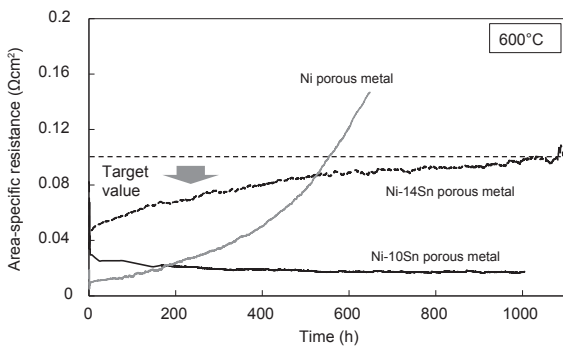


Fig. 6. Changes in the area-specific resistance of the Ni-Sn porous metals with time

It is also inferred that the reason for the high area-specific resistance of the Ni-14Sn porous metal is the effect of Ni_3Sn . More specifically, the Ni-14Sn porous metal forms a higher amount of Ni_3Sn than the Ni-10Sn porous metal. The electrical conductivity of Ni_3Sn is lower than that of a solid solution of Sn in Ni. Consequently, it is likely that the difference in the amounts of Ni_3Sn determines the area-specific resistances of the Ni-Sn porous metals prepared in this study.

4-1-3 Prototype SOFCs incorporating the porous metal as the cathode current collector and the power generation evaluation

Figure 7 shows the IV and the power output characteristics, and the evaluation results of SOFCs with cathode current collectors made of Pt mesh or the Ni-10Sn porous metal. Both the SOFCs exhibited OCVs of 1.2 V several hours after the introduction of hydrogen that is approxi-

mately equal to the theoretical value. This validates the construction and evaluation of the prototype SOFCs. At a typical SOFC operating voltage of 0.8 V, the power output from a cell that incorporated the Ni-10Sn porous metal was 7.3 W (115 mW/cm^2), whereas, the power output from a cell that incorporated the Pt mesh was 6.8 W (107 mW/cm^2). Consequently, because the SOFC with the Ni-Sn porous metal delivered the same level of power output as the SOFC with the Pt mesh, the Ni-Sn porous metals demonstrate a current collecting performance comparable to that of the Pt mesh. Hence, they are proven to be suitable for use as cathode current collectors in the 600°C intermediate temperature range.

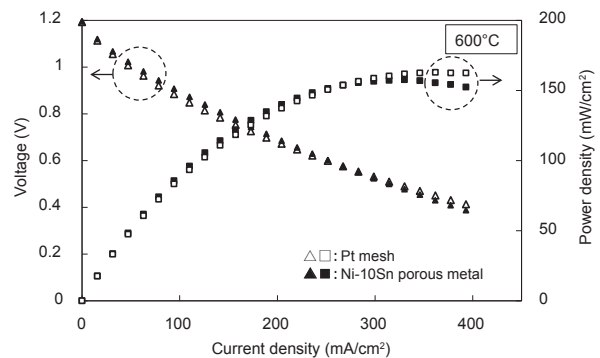


Fig. 7. Power generation characteristics of SOFCs with cathode current collectors made of either Ni-Sn porous metal or Pt mesh

4-2 Application as anode current collectors

4-2-1 Compression testing

Figure 8 shows the results of the compression test conducted for the Ni porous metal at 600°C and 800°C. The Ni porous metal exhibited substantial temperature-dependent variations in the load characteristics. In general, a force of 100–200 kPa, depending on the design, is applied to the

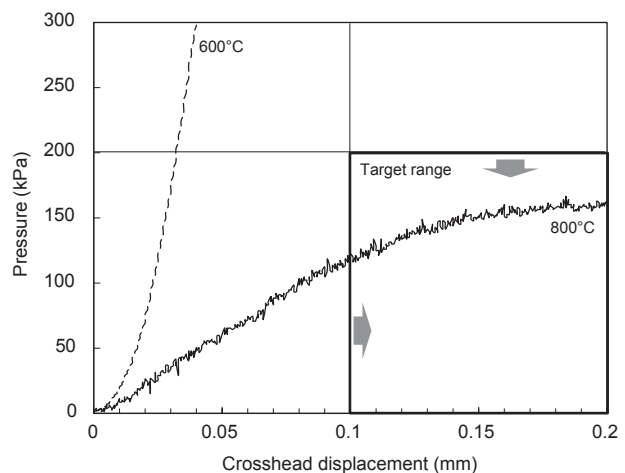


Fig. 8. Compression test results of the Ni porous metal

SOFCs for ensuring their sealing performances and for reducing their contact resistances. The displacement of the Ni porous metal is insignificant at not more than 0.05 mm under a force of 160 kPa and at 600°C. The displacement is close to the machining tolerances for the spacer and the other parts. This might render the design of the stack difficult. Therefore, improvement considerations are currently under study. Meanwhile, at 800°C, the displacement is large at 0.2 mm under the same pressure. Accordingly, it should be possible to achieve an appropriate stack configuration by making allowances for suitable squeezes in the design.

4-2-2 Prototype SOFC (single-cell) and short stack incorporating the porous metal as the anode current collector, and the power generation evaluation

SOFCs with anode current collectors made of Ni porous metal or the Ni-10Sn porous metal were operated at 800°C. Figure 9 shows the IV and power output characteristics, and the evaluation results for these SOFCs.

Both SOFCs exhibited favorable characteristics with OCVs greater than 1 V and sufficiently high power outputs, although the cell incorporating the Ni-10Sn porous metal generated a slightly lower OCV. The test results of this study suggest that the Ni-10Sn porous metal has a sufficient electrical conductivity compared to the Ni porous metal, despite concerns regarding the higher electrical resistance owing to the addition of Sn. The Ni porous metal appears to be usable under the normal SOFC operating conditions, although it needs to be further examined in detail. Meanwhile, with respect to the need for reducing the oxidation of the anode current collector in the case of high fuel utilization, the use of the Ni-Sn porous metal as the anode current collector is likely to be an effective measure.

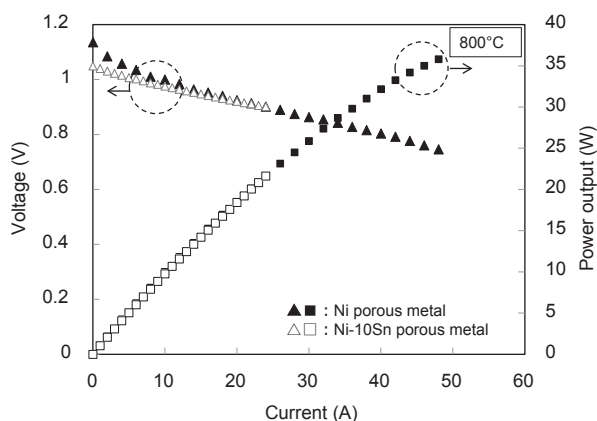


Fig. 9. Power generation characteristics of SOFCs incorporating the Ni and Ni-Sn porous metals, respectively, as the anode current collectors

Photo 1 and Figure 10 depict the prototype short stack and the power generation evaluation results, respectively.

The OCV was 5.16 V and the output was 145 W. This performance is lower than that of the single-cell performance shown in Fig. 9 in terms of the OCV and the power output per cell. However, the power output per cell of the

short stack was 70% of that of the single-cell performance. This result is relatively favorable, as the prototype stack was constructed for the purpose of current collector evaluation. Figure 11 shows the power output of each cell at 2.4 V.

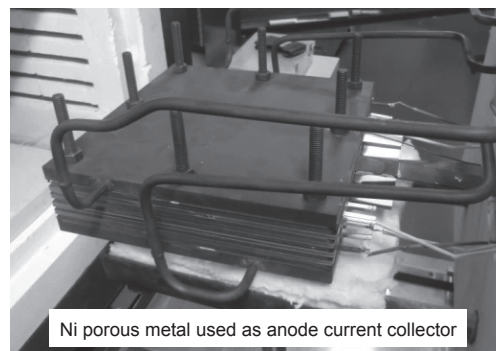


Photo 1. Prototype short stack

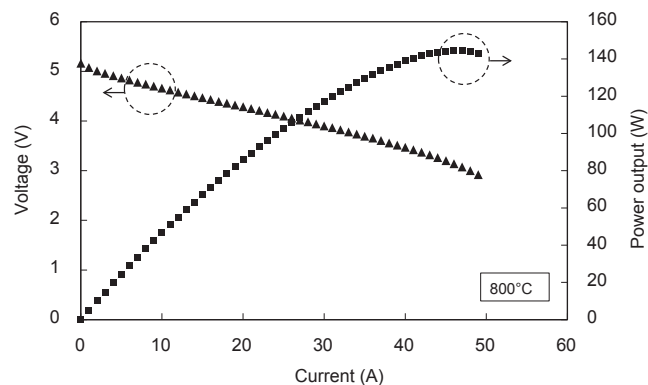


Fig. 10. Power generation characteristics of the short stack

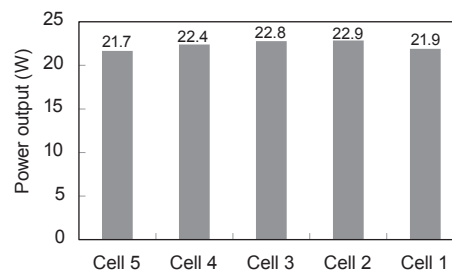


Fig. 11. Power output from each cell in the short stack (under 2.4 V operating conditions)

The variations in the power output of the individual cells were within $\pm 3\%$. At these low level output variations, it can be inferred that the fuel cells are free of uneven gas flows resulting from the non-uniform collapses of the pores in the porous metal. Moreover, the cells did not develop cracks in spite of a considerable pressure applied by the porous metal, proving the potential of the porous metal for use in SOFC stacks.

5. Conclusion

Various porous metals were evaluated with respect to their oxidation resistance and area-specific resistance at high temperatures. The power generation characteristics of the prototype SOFCs were also evaluated. The application of porous metals as the current collectors in SOFCs was examined. The results are shown in Table 3.

Table 3. Current collectors, operating temperatures, and potentially usable porous metals

Operating temp	600 °C	800 °C
Cathode current collector	Ni-Sn porous metal	Not applicable
Anode current collector	To be determined (under development) Suitable depending on the design and operating conditions	Ni porous metal Ni-Sn porous metal

Porous metals are not suitable as cathode current collectors operating at 800°C. However, they seem to be suitable for SOFCs operating in the intermediate temperature range not higher than 600°C, for which the demand is expected to grow in future. In particular, the Ni-10Sn porous metal exhibited favorable characteristics with a 0.14 mg/cm² weight increase owing to oxidation and an area-specific resistance of 0.017 Ωcm² in the case with a heat treatment at 600°C for 1,000 hours. The prototype SOFC incorporating the Ni-10Sn porous metal produced sufficient power output.

Meanwhile, the Ni porous metal appeared to be more suitable as an anode current collector in the 800°C high-temperature range rather than in the 600°C intermediate temperature range. Moreover, for operation at a high fuel utilization, for which a high oxidation resistance is specifically required, the use of the Ni-Sn porous metal that has an excellent oxidation resistance can be effective. Thus, this study has identified the possibility of using an Ni-Sn porous metal in SOFC stacks.

Technical Terms

- *1 Current collector: A component placed on both the electrodes of the cells for efficiently collecting electrons
- *2 Stack: Fuel cells stacked for output power improvement; A stack normally contains 30–50 cells.
- *3 Short stack: A stack that contains 3–10 cells, constructed for performance verification purposes.
- *4 SEM: Scanning electron microscope; Emits electron beams towards the object and detects secondary electrons or others to enable observation.
- *5 YSZ: Yttria-stabilized zirconia; Zirconia stabilized by the addition of yttrium oxide to retard phase transformation at high temperatures; YSZ is used as a solid electrolyte in SOFCs, enabling oxygen ion conduction.
- *6 Open-circuit voltage: Voltage under no-load conditions; The open-circuit voltage is determined predominantly by the fuel gas and the temperature. For hydrogen gas and at 800 °C, the theoretical value of the open-circuit voltage is approximately 1.2 V.
- *7 Oxidation rate constant: The relationship between the oxidation time and the oxide weight follows a parabolic rule, if the diffusion of ions in the oxide films is rate-determining (Wagner's theory). The oxidation rate constant serves as an index of the oxidation rate. The oxidation resistance is higher for a decreasing K_p .

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