FEATURED TOPIC

Application of Heat-Resistant Porous Metal

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Celmet, the unique porous metal product of Sumitomo Electronic Toyama Co. Ltd., has high gas-diffusivity and high electric conductivity. Celmet is a good candidate for the cathode current collectors of solid oxide fuel cells (SOFCs) that require uniform gas-diffusivity and high electric conductivity. Thus far, we have examined the application of nickel (Ni) Celmet to the collectors, however, the desired output power density has not been obtained due to the decrease in electric conductivity caused by the oxidation of Ni at high temperature of the fuel cells. We have developed new nickel cobalt (NiCo) Celmet that forms conductive ceramics, keeping high electric conductivity at high temperature and highly oxidizing atmosphere. This paper introduces the physical properties of the NiCo Celmet and reports on the performance of an SOFC that uses the new Celmet for its cathodic current collector.

Keywords: solid oxide fuel cell (SOFC), Celmet, porous material, current collector, high heat resistance

1. Introduction

In recent years, hydrogen has been expected to be a new energy source with low environmental impact. In particular, fuel cells are clean since they generate electricity directly from hydrogen and oxygen with high energy-conversion efficiency and generate only water as a reaction product. Because of such advantages, fuel cells are attracting attention as batteries for household, industrial, and even on-vehicle use.[(1),(2)] Among these fuel cells, solid oxide fuel cells (SOFCs), which operate at temperatures as high as 700°C or more, do not need such an expensive, rare catalyst as platinum.[(3),(4)] Thanks to such advantage, SOFCs are expected to expand their applications in the future. On the other hand, SOFCs' structural members are required to be highly resistant to heat. It is crucial to reduce the cost of the structural members.[(5),(6)]

Interconnectors*[1] with gas flow channels are used in a typical SOFC stack to evenly diffuse the supply gas, as shown in Fig. 1 (a).[(7)] Since the interconnectors are exposed to a high-temperature oxidizing atmosphere on their cathode side, studies have been conducted on the use of Fe-Cr and other high heat-resistant alloys as interconnector materials. However, the catalytic activity of these materials is likely to degrade due to Cr-poisoning. In addition, SOFCs may be deformed when operated or heated/cooled, reducing the degree of contact between the interconnectors and the cell. To ensure an adequate degree of contact between the interconnectors and the cell for a long period, it is desirable to place a Cr-free current collector between the cell and each interconnector. Celmet, a product of Sumitomo Electric Toyama, is a three-dimensional network-structured porous metal with a maximum porosity of 98%. Taking advantage of this feature, Celmet has already been used widely as the current collectors and electrolytic substrates of various energy devices. When used as a current collector of an SOFC, Celmet deforms integrally with the cell, ensuring a sufficient degree of contact between the interconnectors and the cell. Further, due to its high porosity, Celmet sufficiently diffuses the supply gas, reducing interconnector cost by eliminating the need for grooving (Fig. 1 (b)).

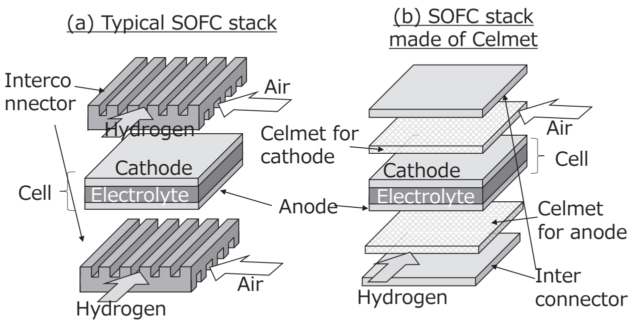

Fig. 1. Concept of use of Celmet for SOFC

Although mass-produced Ni Celmet has already been confirmed to be useful in anode current collectors,[(8)] cathode current collectors made of Ni are oxidized when heated to a high-temperature of 700°C or more and increase their electrical resistance. Therefore, Ni Celmet is unsuitable for use in such a high-temperature atmosphere.

We have developed nickel cobalt (NiCo) Celmet as a cathode collector material that forms electrically conductive ceramics when heated to a high temperature, and therefore can be used even in a high-temperature atmosphere. In this study, we evaluated the electrical conductivity, gas diffusivity, and compressive load characteristics required of an SOFC current collector, as well as the output power performance of an SOFC comprising a NiCo Celmet component.

2. Development Milestone

To check the applicability of NiCo Celmet in the cathode current collector of an SOFC, we evaluated this alloy in terms of electrical resistance in a high-temperature oxidizing atmosphere, pressure loss when air is passed through it, and stacking load-bearing performance. We also checked whether or not this alloy would satisfy the performance required when built into an SOFC. For these evaluation items, the development milestones determined from conventional stack design values are shown in Table 1.

Table 1. Development milestone

Item	Target value
Electrical resistance	When measured in an 800°C air atmosphere, the electrical resistance during the initial 1000 h shall be 200 mΩ · cm² max. (Design value for in-house made stacks)
Pressure loss	Acquisition of measured value
Breaking strength	Shall be 0.2 MPa min., which is the load exerted onto an SOFC stack
Power density of SOFC	Shall have a performance equivalent to that of a single cell stack for comparison (a combination of a grooved interconnector and a stainless steel mesh current collector)

3. Experiment Method

3-1 Preparation of NiCo Celmet

NiCo Celmet was manufactured using the processes of (1) electro-conductive treatment of the surface of a foam resin having a three-dimensional network structure, (2) deposition of a predetermined quantity of NiCo on the resin's surface by electro-plating, (3) decomposition and removal of the resin by heating the NiCo-plated resin to 800°C, and (4) heat-treatment of the NiCo film in a reducing gas atmosphere maintained at approximately 1000°C. Subsequently, the manufactured NiCo Celmet was passed through a roll press to adjust the thickness to 0.5 mm. The major physical properties of the produced NiCo Celmet are shown in Table 2.

Table 2. Major physical properties of NiCo Celmet

Item	Physical property
Thickness (mm)	0.5
Mean pore diameter (μm)	450-850

3-2 Electrochemical measurement

The electrical resistance of the prepared NiCo Celmet was measured by sandwiching it on both sides by a flat SUS 304 plate jig with a platinum mesh and platinum wire (see Fig. 2). Further, to simulate the use of NiCo Celmet in an SOFC, an SUS block was placed on the evaluation jig to apply a load of 0.12 MPa onto NiCo Celmet. The electrical resistance was measured by a four-terminal method at 800°C in a thermostatic oven.

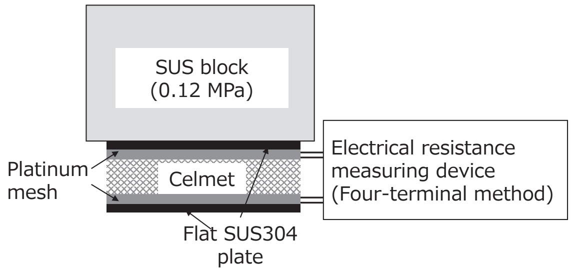

Fig. 2. Schematic illustration of electrical resistance measurement method

3-3 Pressure loss measurement method

As a gas diffusivity index of NiCo Celmet, its pressure loss was measured. For the measurement, a Celmet sheet was machined to a predetermined shape, fixed to an SUS304 jig, and heated to 800°C in a high-temperature oven. In the heating process, a predetermined volume of air was injected from the Jig's air inlet to outlet through the Celmet. The pressure difference between the inlet and outlet was defined as the pressure loss.

3-4 Compressive strength measurement method

NiCo Celmet embrittles when oxidized. To allow this alloy to be used in SOFCs, it must be capable of withstanding the load that is ordinarily produced inside them. To check the compressive strength of this alloy, we prepared a 25 mm square test piece and measured its compressive strength by compressing it at 3 μm/s.

3-5 SOFC performance evaluation method

To evaluate the performance of an SOFC comprising a NiCo Celmet component, we combined a commercially available φ120 mm YSZ*2 cell made by Elcogen Co. with a Ni felt anode current collector and a NiCo Celmet cathode current collector. For comparison, we also fabricated a single cell stack*3 using a stainless steel mesh. The output power performance of the above two samples at 750°C were evaluated. Groove-less interconnectors were combined with the NiCo Celmet current collector, while interconnectors with gas flow channel were combined with the single stainless-steel-mesh stack.

4. Experimental Results

4-1 Electrical resistance measurement result

To apply newly developed NiCo Celmet to cathode current collector, this alloy should maintain a high electric conductivity over a long period in a high-temperature oxidizing atmosphere. It has been known that NiCo alloys, when oxidized, form spinel oxides*4 whose structural formula is expressed as A_2BO_4.[7]

This formula tells us that, when the composition of a NiCo alloy changes, the elements corresponding to the symbols A and B change accordingly. The electric conductivity of these alloys is considered to be significantly affected by their composition. To clarify the dependence of the electrical conductivity of these alloys on their composition, the electrical resistance of alloys of different Co concentrations was measured after heat treatment at 800°C for 1000 hours in an air atmosphere. As a result, the electrical resistance began to decrease sharply when the Co concentration was 30 wt% or more, and the decrease peaked when the concentration was around 50 wt%. As a whole, NiCo alloys showed a tendency to decline in electrical resistance as their Co concentration increased (see Fig. 3). For NiCo Celmet to be usable in SOFCs, the content of relatively expensive Co should be as low as possible. A Co concentration of 30 to 40 wt% was concluded to be optimal.

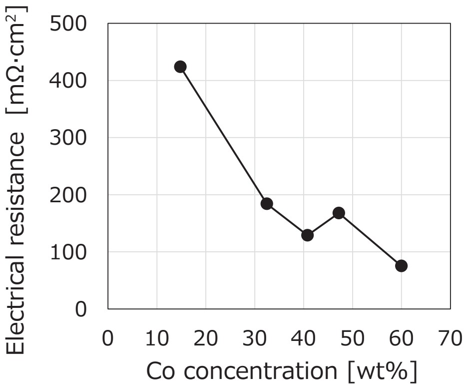

Fig. 3. Correlation between Co concentration and electrical resistance (Electrical resistance after heat treatment at 800°C for 1000 h)

Figure 4 shows the change with time of the electrical resistance of NiCo Celmet with a Co concentration of around 35 wt%. During the initial several tens of hours, the electrical resistance of this alloy increased, probably due to its transformation from a metal to an oxide. After that, the alloy maintained a stable electrical resistance at an almost constant level, demonstrating that it would ensure a long-lasting stable performance when used in SOFCs. For the evaluation of various other physical properties, the Co concentration of NiCo Celmet was controlled to approximately 35 wt%.

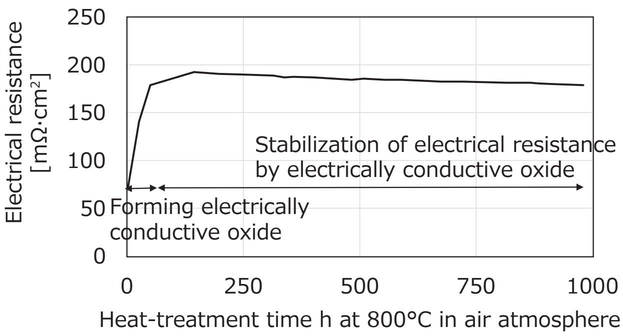

Fig. 4. Long-term measurement result for the electrical resistance of NiCo Celmet

4-2 Pressure loss evaluation results

The correlation between the pore diameter*[5] and the pressure loss of NiCo Celmet was tested. As a result, the pressure loss was found to decrease as the pore diameter increased. In particular, increasing the pore diameter from 450 to 850 μm resulted in a 20% or more decrease in pressure loss.

4-3 Compressive strength test results

Inside an SOFC, a load is applied in the thickness direction to ensure adequate strength of contact between the current collectors and interconnectors and between the current collectors and the cell. To apply NiCo Celmet to cathode current collectors, it is crucial that this alloy ensures the required durability even after it is oxidized. To check the durability of this alloy, we carried out a compressive load test. In the test, the test specimen was fully oxidized by heat-treating it at 800°C for 300 h in an air atmosphere. The measured breaking strength of this alloy exceeded 0.6 MPa as shown in Fig. 5, verifying that this alloy would sufficiently withstand the standard SOFC internal pressure of 0.1 to 0.2 MPa.

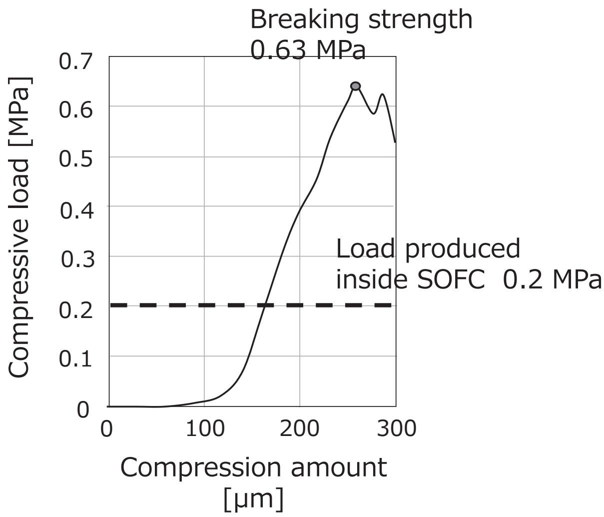

Fig. 5. Breaking strength test for oxidized NiCo Celmet

4-4 Evaluation of SOFC single cell stack

The IV characteristics and output power performance of an SOFC comprising a NiCo cathode current collector were evaluated. For the evaluation, groove-less flat stainless steel plates were used as interconnectors. For the gas utilization ratio,*[6] the fuel and air utilization ratios were adjusted to 60% and 30%, respectively, at a current density of 0.3 A/cm^2. As a result, the test SOFC demonstrated a performance equal to or better than that of a conventional SOFC comprising a combination of a conventional stainless steel mesh and interconnectors with gas flow channel

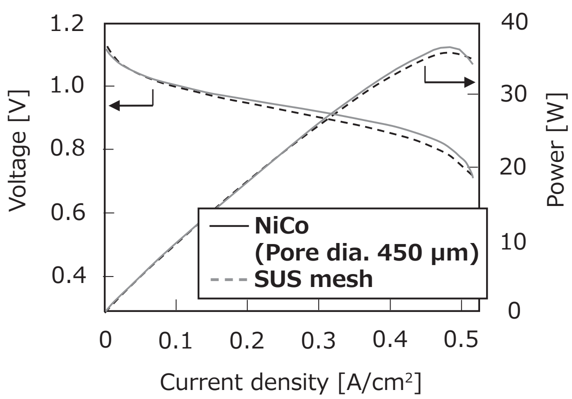

Fig. 6. Evaluation of electricity generation by SOFC in which NiCo Celmet is used

(see Fig. 6). The above result verified that NiCo Celmet is a promising current collector material for SOFCs, which can reduce the high interconnector grooving cost.

The gas diffusivity of NiCo Celmet as a cathode current collector was additionally evaluated. In particular, the test SOFC was operated by reducing the air gas flow rate so that the air utilization ratio would become 100% at a current density of 0.3 A/cm^2.

The result revealed that increasing the pore diameter of NiCo Celmet from 450 to 850 µm is effective in increasing the output power of the SOFC at a high current density or a high air utilization ratio (see Fig. 7). Since the pressure loss of NiCo Celmet tends to decrease as its pore diameter increases as described in Section 4-2, an increase in the pore diameter to 850 µm is considered to have improved the gas diffusivity of this alloy and increased the output power of the SOFC.

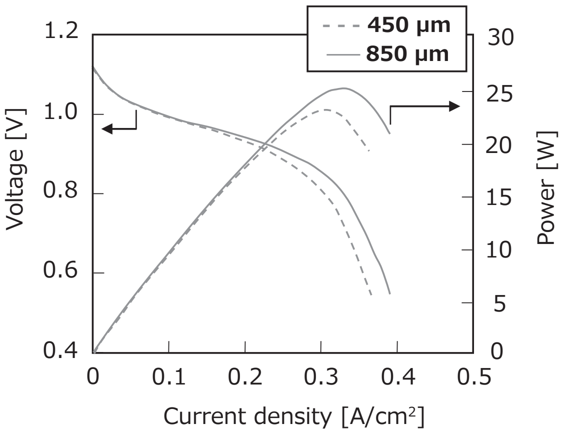

Fig. 7. Effect of the pore diameter of NiCo Celmet on electricity generation capacity

5. Conclusions

As a promising material for the cathode current collectors of high-temperature SOFCs that is required to be highly heat resistant, we developed NiCo Celmet and measured its physical properties to check whether or not it could be used in SOFCs. After confirming from the measurement results that NiCo Celmet with a Co concentration of 30 to 40 wt% is optimal for SOFCs in terms of cost and electrical resistance, we evaluated the pressure loss of NiCo Celmet and tested its breaking strength. The results verified the usability of this alloy in SOFCs. Further, we fabricated a prototype SOFC comprising a NiCo cathode current collector with a Co concentration of 35 wt%, and evaluated the electricity generation capacity of the prototype. As a result, it was confirmed that an SOFC comprising a NiCo cathode current collector exhibits a high output power performance even when the interconnectors don't have gas flow channel. The dependence of SOFC's output power on the pore diameter of NiCo Celmet was also tested. The test results showed that the pressure loss of NiCo Celmet tends to decline as its pore diameter increases and, as a result, the SOFC increases its output power. As described above, the use of the newly developed NiCo Celmet as the cathode current collectors eliminates the need for grooving the interconnectors, which is a factor increasing the cost of SOFCs, thereby contributing to stack cost reduction.

Technical Terms

∗1 Interconnector: A wall used to prevent the hydrogen and air supplied to a fuel cell from mixing with each other. The interconnector is usually grooved to evenly diffuse the hydrogen and oxygen.

∗2 YSZ: An abbreviation for yttria-stabilized zirconium, a material used for the solid electrolyte of SOFCs. The phase transition of zirconia at high temperatures is suppressed by adding yttrium oxide.

∗3 Stack: A structure in which a cell, which is an electricity generation body, is sandwiched between a cathode current collector, an anodic current collector, and interconnectors. A typical SOFC comprises laminated stacks. A stack constructed of a single cell to evaluate the basic performance of the stack is called a single cell stack.

∗4 Spinel oxides: A crystalline structure that is usually expressed by the structural formula A_2BO_4. The spinel structure has the property of being electrically conductive at high temperatures.

∗5 Pore diameter: The mean distance between the frames of Celmet.

∗6 Gas utilization ratio: An indicator of how effectively the hydrogen or air supplied to a fuel cell is consumed for electricity generation. The fuel cell consumes a large volume of the gas when generating a high electric current, and increases the gas utilization ratio.

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