JTTEE5 9:360-363

Development of Metallic Substrate Supported Planar Solid Oxide Fuel Cells Fabricated by Atmospheric Plasma Spraying

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(Submitted 23 December 1999; in revised form 7 April 2000)

A planar solid oxide fuel cell (SOFC) consisting of a cell supported with a porous metallic substrate and a metallic separator has been developed. In the fabrication of the cell, anodes and electrolytes were formed on sintered Ni-felt substrates using flame spraying (FS) and atmospheric plasma spraying (APS), respectively. The APS is also applied to form (LaSr)MnO_3 protective coatings on the metallic separators. With these metallic cells and separators, a 3 kW-class stack, which consisted of 30 cells (15-cell block × 2) was constructed and operated. The active electrode area of the cell was 600 cm^2. The stack generated 3.3 kW at 970 °C when the current density was 0.3 Acm^{-2} and the fuel utilization 50%. It did not show any degradation for the initial 2100 h, but a few cells in the lower 15-cell block became unstable after 2100 h. On the other hand, the upper 15-cell block was stably operated for 3200 h.

Keywords APS, planar SOFC, protective coating, metallic substrate, seal-less structure

1. Introduction

Solid oxide fuel cells (SOFCs) are promising candidates for future generation systems on account of their high energy conversion efficiency and low enviromental hazards. Many investigations have been carried out with regard to the choice of materials and processing techniques. However, there are few processes that can be used to fabricate high performance cells quickly and inexpensively. Plasma spraying is a promising candidate for such a process.

A planar SOFC consisting of a cell supported with a porous metallic substrate and a metallic separator was developed. The principal advantage of this construction is to allow enlarging the cell area and improving its mechanical properties. Flame spraying and atmospheric plasma spraying can be used to form electrodes and electrolytes of such cells and to form the protective coating of the metallic separators.

Another characteristic of the design is to adopt a *seal-less* disk configuration. Fuel gas and oxidant gas are fed to each separator independently through tubes from outside. The gases fed inside blow out from the center of the separator and spread to the electrodes' surface. In this way, there is no need to consider unreliable seals.

This paper presents the fabrication procedure of the cells and separators and the test results of a 3 kW-class stack constructed using these technologies.

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2. Fabrication Process of Cells

In the fabrication of cells, Ni felts were used as porous substrates. Three sheets of Ni felts were pressed together and sintered in vacuum. Then, anodes and electrolytes were formed on the Ni-felt substrates using FS and APS, respectively. Each gun was fixed on the top of the robot, and the films were formed by the guns traversing repeatedly above the substrates at a specific speed. The spray conditions and the gas permeability of the anode and the electrolyte are given in Table 1.

After forming eletrolytes by APS, Y_2O_3-doped CeO_2 (YDC) thin layers were applied using a dip coating method on the surface of the electrolyte layers in order to enhance the catalytic activity of cathodes. Then, cathodes were coated onto them with a slurry coating method and were *in-situ* sintered during operation of the cells. Figure 1 shows the appearance of the 600 cm^2 Ni-felt substrate supported cell, and Fig. 2 shows the scanning electron microscope (SEM) image of the cell.

3. Protective Coatings for Metallic Separators

3.1 Advantages of Metallic Separators

$LaCrO_3$ is often used as the material for a ceramic separator, because it is stable in both fuel and air atmospheres ($Po_2 = 10^{-1}$ to 10^{-18}) and also because its thermal expansion coefficient matches that of the electrolyte (Y_2O_3-stabilized ZrO_2). On the other hand, some investigations have been carried out with metallic separators,[1,2,3] because they are inexpensive and have higher thermal and electrical conductivities than ceramic separators. However, if one wants to use metal alloys as separators of SOFCs, then a suitable coating is needed to reduce the growth rate of scales caused by oxidation and to keep electrical resistance low and stable. In our stack, Ni22Cr superalloy was used as a metallic separator material and (LaSr)MnO_3 protective coatings were applied on the cathode side surface of the separators using APS.[4]

Table 1 Spray conditions of anodes and electrolytes

(a) Anodes	
Fabrication method	FS
Powder—material	NiO—8 mol pct YSZ
—particle size	45 to 106 μm
Flame gas	$C_2H_2 + O_2$
Spray distance	100 mm
Gun traverse speed	500 mm s^{-1}
Gas permeability	8.34×10^{-2} cm^4 g^{-1} s^{-1}
(b) Electrolytes	
Fabrication method	APS
Powder—material	8 mol pct YSZ
—particle size	5 to 25 μm
Plasma gas	$Ar + H_2 + N_2$
DC input power	40 kW
Spray distance	50 mm
Gun traverse speed	1000 mm s^{-1}
Gas permeability	7.79×10^{-8} cm^4 g^{-1} s^{-1}

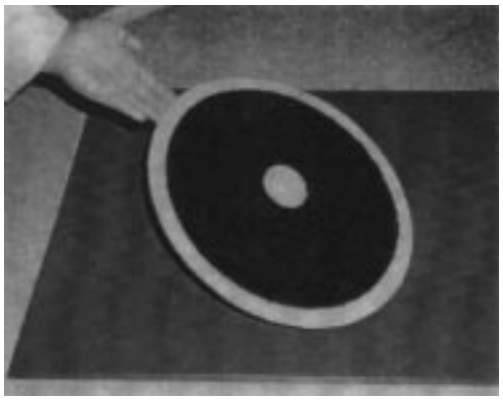

Fig. 1 Appearance of a 600 cm^2 Ni-felt substrate supported cell

3.2 Long-Term Stability of Metallic Separators

To examine the long-term stability of the metallic separators, preliminary experiments were carried out as follows. $(LaSr)MnO_3$ was sprayed on both sides of 25×25 mm^2 NiCr superalloy samples using Ar/N_2 plasma at an input power of 35 kW. The thickness of the film was 150 μm. The plasma-sprayed samples were sandwiched between Pt sheets, and electrical resistance was measured using an AC four-probe technique at temperatures of 950 and 1000 °C for several thousand hours in air.

Figure 3 shows the resistance change of the $(LaSr)MnO_3$-coated Ni22Cr superalloy with time at 950 °C and 1000 °C in air. It can be seen that the resistance of the Ni22Cr superalloy remains lower than 25×10^{-2} Ω cm^2 for about 3000 h, although a gradual increase in resistance is observed. Thus, the voltage drop caused by oxidation of a metallic separator remains less than 7.5×10^{-3} V at the current density of 0.3 A cm^{-2} in this term. Figure 4 presents an SEM image of another sample of $(LaSr)MnO_3$-coated Ni22Cr after aging at 1000 °C in air for 10,000 h. The coating shows good adherence to the metal in spite of mismatching of its thermal expansion coefficient ($(LaSr)MnO_3$: 12×10^{-6} K^{-1}, and Ni22Cr superalloy: 16×10^{-6} K^{-1}). However, chromia scales can be seen between the coating and the metal

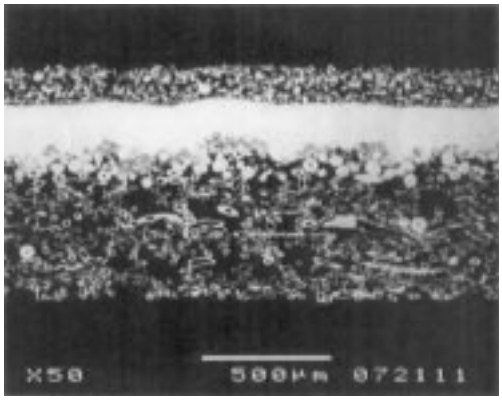

Fig. 2 Cross-sectional SEM image of a cell

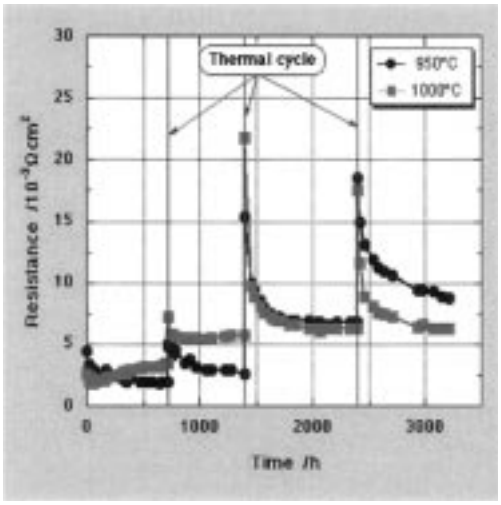

Fig. 3 Resistance change of the $(LaSr)MnO_3$-coated Ni22Cr superalloy with time

underneath because some oxygen and/or oxygen ions can permeate through the protective coating. It is considered that the increase of electrical resistance is caused by the growth of these scales. These experimental results suggest that the electrical resistance of metallic separators can be kept low and stable for at least 3000 h in SOFC operating conditions by the application of $(LaSr)MnO_3$ protective coatings.

4. 30-Cell Stack Test

4.1 Stack Design

A stack with a seal-less disk structure, which does not use any sealing materials, was devised (Fig. 5). In this structure, gases are supplied from gas distributors to each cell independently, thereby eliminating the need of sealings.

Although they are not shown in the figure, air and fuel gas flow paths were formed between the cells and separators. $(LaSr)MnO_3$ sticks were arranged radially for air flow paths and Fe-Cr alloy radial ribs were used for fuel gas flow paths.

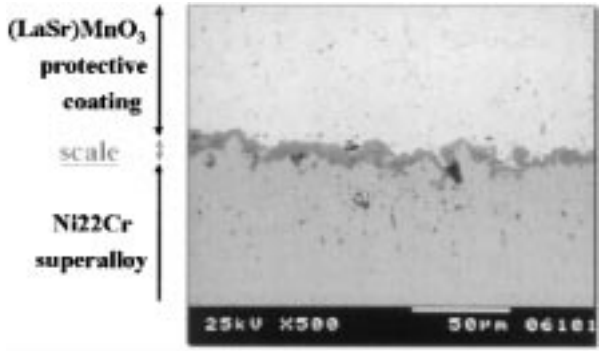

Fig. 4 Cross-sectional SEM image of a (LaSr)MnO_3 sprayed NiCr separator after keeping at 1000 °C for 10,000 h in air

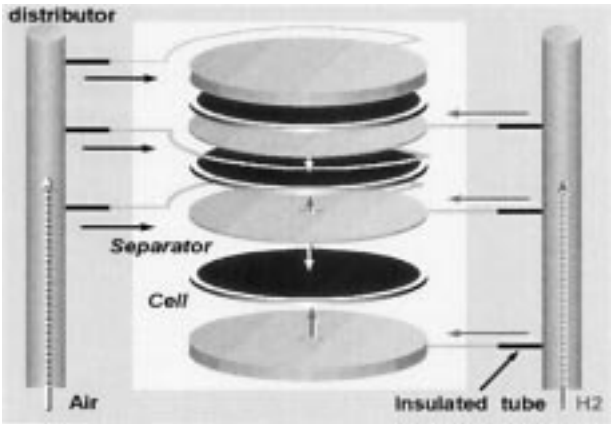

Fig. 5 Schematic diagram of the *seal-less* SOFC stack

Fig. 6 Overview of the seal-less 30-cell stack

A 3 kW-class stack with the seal-less structure was constructed using the metallic cells and separators. The stack consisted of 30 cells, which were divided in two blocks: an upper 15-cell block and a lower 15-cell block. The diameter of each cell and separator was 340 mm and the active electrode area of

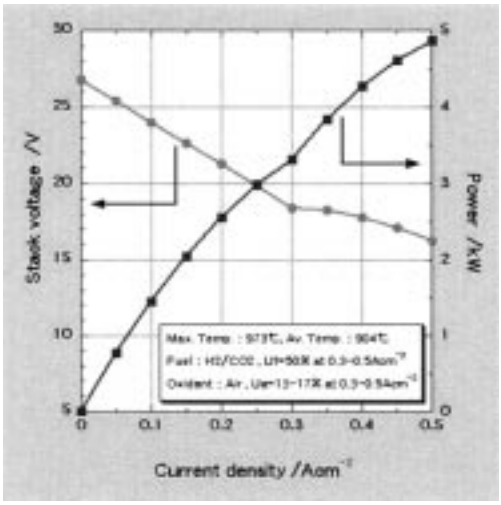

Fig. 7 I—V and I—P characteristics of the 30-cell stack

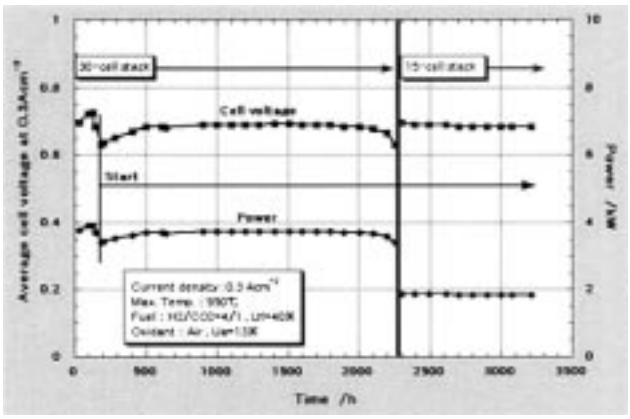

Fig. 8 The stack voltege change with time

the cell was 600 cm^2. The fuel was a hydrogen/carbon dioxide mixture (the ratio of 4 to 1) and the oxidant was air. The overview of the 30-cell stack is shown in Fig. 6.

4.2 Results of the 3000 h Test

Figure 7 shows the I-V and I-P characteristics of the 30-cell stack after an initial 300 h of operation. At 970 °C and a fuel utilization (U_f) of 50%, the stack generated 3.3 kW when the current density was 0.3 A cm^{-2}. The output power reached almost 5 kW when the current density was increased to 0.5 A cm^{-2}.

Figure 8 shows the stack voltage change with time. The life test was carried out for 3200 h at the current density of 0.3 A cm^{-2} and at U_f of 40%. The stack did not show any degradation during the initial 2100 h, but a few cells in the lower 15-cell block became unstable after 2100 h. Therefore, only the upper 15-cell block was operated for 3200 h. The upper block showed good stability during the life test.

The I-V and U_f-V characteristics of the upper 15-cell block were measured after 3200 h operation. The results are shown in Fig. 9 and 10, respectively, and are compared with the results from the initial stage.

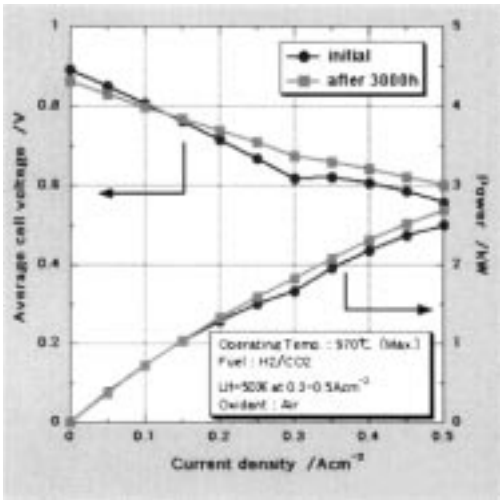

Fig. 9 I-V characteristics of upper 15-cell block at initial stage and after 3200 h operation

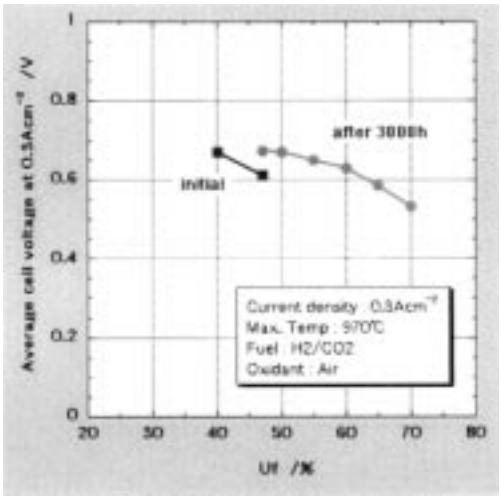

Fig. 10 U_f-V characteristics of upper 15-cell block at initial stage and after 3000 h (0.3 A cm^{-2})

As shown in the figures, the I-V and U_f-V characteristics after 3200 h operation were remarkably improved in comparison with those of the initial stage. At the initial stage, the stack voltage became unstable when it was operated with fuel utilization higher than 50%. However, it was stable even with 70% fuel utilization after 3200 h operation. The reasons for this improvement are considered as follows. The catalytic activity of cathodes was gradually enhanced because cathodes and YDC layers were *in-situ* sintered during the operation. In addition, the cross-leakage of air and/or fuel gases through electrolytes was reduced during the operation. That reduction was caused by the electrolyte films sintering at operating temperature. These phenomena were found by observing the cells after 3200 h operation with a SEM.

After all the tests were finished, the stack was dismantled and the cause of the instability of the lower block was investigated. As a result, deposits were observed on the cathode and they choked the air flow path, which seemed to cause degradation. From the fluorescent x-ray analysis of deposits and the cross-sectional SEM obsevations of degradated cells, the deposits was determined to be a mixture of ZrO_2 and Fe_2O_3. The Fe in Fe_2O_3 originated from the Fe-Cr alloy, which was used for radial ribs for the fuel gas flow paths. These deposits were caused by the local temperature increase that resulted from microcracks of electrolyte films. It can be suspected that generation of microcracks is ascribed to concentrated loads at particular sites.

5. Conclusions

A *seal-less* planar SOFC consisting of a cell supported with a porous metallic substrate and a metallic separetor has been developed. An anode and an electrolyte are fabricated using FS and APS, respectively, and APS is also used to form a protective coating of the separator. Long-term stability of the metallic separator was examined, and it was shown that the electrical resistance of the separator can be kept lower than $25 \times 10^{-3}\ \Omega\ cm^2$ for at least 3000 h by the application of $(LaSr)MnO_3$ protective coatings. A 3 kW-class stack (the active electrode area of each cell was 600 cm^2) was constructed using those technologies, and it generated 3.3 kW at 970 °C when the current density was 0.3 A cm^{-2} and the fuel utilization 50%. Also, the upper 15-cell block was stably operated for 3200 h.

From the results mentioned above, APS proved to be a promising technology to fabricate SOFCs.

Acknowledgments

This research was carried out as an R & D program of the New Energy and Industrial Technology Development Organization (NEDO) under the New Sunshine Project of the Agency of Industrial Science and Technology, MITI.

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