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

Shunji Takenoiri, Naruaki Kadokawa, and Kazuo Koseki

(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)MnO₃ 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 cm². The stack generated 3.3 kW at 970 °C when the current density was 0.3 A cm⁻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.

1. Introduction

Solid oxide fuel cells (SOFCs) are promising candidates for future generation systems on account of their high energy conversion efficiency and low environmental 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.

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 electrolytes by APS, Y₂O₃-doped CeO₂ (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 cm² 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

LaCrO₃ is often used as the material for a ceramic separator, because it is stable in both fuel and air atmospheres (P₂O₅ = 10⁻⁶ to 10⁻¹⁶) and also because its thermal expansion coefficient matches that of the electrolyte (Y₂O₃-stabilized ZrO₂). On the other hand, some investigations have been carried out with metallic separators,[1-3] 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)MnO₃ protective coatings were applied on the cathode side surface of the separators using APS.[4]
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)MnO₃ was sprayed on both sides of 25 × 25 mm² NiCr superalloy samples using Ar/N₂ 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)MnO₃-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 cm² 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. 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)MnO₃-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 cm² 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)MnO₃-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)MnO₃; 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 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)MnO₃ 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)MnO₃ sticks were arranged radially for air flow paths and Fe-Cr alloy radial ribs were used for fuel gas flow paths.