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Application of Plasma Spraying to Tubular-Type Solid Oxide Fuel Cells Production

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Solid oxide fuel cells (SOFCs) feature the highest energy conversion efficiency of any type of fuel cell yet developed. This article describes SOFC production by means of plasma spraying and presents the resulting SOFC performance. The application of plasma spraying to tubular SOFC production has realized good performance on the order of 40 W or greater in terms of electricity generation per cell stack under standard conditions of 200 mA/cm^2.

Keywords cell potential, fabrication, SOFC, YSZ

1. Introduction

Electric power generation is continuously demanding increased conversion efficiencies. Decreased emissions of carbon dioxide are also being called for in order to protect the earth's environment, and the importance of highly efficient generation systems is greater than ever. Fuel cells directly convert the chemical potential of fossil fuels to electricity, and their high conversion efficiencies make them candidates for next generation power systems. At present, SOFCs feature the highest conversion efficiency of any type of fuel cell yet developed. A SOFC structure consists of the lamination of functional ceramic films, and plasma spraying is a suitable production method.[1] This article describes SOFC production by means of plasma spraying and presents the resulting SOFC performance. The authors are now changing the production method from plasma spraying to cosintering, and the application of cosintering for SOFC production is also briefly described.

2. Principle and Features of SOFCs

Figure 1 shows the SOFC operating principles. The basic element consists of solid oxide electrolyte layer in contact with a porous air electrode and fuel electrode on either side. The fuel and oxidant gases flow past the reverse sides of the air electrode and fuel electrode, respectively, and generate electrical energy by means of the electrochemical oxidation of fuel and the electrochemical reduction of oxygen. The transport rate of oxygen ions in the solid oxide electrolyte is adequate for practical applications at a high temperature of about 1273 K using presently available electrolyte materials and designs.

The cell potential is decreased from the equilibrium value of 1 V at 1273 K because of irreversible losses in practical fuel cell operation. The losses originate primarily from three sources: (1) ohmic polarization, (2) concentration polarization, and (3) activation polarization. These losses result in a cell voltage being less than the equilibrium potential. Materials and material processing play a key role in reducing these losses and thereby improving cell performance.

Table 1 shows the main SOFC components, the required SOFC characteristics, and examples of applied materials. Since the solid oxide electrolyte is lower in conductivity than the other component materials, the increase in conductivity and reduction in resistance achieved by reducing the layer thickness have a substantial effect on the improvement of cell performance. Yttria-stabilized zirconia (YSZ) is usually utilized as a solid oxide electrolyte, because of its high ionic conductivity and easy availability. The air electrode material used here is lanthanum composite oxide (for example, $LaCoO_3$) having a perovskite structure, because of its stability and high conductivity in a high temperature-oxidizing atmosphere.

As metallic material for the fuel electrode in a reducing atmosphere, a Ni alloy cermet with YSZ is used. The electrode structure is required to be porous in order to provide an extensive electrode/electrolyte interfacial region for the electrochemical reaction and to transport the gaseous reactants.

In order to equalize the thermal expansion with that of the cell components, especially the YSZ electrolyte, a porous material of calcia-stabilized zirconia (CSZ) is used as a support tube. Although plasma spraying has been considered inappropriate for producing a dense electrolyte coating, such a coating with a quality corresponding to a sintered layer has recently become possible to produce, and a relatively high level of practicality has also been obtained.

The SOFC power generator based on the aforementioned principles has many favorable characteristics as an energy conversion system, including the following: (1) high-energy conversion efficiency (Fig. 2), (2) flexibility of fuel use, (3) cogeneration capability, and (4) very low chemical and noise pollution.

3. Application of Plasma Spraying to Cell Production

The SOFC structures can be divided into two types, tubular and planar, and both types have been developed for stationary power generation, on-site power generation, and mobile power

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sources. Tubular-type SOFCs have advanced further to near practical use as compared to planar ones.[2,3,4]

Plasma spraying has been applied to the production of tubular-type SOFCs, and Fig. 3 shows pictures of such cells. Multiple circular-striped cells are formed on the surface of a support tube of about 20 mm diameter (hereinafter called cell stack). Figure 4 shows the structure of the transaxial section of a cell stack. On the support tube, multiple ring-shaped cell structures are deposited, each comprising the fuel electrode, the electrolyte, and the air electrode. The electrodes of adjacent cells are connected by means of an interconnecting coating. Since the interconnector material is a cermet of a Ni alloy and Al_2O_3, the Al_2O_3 protective coating for resistance to oxidation is formed on the interconnector coating. The electrolyte coating, which requires especially high density, is deposited by low pressure plasma spraying. The fuel electrode coating made of cermet, the interconnector coating, and the ceramic protective coating are all deposited by atmospheric plasma spraying.

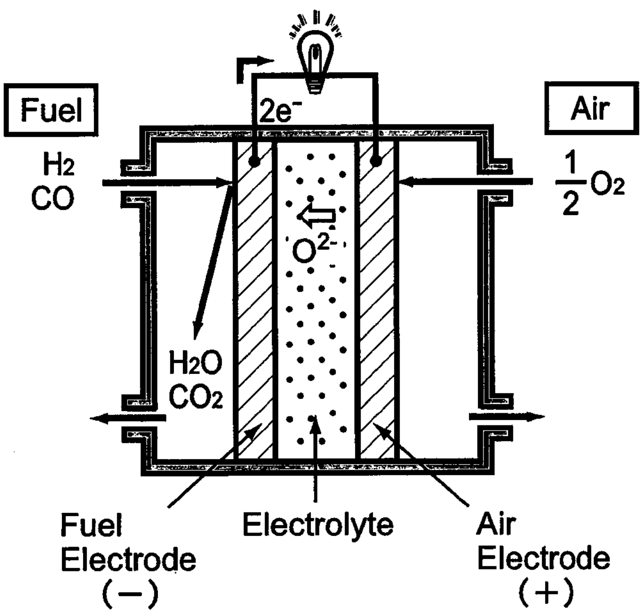

Fig. 1 Principle of SOFC

Figure 5 shows a comparison of the coefficient of gas permeability for the YSZ coating when deposited by low pressure plasma spraying (LPS) and by atmospheric plasma spraying (APS), including changing of the spray particle diameters. The gas permeability of the YSZ coating deposited by LPS is lower in value by one order of magnitude compared to that of the coating deposited by APS, and it can be improved further by reducing the spray particle diameter. The LPS type YSZ coating has the advantage of being dense in structure and high in strength, making LPS indispensable for cell production. The sectional structure of a cell portion with coatings formed by plasma spraying is shown in Fig. 6.

Each of the component coatings is adequately formed on the support tube, and the adhesion between them is reliable. For the interconnector coating, the thermal expansion coefficient in relation with the support tube must be reduced, as well as the thermal stress, which occurs in the thermal cycle while the SOFC is in operation. Therefore, the interconnector is a composite coating of ceramic and metallic materials, which is formed by plasma spraying.

Figure 7 shows the relation between the mixing ratio of Al_2O_3 to Ni alloy and the resistivity of the coating. Even when the mix-

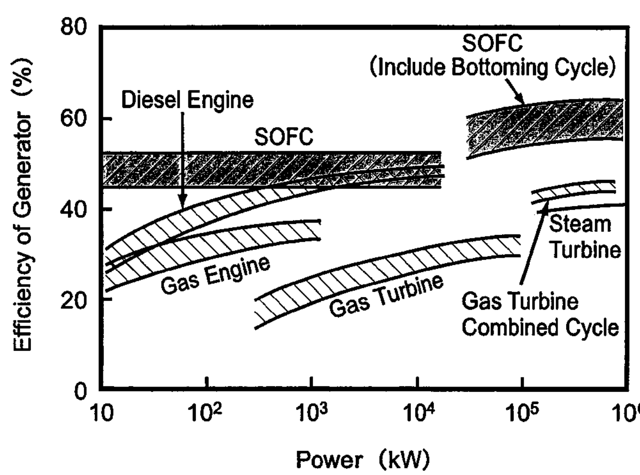

Fig. 2 Efficiency of generators

Table 1 Components of SOFC and required characteristics

Component	Characteristics	Structure	Materials
Air electrode	• High ionic and electronic conductivity • Stable in high-temperature oxidizing atmosphere • Thermal expansion matching with other components	Porous	$LaCoO_3$ $LaMnO_3$ $LaSrMnO_3$
Fuel electrode	• High electronic conductivity • Stable in high temperature • Thermal expansion matching with other components	Porous	Ni Ni-ZrO_2 Ni-Al_2O_3
Electrolyte	• High ionic conductivity and high ionic transport • Stable in high temperature • No gas permeability	Dense	YSZ
Interconnector	• High electronic conductivity • No gas permeability • Stable in high- temperature oxidizing and deoxidizing atmosphere	Dense	Ni alloy-Al2O_3 Ni alloy-CSZ $LaCrO_3$
Support tube	• High gas permeability • Electric insulation • Thermal expansion matching with other components • Low cost	Porous	CSZ

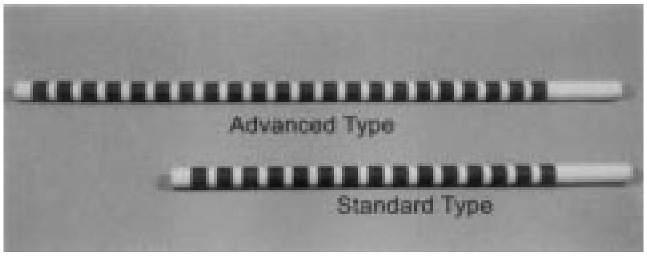

Fig. 3 Appearance of tubular-type SOFC

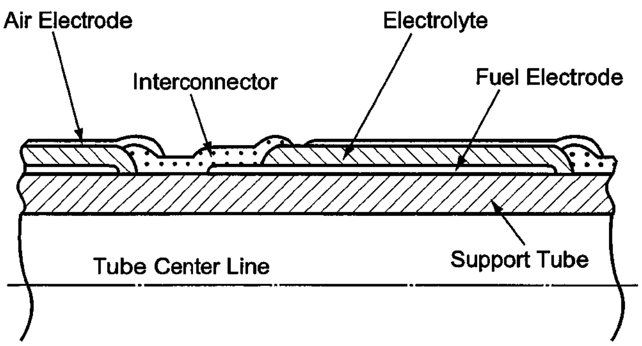

Fig. 4 Tubular cell configuration

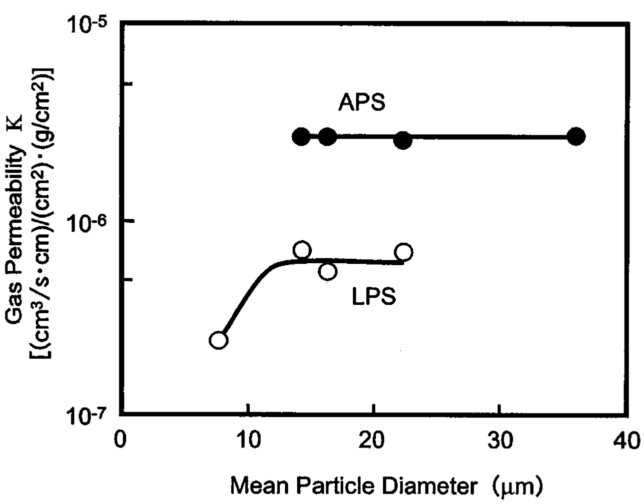

Fig. 5 Effect of particle diameter on gas permeability of YSZ plasma-sprayed coating

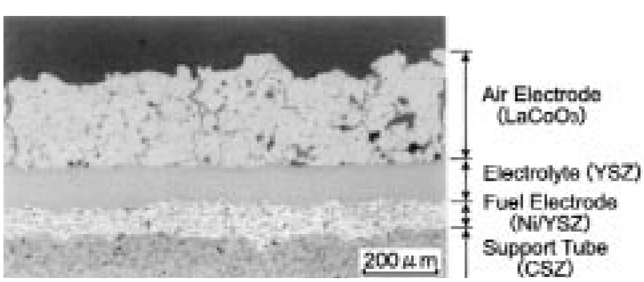

Fig. 6 Microstructure of SOFC formed by plasma spraying

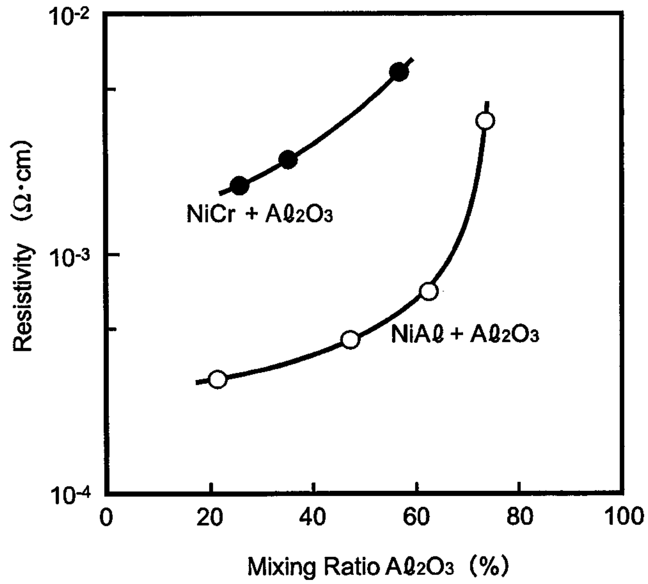

Fig. 7 Effect of mixing ratio of Al_2O_3 on resistivity of Ni alloy-sprayed coating

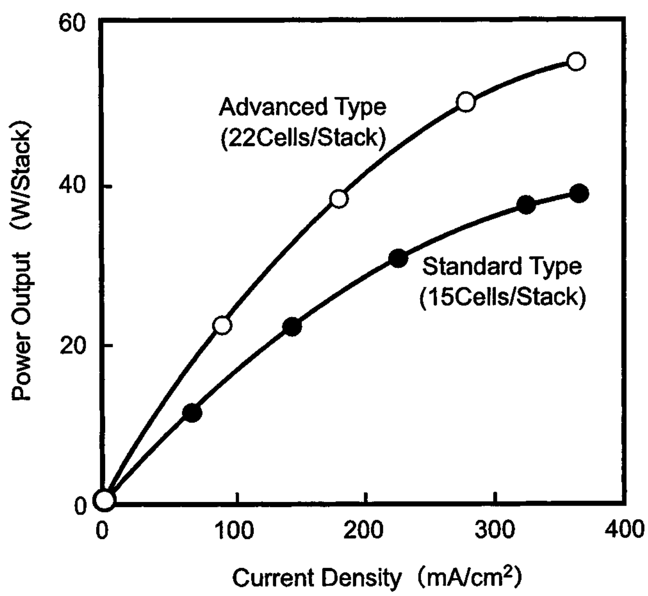

Fig. 8 Example of cell performance

ing ratio of Al_2O_3 is moderately high, a relatively low resistivity is shown.

Since the coefficient of linear thermal expansion is proportional to the mixing ratio of metal to ceramic, control of this ratio allows the achievement of both compatibility between the coefficients of linear expansion and acceptable conductivity. Plasma spraying is suitable for depositing such a coating at a high rate, because it permits deposition of a wide range of material compositions.

Figure 8 shows the performance of cell stacks using the developmental results of the material described above. Under standard conditions of 200 mA/cm², a cell stack consisting of 22 cells in a series has an electricity generation capability of 40 W or more. Cell stacks were used for a pressurized 10 kW class module, which is presented next.

4. Development of Pressurized 10 kW Class Module

The structure of a pressurized 10 kW class module is shown in Fig. 9, with specifications indicated in Table 2. This module consists mainly of four parts: the fuel plenum, the spent fuel plenum, the reactor chamber, and the air preheater. All these parts are installed in the pressure vessel.

The authors have adopted a suspended stack structure for relaxation of thermal stress and easy stack maintenance. The fuel is fed from the top of the module and introduced to the fuel plenum, distributed to each cell stack through injection tubes, and utilized for the cell reaction. The open end of the cell stack was fixed at the fuel plenum. Fuel was fed from this open end to the cell stack, while air was supplied from the bottom of the module to the reaction chamber. The spent fuel is exhausted through the spent fuel plenum.

The performance curve of the pressurized 10 kW class module is shown in Fig. 10. The maximum power output was 21 kW and the efficiency was 35% at 75% fuel utilization without a fuel recycle system. Module power output was stable over all operation conditions. The deterioration rate is about 1 to 2% per 1000 h. Figure 11 shows the system flow diagram of the pressurized 10 kW class module.

Reduction of production cost is the remaining hurdle that must be cleared in order to bring SOFCs to the market. The following measures are considered to be effective in reducing SOFC (plasma spraying) production cases.[5]

- Improvement of the deposition efficiency of sprayed material.
- Development of automated production equipment (including automatic masking).
- However, given the reasons presented below, it was decided that fewer barriers to practical use would be encountered if the SOFC production method were changed from plasma spraying to cosintering.
- High raw material yield of cosintering as compared with plasma spraying.
- Lower equipment cost for cosintering as compared with plasma spraying.

Table 2 Specifications of pressurized 10 kW class module

Power output	150 kW DC (nominal) 200 kW DC (maximum)
Operation voltage	250 V
Operation current	57.6 A (200 mA/cm²)
Stack type	Advanced type
Number of stacks	414
Operation temperature	900 °C
Operation pressure	0.59 Mpa (5 atg)

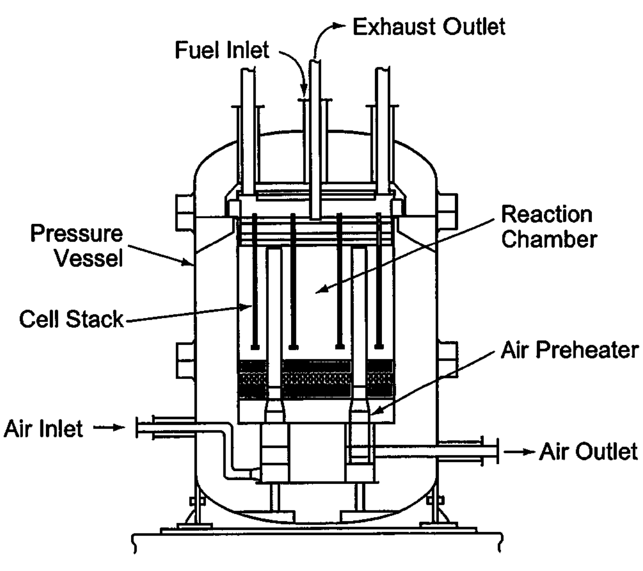

Fig. 9 Structure of pressurized 10 kW class module

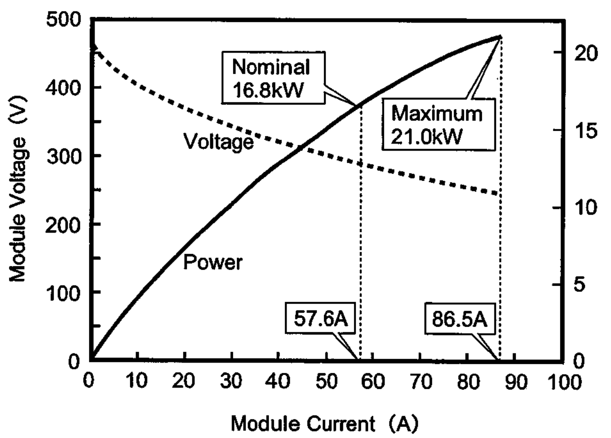

Fig. 10 Performance curve of pressurized 10 kW class module

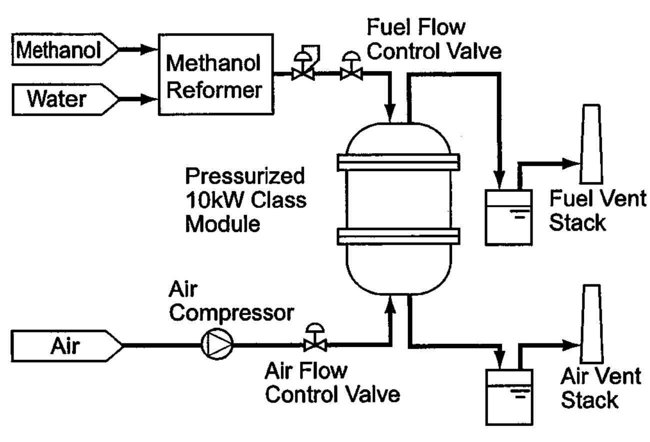

Fig. 11 System flow diagram of pressurized 10 kW class module

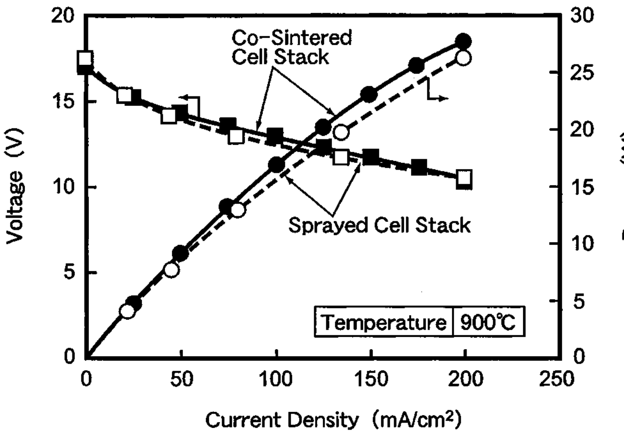

Fig. 12 Example of cosintered cell stack performance

The performance of a cosintered cell stack is shown in Fig. 12, where it is also compared with that of the plasma-sprayed cell stack. It can be seen that the performance is the same for both cell stacks. The endurance performance of a 1 kW module using cosintered cell stacks is shown in Fig. 13. This module has successfully operated for 2000 h, including three thermal cycles. Details of procedures relating to cosintered cell stacks are available elsewhere.[6]

5. Conclusions

The application of plasma spraying to tubular SOFC production has resulted in cells with good performance, on the order of 40 W or higher, in terms of electricity generation per cell stack under standard conditions of 200 mA/cm^2. This achievement has been made possible by the improvement of plasma spraying technology for higher density electrolyte deposition, by better adhesion between cell components, and by improved cell configuration. A pressurized 10 kW class module consisting of 414 cell stacks was successfully operated.

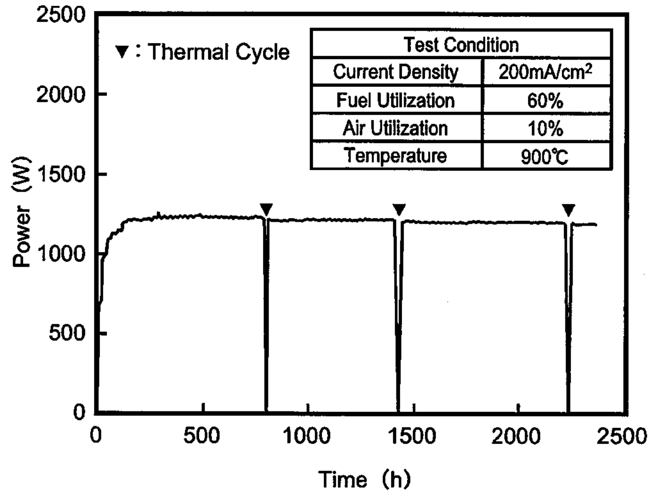

Fig. 13 Endurance test of 1 kW module by cosintered cell stack

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