A STUDY OF ANODE MATERIALS AND STRUCTURES FOR SOFC

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ABSTRACT

We have been developing SOFC manufacturing techniques that employ self-supporting cathodes and are based on the application of film-forming techniques, such as the plasma spray coating method. We have been investigating film-forming techniques suitable to produce electrolyte films by plasma spray and self-supporting cathodes by extrusion-sintering that are ex of maintaining consistency during thermal expansion with the electrolyte (1-6). This report describes the improvements in anodes that we have achieved in pursuit of higher performance and longer operational life.

INTRODUCTION

For achieving a higher performance and longer operational life in cells, it is important to prevent exfoliation between the electrolyte and the anode. That originates from the heat cycles. As a countermeasure, we propose obtaining matching thermal expansions between the electrolyte and the anode by gradually changing the Ni/YSZ content ratio in the anode in order to vary the coefficient of thermal expansion. In effect, we have successfully developed a technique to implement this by forming films using the plasma spray coating method (Functionally Gradient Material anode: FGM anode). As for any increase in polarization due to sintering and cohesion of Ni particles during the operation, which is the other important issue related to the anode, we have studied the application of a monolayer particle coated powder to the Ni/YSZ electrode obtained by plasma spray coating.

This report mainly deals with the performance of cells consisting of FGM anodes and of cells that are composed of anodes made by the plasma spray coating methods with a monolayer particle coated powder.

EXPERIMENTAL

Improvement of Cell Performance with FGM anodes

In general currently available anodes are made of a cermet, which is obtained by mixing Ni and YSZ at a certain ratio. To improve the performance of anodes, it is desirable that the Ni content be as high as possible, but too high a Ni content makes it impossible to match its thermal expansion to that of the YSZ. FGM solves both of these problems, besides providing excellent cell characteristics for a long period of time. An actual FGM film consists of a film that has a high YSZ content on the
electrolyte side, but whose Ni content increases as it goes farther from the electrolyte along the film thickness. When anodes are made of FGM films, the field of reaction called the 3-layer interface is expected to expand in the direction of the film thickness.

Two types of materials with different ratios of NiO/YSZ were prepared (each one of these materials is a mixture of Ni and YSZ, and termed a composite powder). These material is supplied to a spray gun through two powder feeders designed to control the feed volume of the material, forming a plasma-spray film at any desired ratio. The film produced was observed by EPMA to confirm that it was a film with a gradient of ratios of NiO and YSZ. Also, a heat cycle of room temperature - 1000 degrees C was repeated on the film to evaluate its heat-cycle characteristics and possible exfoliation from the YSZ. Once the absence of exfoliation in the film was confirmed, cells were finally formed and the anode polarization characteristics measured. Fig. 1 illustrates the cell.

Fig. 2 shows a cross-sectional EPMA of FGM anode following the plasma spray coating process. Since the film had been formed at a certain ratio by the plasma spray coating method, it was verified that the contents of Ni and YSZ varied in the direction of the film thickness. Moreover, Fig. 3 represents the results of a cross-sectional SEM observation made after the heat cycle test on the film. This figure confirmed that no exfoliation from the YSZ base material took place even after 20 heat cycles had been repeated on the film. Cells were made using this film. Fig. 4 provides the results of the measurement of variations in the polarization of the anodes. For comparison purposes, the polarization characteristics of the anodes, which have conventionally been employed, are given in Fig. 5. It can be seen that the increase in polarization was less in the FGM anodes as compared to the plasma spray film using a composite powder.

Improvement in Anode by A Monolayer particle Coated Powder

At the working temperature of the SOFC in the neighborhood of 1000 degrees C, Ni is deformed by having toward a smaller specific surface area. However, one of the major factors to prevent cell performance from degrading is to have a large Ni specific surface area and to maintain an ample 3-layer interface. Each individual Ni particle is coated with fine YSZ powder in order to limit the degradation of Ni, thereby preventing the sintering and cohesion of Ni and, therefore, any loss in cell performance.

When this powder is used for the plasma spray coating method, it can be expected to prevent cohesion of Ni during the plasma spray.

In our test, we adopted a dry manufacturing method based on physical techniques from among several available YSZ coating methods. Fig. 6 gives an schematic diagram of the equipment we used and the manufacturing process. This equipment disperses the powders into the gaseous phase and gives each powder mechanical / thermal energy to effectively and repeatedly embed or film the fine powder onto the surface of core powder repeatedly by a rotor which rotates at a very high speed for a very short time.

Materials with the compositions shown in Table 1 were prepared, and the Ni was coated with YSZ by thermal and mechanical techniques. Powder was produced under
the coating conditions of 8,000 rpm, a nitrogen atmosphere, and a processing time of 10 minutes. The obtained powder was subjected to an oxidizing treatment at 700 degrees C, and further transformed into a powder suitable for the plasma spray coating process. The produced material was then sprayed. Conductivity and gas permeability were measured on the films after the plasma spray coating. Cells were made of the film that offers the best characteristics among those produced, and the polarization characteristics of anode were then measured. These cells have the same form as the one adopted in the FGM test.

Fig. 7 depicts a SEM observation of the powder after monolayer particle coated. It can be seen that the YSZ particles are coated on the Ni surface. This powder was first treated by oxidation prior to the plasma spray coating process, and then sprayed at atmospheric pressure to form a film. Also, for comparison purposes, Fig. 8 is a cross-sectional EPMA observation of the plasma spray coating film made of both the composite powder and the monolayer particle coated powder with the same Ni/YSZ ratio. It can be seen in these figures that Ni is dispersed to a greater extent in the film made from the monolayer particle coated powder than in the sprayed film of the composite powder. A cell was made of the former film in the same cell form as that of the FGM anode. Fig. 9 represents the anode polarization characteristics of the cell during power generation. Fig. 5 indicates that the polarization in this cell is lower than that of the anode produced from a composite powder.

Materials with the compositions shown in Table 2 were prepared, and the large size Ni was coated with small size Ni and YSZ using thermal and mechanical techniques. Powder was produced under the coating conditions of 8,000 rpm, a nitrogen atmosphere, and a processing time of 10 minutes. The obtained powder was subjected to oxidizing treatment at 700 degree C. After this powder was coated on the YSZ film by the slurry method, the coated film was dried and sintered. This film was observed using EPMA, and its conductivity measured.

Fig. 10 represents a SEM observation of the powder produced by monolayer particle coated. It can be seen that Ni and YSZ as fine particles are fixed to the Ni surface. Also, an EPMA observation of the film made of this powder by the slurry method is given in Fig. 11. YSZ fixed on the Ni surface was observed. Fig. 12 shows the conductivity, which is expressed in values computed from the porosity with the aim of simulating the conductivity of a dense bulk. The conductivity initially decreases, but remains constant after reaching a certain value.

RESULTS AND DISCUSSION

When anodes are built with the FGM Ni/YSZ, small variations in polarization and longer operational life are expected. Also, when Ni fixation treatment is applied to a powder, the anode is expected to exhibit a higher Ni dispersion, which contributes to the improvement of the characteristics of the anode, with a resultant higher cell performance. While it is highly likely that cells with longer operational life and higher performance will be produced in the future through the proper combination of these two techniques, further studies will have to be dedicated to the manufacture of monolayer particle coated powders. Meanwhile, in order to create films with perfect Ni fixation, it is necessary to use a slurry or other methods, not the plasma spray...
method.

ACKNOWLEDGMENT

This work has been performed as a R&D program of the New Energy and Industrial Technology Development Organization (NEDO) under the New Sunshine Project of Agency of Industrial Science Technology, MITI. We appreciate their advice and support.

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A plane figure

A cross-sectional figure

Electrolyte

**Fig. 1** Illustration of the cell form

**Fig. 2** A cross-sectional EPMA of FGM anode
Fig. 3 A cross-sectional SEM observation made after the heat cycle test.

Fig. 4 The results of the measurement of variations in the polarization of the anodes.

Fig. 5 The polarization characteristics of anodes which have conventionally been employed.
Table 1: To investigate attaining higher dispersion of Ni materials with the compositions

| Material | Ni | YSZ |
|----------|----|-----|
| Particle size | 3-7μm | 0.1μm |
| weight % | 60 | 40 |

Fig. 7 A SEM observation of the powder after monolayer particle coated powder

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Fig. 8 EPMA observations of cross-sectional high dispersion and composite powder with the same Ni/YSZ ratio.

Fig. 9 Measurement of anode polarization characteristics of the cell in power generation by a high Ni dispersion.

Table 2 Ni and YSZ materials with the compositions

| Material   | Ni   | YSZ  |
|------------|------|------|
| Particle size | 3-7um | 0.5um | 0.1um |
| Weight %    | 50   | 10   | 40   |

Fig. 10 A SEM observation of the powder produced with monolayer particle coated.
Fig. 11 An EPMA observation of the film made of monolayer particle coated powder

Fig. 12 The conductivity, which is expressed in values computed from the porosity with the aim of simulating the conductivity of a dense bulk