SINTERING BEHAVIOR AND PERFORMANCE OF ANODE MATERIALS FOR SOFC

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ABSTRACT

The powder mixture of fine particle nickel oxide (NiO) and fine particle yttria stabilized zirconia (YSZ) had been used as anode material for solid oxide fuel cells (SOFC) in our laboratory. Performance of single cells with this material showed sharp degradation within tens of hours. Results of investigations on this phenomena showed that the deterioration of this anode led to the drop in the cell performance.

Particle size controlled powders were applied to the new anode material by blending YSZ and NiO. Changes of shrinkage and porosity with these new materials were smaller than those with conventional one. The cell with the best new material anode accomplished longer lifetime, over 2,500 hours, and the drop rate of cell voltage was 2.2 % per 1,000 hours.

INTRODUCTION

In order to use SOFC for practical applications, it is necessary to achieve lower production costs(1) and more performance stability. Authors already have confirmed the excellent initial performance of cells as shown in our previous reports(2–3). However, these cells degraded sharply within tens of hours. The cause for this behavior is not related to interfacial reaction between cathode and electrolyte(4–6). Changes in anodic and cathodic overpotentials with operation time were measured, and the microstructures before and after power generation were compared. As a result of these investigations, it was ascertained that the property and the structure of cathode did not change during operation test. On the other hand, the anode was found degraded and it was obvious that the anodic degradation was caused by cohesion of nickel(Ni) particles and shrinkage of the fuel electrode. This anodic phenomenon decreased electric conductivity, gas diffusibility and electrocatalytic activity. In general, anode material for SOFC is composed of nickel oxide(NiO), reduced to metal Ni during cell operation, and yttria stabilized zirconia(YSZ). Frequency of Ni particles, dispersed in the material, affects the number of electrode reaction points, called three phase boundary(7), and formation of current passages(8–9). Therefore, as Ni particles cohere, the reaction points and the current passages diminish gradually. The shrinkage of electrode also causes important problems; such as occurrence of thermal stress,
decrease of gas permeability and increase of contact resistance between the electrode and the current collector.

New anode materials were developed by blending YSZ with NiO in order to solve the problems with the conventional anode. Particle size controlled powders of coarse YSZ, NiO and fine YSZ were mixed to prevent the change in their particle sizes. The coarse YSZ (i) corresponds to thermal expansion of YSZ electrolyte, (ii) prevents sintering shrinkage, and (iii) forms and retains micro pores in the layer. The NiO particles were dispersed around the coarse YSZ particles like plugging up spaces between the coarse YSZ. The fine YSZ is added at the final manufacturing stage and plays an important role in shrinkage control of the material, fixation of Ni particles, and extension of three phase boundary. Changes in porosity and shrinkage in the new materials were much smaller than in conventional material, after reduction at 1000 °C. Figure 1 shows the conceptual microstructure of this new anode. A single cell with the new anode has been tested over 2,500 hours with stable performance; this lifetime is about one hundred times as long as that of the former cell.

EXPERIMENTAL

Preparation of Anode Materials

Two kinds of anode were investigated in this study. Their preparation processes are shown in figure 2. The conventional anode was prepared from a powder mixture of NiO (40 volume % after reduction, Wako Pure Chemical Industrial Ltd.) and YSZ (TZ-8Y, TOSOH Corp.). The powder was heated at 1,400 °C for 2 hours, and then crushed in a rotary ball mill. New anodes were processed in the following steps. The first stage was the preparation of several raw powders. Coarse YSZ was obtained through heat treatment at 1400 °C for 20 hours and sieving with a 330 mesh screen. Fine YSZ (TZ-8Ys, TOSOH Corp.) and NiO (Nakalai-tesque Inc.) were made by crushing in a ball milling machine. At the second stage, these powders were mingled in a procedure as shown in figure 2 and amount prescribed in table I. In this report, the individual materials were named FEM-xyz (x,y,z: these numbers mean the weight ratio), in table I.

Reduction Experiment and Electrical Measurement

Individual powders were press-molded and sintered for measurements of porosity and shrinkage after reduction. Porosity of the individual sample anodes are shown in table I. Samples were held in H₂ atmosphere at 1000 °C for prescribed hours, measured and weighed to calculate the porosity and volume.

The single cells with electrode area of 3.1 cm² were fabricated for investigation of the anodic polarization and any degradation. Several of the cathode, (La₀.₈Sr₀.₂)₀.₉₇MnO₃, with average particle size of 10μm and the anode described above were mixed with turpineol (Wako Pure Chemical Industrial Ltd.) and coated onto
the respective surfaces of thin YSZ plate (Nippon Shokubai Kagaku Co., Ltd). Details of the cell configuration and measurement equipment have been described previously(2). \( \text{H}_2\text{--H}_2\text{O} \) gas as fuel and air as oxidant were supplied to the anode side and the cathode side, respectively. Gaseous hydrogen was humidified by bubbling in water at room temperature. The anodic polarization was measured with a galvanostatic current interruption technique, which can distinguish among the electrode overpotentials and the electrolyte polarization(IR-drop)(10). The microstructures of these anodes were observed with an electron micro probe analyzer (EPMA, JEOL Ltd., JXA–8900R).

RESULTS AND DISCUSSION

Changes in Volume after Reduction

Change rates of the volume shrinkage after the anode samples were reduced for prescribed time are shown in figure 3. The rates were estimated from the relative volumes before and after the reduction. All samples showed volume decrease, and FEM–010 shrunk most of all; it is indicated that sintering shrinkage of Ni particles made the volume to be contracted about 50% after 300 hours reduction. The conventional anode, FEM–000, shrunk about 17% after 300 hours, and the slope of the curve after 300 hours implied that this sample would continue shrinking, if it remained in the same condition.

In the case of the new materials, sintering shrinkage changed little less than 5%, and the volumes were constant from after about 50 hours on. These were most different from that of FEM–000 and FEM–010. It seems to suggest that the coarse YSZ forms a solid framework in the new materials and prevents configurations from transforming.

Change in Porosity

Figure 4 shows the porosity change rates. The positive and the negative values mean decrease and increase of porosity, respectively. While the porosity of all samples except FEM–010 increased temporarily at the beginning of the reduction, the values showed tendency to decrease after that time. The porosity of new anodes, with time, decreased within at most 2 % after 300 hours; that of FEM–731,641 and 461 became approximately 35 %. For the new materials, it seems that, before reduction, the Ni content was higher and the porosity was lower, but the porosity after reduction for a short time was higher. This is explained as follows: when NiO is reduced to Ni metal, the volume decreases and cohesion of Ni particles starts simultaneously. However, the apparent volume changes very little because of the coarse YSZ building up the framework. Therefore, only Ni particles existing around the coarse YSZ cohere slowly and the porosity increases in about 50 hours. It is assumed that FEM–010 has almost the same behavior as the NiO particles in the new anode. However, since agglomeration of Ni particles occurs rapidly, it was impossible to measure the porosity.
Through examinations of the volume and the porosity, it was found that the additional YSZ, which was applied to the anode for the fundamental purpose of matching the anodic thermal expansion to that of the electrolyte, was effective in preventing progressive sintering. In particular, the coarse YSZ in the new materials is more effective action against this sintering.

SOFC performance and anodic polarization

On the basis of the experimental facts mentioned above, the FEM-461 material was applied to the anode. The electric load current was set as shown in table II. It has been established that this set current was able to flow through the former cell with FEM-000, and that the performance degraded rapidly at higher current conditions. However, the voltage of the cell with FEM-461 dropped gradually as the voltage hovered within a range of about 0.10 V, even if current density was set at 1.3 A/cm². After 500 hours from start, the cell performance stabilized at about 0.62 V. Figure 5 shows lifetime of the cell with FEM-461. The drop rate of the voltage was 2.2%/1000 hours within a period from 520 to 2,375 hours after starting this measurement. The cell voltage dropped within the range of about 0.20 V, when an earthquake occurred after about 2,400 hours. The measurements on the current density − cell voltage (j−V) characteristics of this cell every 500 hours showed that the performance did not change substantially within a period from 500 to 2,000 hours. Life of FEM-461 was longer than that of FEM-000 by about one hundred times.

Figures 6 and 7 show the anodic polarizations of FEM-000 and FEM-461, respectively. Measurements on the properties of FEM-000 during generation show that: (i) nonlinear Faradic resistance of the anode increased, (ii) the active overpotential increased and exchange current density was less than one tenth after 44 hours, and (iii) as the generation time elapsed, the concentration polarization shifted down to lower current range. With regard to FEM-461, the overpotential after 500 hours was higher by about 0.08 V at 0.40 A/cm² than that after 215 hours, while there was no difference in the properties from 500 hours on. In addition, the concentration polarization of FEM-461 did not change remarkably, such as observed with FEM-000. It seemed that this new anode would degrade scarcely, if the current was not set over 0.40 A/cm².

Observation of Microstructures

The microstructure and the elemental distributions of Ni and Zr in the FEM-000 are shown in figure 8. There were no distinctions in the scanning electron microscope (SEM) images between before and after generation test. However, it was found that Ni particles, which were dispersed very finely and came into contact with themselves before generation, agglomerated at some place and broke the contacts off after generation test. Figure 9 shows the EPMA images with FEM-461 after generation.
test. It was observed that the connective lines of Ni particles extended from the electrolyte/electrode interface to the opposite side of anode layer. On the Zr elemental distribution map, since the dark and/or white gray lines were expanding like whiskers from coarse YSZ particles, it was estimated that fine YSZ particles existed in these places and fixed the Ni particles.

CONCLUSIONS

It was obvious that increasing shrinkage and diminishing porosity in anode, which was prepared from a mixture of fine NiO and fine YSZ, occurred slowly and infallibly with the anode reduced. This anode degraded rapidly with the operation time.

On the contrary, there was no obvious deterioration in the new anode fabricated in this study. The coarse YSZ forms a solid framework and prevents changes in the configuration and porosity, and Ni particles around the coarse YSZ are fixed by the fine YSZ. The results obtained in this experimental study provide conceptual design of the anodic microstructure for long lifetime.

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Table I Preparation conditions and porosity before reduction of samples.

| Sample name (FEM-xyz) | Mixture ratio of several powder (wt%) | Porosity before reduction (%) |
|-----------------------|--------------------------------------|------------------------------|
|                       | coarse YSZ  
(27.0 μm)  
NiO powder  
(12.8 μm)  
fine YSZ  
(0.6 μm) |                              |
| xyz                   | 7 3 0                                      | 45.5                         |
| 730                   | 7 3 0                                      | 45.5                         |
| 731                   | 7 3 1                                      | 34.3                         |
| 641                   | 6 4 1                                      | 25.2                         |
| 461                   | 4 6 1                                      | 22.1                         |
| 000                   | 40vol% Ni–YSZ (conventional material)    | 14.6                         |

\(a,b,c\) The number in parentheses shows average particle size of the individual powders.

Table II Set values of generation test.

| Time elapsed (hours) | Current density (A/cm\(^2\)) | Flow rate of H\(_2\) (l/min.) | Flow rate of air (l/min.) |
|----------------------|------------------------------|-------------------------------|---------------------------|
| 0 – 108              | 0.40                         | 0.25                          | 1.00                      |
| 110 – 204            | 0.70                         | 0.25 – 0.27                   | 1.00 – 1.10               |
| 205 – 300            | 1.00                         | 0.27                          | 1.10                      |
| 303 – 400            | 1.30                         | 0.30                          | 1.50                      |
| 404 – 502            | 0.70                         | 0.30                          | 1.50                      |
| 509 –                | 0.40                         | 0.25                          | 1.00                      |

Fine YSZ particle
Coarse YSZ particle
NiO particle
Ni particle
(a) before operation
(b) after operation

Fig.1 Conceptual design of anodic micro structure.
Fig. 2 Production processes of anode materials.

(a) conventional process

- YSZ (raw powder) → Mixing by a rotary ball mill → Firing at 1400°C for 2 hours → Crushing by a rotary ball mill → Powder

(b) new process

- Coarse YSZ powder (controlled particle size) → Mixing NiO with 8YSZ by a rotary ball mill → Fine YSZ powder (controlled particle size) → Blending by a rotary ball mill → Powder

Fig. 3 Volume decrease after reduction of the sample anodes.

Number of xyz represents as FEM–xyz.

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Fig. 4 Porosity change after reduction of sample anodes. Number of xyz represents as FEM-xyz.

Fig. 5 Cell life with FEM-461 anode material.
Fig. 6 Polarization behavior of FEM-000.

-●: after 5 hours
-■: after 10 hours
-▲: after 43 hours

Fig. 7 Polarization behavior of FEM-461.

-●: after 215 hours
-■: after 500 hours
-▲: after 1000 hours
-○: after 1500 hours
Fig. 8 SEM images and elemental distributions of polished cross section of FEM-000 before and after operation.

Fig. 9 SEM images and elemental distributions of polished cross section of FEM-461 after operation.