OPTIMIZED MIXTURE RATIO IN YSZ-SUPPORTED NI-YSZ ANODE MATERIAL FOR SOFC

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ABSTRACT

Ni-YSZ cermets are generally used as anodes in SOFCs. The authors have proposed a new concept for the microstructure of anodes, referred to as “YSZ-supported anodes.” A feature of this material is that, unlike other materials, the YSZ powders are divided into coarse and fine particles. Comparative analysis of the properties of the material has revealed improved long-term stability. Samples were prepared with varying levels of coarse and fine YSZ and NiO powders, with average particle sizes of 27.0, 0.4 and 1.0 μm, respectively. To optimize the mixture ratio of the three powders, volume shrinkage, porosity ratios and electrical conductivity were investigated under both SOFC fabrication and operation atmospheres. Electrode performances were also measured and compared. The results provide evidence for an optimal mixture ratio for YSZ-supported anodes.

INTRODUCTION

To use solid oxide fuel cells (SOFCs) for practical applications, it is necessary to both reduce fabrication costs (1) and to achieve higher and more stable levels of performance. Electrodes for fuel cells provide sites for electrochemical reactions and electrical paths under operation conditions. In SOFCs, nickel (Ni) and yttria stabilized zirconia (YSZ) cermets, which are generally used as the anode, are made by heat-treating in air after powder mixtures of nickel oxide (NiO) and YSZ, and then NiO is reduced to Ni in initial cell operation. YSZ particles are added to the anode material to make its thermal expansion behavior compatible with other components, particularly the YSZ electrolyte, and to inhibit the agglomeration of Ni particles (2). An optimal distribution of Ni particles would increase the amount of the reaction sites, that is, the length of the three-phase boundary (3) and would form a current path (4,5). A network of micro-pores in the anode is also required to provide a diffusion path for gaseous reactants and products. These functions are greatly dependent on the morphology of the anode, consisting of the Ni particles, the added YSZ and the micro-pores.

In the research and development of SOFCs at CRIEPI, serious reductions in cell performance have been observed due to deterioration of the anode, which, in turn, is due to the agglomeration of the Ni particles and the resulting shrinkage of the anode (6-8). A new concept for the microstructure of anode has been proposed to solve this problem. A feature of this material, referred to as “YSZ-supported anodes,” is that the YSZ powders are divided into coarse and fine particles. Measurements of cell performance...
have indicated improved long-term stability compared to the previous material. Analyses of the configuration and the electrical behavior of the anode, tested with the total Ni volume ratio set at 40%, have shown that the YSZ structure made from the two different particle sizes leads to more stable properties (9).

In this paper, experimental results are discussed concerning the changes and differences in the dimensional stability, electrical conductivity and electrode characteristics of different YSZ-supported anode samples under both cell fabrication and cell operation atmospheres. Furthermore, based on these results, the optimal mixture ratios for the three powders are determined.

**EXPERIMENTAL**

**Sample Preparation**

The preparation procedure for the YSZ-supported anode consists of two main steps. The first step is the control of the particle size distribution and the second is the mixing of the powders. Details of this process have been described elsewhere (6-9). The mixture ratios for the samples are shown in Fig. 1. The weight ratio values are expressed in the form, x-y-z, (where x + y + z = 100, apart from the series 4-6-z) for the coarse YSZ, the NiO and the fine YSZ, respectively.

**Measurement of Anode Characteristics**

For reduction tests and electrical conductivity measurements, the anode powders were molded and then sintered at 1673 K for 10 h. The samples were placed in an alumina tube and were held at 1273 K for 12 to 300 h in a H2 flow, humidified by water at around 293 K at about 100 cm³/min. The sizes and weights of the samples were then measured to derive their volumes and porosities. Electrical conductivity measurements were conducted after the reduction tests with either an ac impedance spectroscopy or the dc four-probe method in a H2 atmosphere at 1273 K. The samples were set in a special rig, similar to that used by MacDonald (10).

Two anodes, one with and the other without fine YSZ (z=0 and z=2 in the series of 4-6-z samples, respectively), were used to examine anodic polarization. YSZ disks with relative densities of > 95.0% and about 1.0 mm in thickness were used as electrolytes. Anodes were slurry-coated with an electrode area of 0.8 cm² and fired at...
1673 K onto one side of the disks. Cathodes, (La$_{0.8}$Sr$_{0.2}$)$_{0.97}$MnO$_3$, were also slurry-coated and baked at 1423 K on the opposite sides. A reference electrode was made with platinum (Pt) and Pt wire at the edge of the cathode side of the disks. In the electrochemical measurements, gaseous H$_2$ humidified by water at 293 K (50 cm$^3$/min) as a fuel and air (200 cm$^3$/min) as an oxidant were supplied to the anode and the cathode, respectively. Anode characteristics were measured using an impedance technique. Data concerning current flow through the cell and steady-state impedance spectroscopy were measured simultaneously within conditions of almost open circuit voltage and anodic polarization. At least 20 minutes was allowed for stabilization before each impedance run. After measurements, the polished cross sections of the anodes were observed with an electron-probe micro-analyzer (EPMA, JEOL Ltd., JXA-8900R).

RESULTS AND DISCUSSION

Configurational Stability

Configuration stability and compatibility with other components in terms of thermal expansion behavior are important factors for anodes. The thermal expansion behaviors of both NiO-YSZ composites and Ni-YSZ cermets have been already clarified in air and in H$_2$ atmospheres (11,12). As Dees et al. reported (13), the agglomeration of Ni particles under SOFC operating conditions leads to a reduction in reaction sites and the cutting-off of current paths. Furthermore, shrinkage of the electrode upon firing also leads to decreases in the gas permeability of the electrode layer, the occurrence of shear stresses at the electrolyte/electrode interfaces, and increases in contact resistance between the electrode and the current collector when assembled as a stack.

Figure 2 shows the changes in linear shrinkage for the various YSZ-supported samples and “YSZ composites” which consisted of only coarse and fine YSZ ($y=0$ series) after sintering in air. The shrinkage in the samples decreases gradually with increases in the content of coarse YSZ. From the values of the raw materials it is clear that the NiO densified more than the coarse YSZ, but less than the fine one.

![Fig. 2 Linear shrinkage, $\Delta L$, for the various anodes after sintering at 1673 K in air for 10 h.](image)

(a) $z=0, 9, 23$
(b) $y=0, y=56$
(c) $4-6-z(z=0, 1, 2, 3, 5, 7, 9)$
Figure 3 shows the volume shrinkage for the \( z = 0 \) sample as a function of retention time in the \( \text{H}_2 \) atmosphere at 1273 K. When the NiO only sample (0-100-0), indicated by a gray square, was reduced and held for 300 h, the porous specimen became agglomerated and shrank by more than 50%. However, the shrinkage for the \( z=0 \), coarse YSZ added NiO (apart from the 0-100-0 sample), decreased with increases in the content of coarse YSZ. This indicates that added coarse YSZ inhibits the coarsening of Ni particles and the resultant dimensional changes. From a comparison of the data for the 0-100-0 sample and the 0-91-9 sample, it is also clear that fine YSZ had a similar effect. All samples for which the ratio \( x/(x+y) \) was below 0.4 showed remarkable volume decreases during the initial 50 h, and then became constant over time. With increases in the content of coarse YSZ, volume contractions became milder and only small differences were seen at \( x/(x+y)>0.5 \).

The linear shrinkage for our previous anode after sintering in air was 15.6 %. When sintered with either a 3 m/o YSZ plate (4 cm diameter and ca. 300 \( \mu \)m) or an 8 m/o YSZ plate (10 cm diameter and ca. 300 \( \mu \)m) using the slurry-coating and firing process, the anode caused warping of the plates due to large shrinkage. During long-term SOFC operation, this anode deteriorates remarkably after about 20 h because the anodic over-potential curve at 0.2 A/cm\(^2\) rises abruptly. From the results of reduction test, this anode contracted at a rate of about 15.0 % after 24 h, and continued to shrink even after 300 h. These phenomena would be accompanied by strong agglomeration, and would cause shearing stress at the interface with the electrolyte under SOFC fabrication conditions. In general, for materials with isotropic volume change behavior, the linear expansion is one third of the volume. Therefore, the permissible linear shrinkage can be calculated to be 5.0 %. Figure 4 shows the total linear shrinkage for samples, excluding \( y=0 \) sample, which were added to the rate after sintering in air to the rate after 300 h.
reduction. This clearly shows the suitable range for permissible shrinkage.

Changes in Porosity

The porosity of electrode is also an important factor, because of its effect on gas permeation, where low permeability can give rise to increases in over-potential related to gaseous diffusion. For our previous anode, over-potential occurred at about 10 h after commencing operation. The porosities for the z=0, 9, 23 samples after sintering in air increase with decreases in the content of fine YSZ, and a similar behavior was observed for other samples. However, the curve for changes in porosity for the z=23 sample shows a gradual increase from 3.2 % up to 17.8 % with increases in the $x/(x+y)$ value, while the changes for the samples $z=0$ and $z=9$ show only increases in the minimum region. The respective porosities of the coarse YSZ only, the fine YSZ only and the NiO only were 43.5 %, 1.5 % and 32.0 %. The differences in the porosity of the samples, made from three different powders, are due to different sintering properties of each of the powders.

During reduction, the large initial increase in porosity, which occurs for all samples apart from the x-0-z sample, is due to the reduction in NiO to Ni with a simultaneous decrease in the volume and an agglomeration of Ni particles. Samples with high fine YSZ contents and samples for which $x/(x+y)>0.5$ did not show any changes after the initial increment. Figure 5 shows the final porosities of the $z=0$, 9, 23 samples after sintering in air and reducing at 1273 K for 300 h, and the applicable range for SOFC anodes. Porosity was below about 30 % and the decrease to 20 % was continuous, as reported in ref.(1). Therefore, samples with a porosity of less than 30 % are unsuitable for SOFC anodes.

Change in Electrical Conductivity

The electrical conductivities of all the Ni-YSZ cermets were measured in a H₂ atmosphere at 1273 K. As reported and discussed with respect to the change in conductivity for the $y=56$ sample (9), samples that have low NiO contents compared to either coarse or fine YSZ have low conductivities because the connections between the Ni particles are lost. Dees et al. (13) state that normally more than 1 h was required to attain steady states for their samples, although more than 90% of the change occurred within the first 10 min. In contrast, some of the YSZ-supported anodes required more than 50 h to stabilize.
Figure 6 shows the electrical conductivities for the $z=0, 9, 23$ samples maintained in a reducing condition for 300 h, as a function of $x/(x+y)$. Conductivity was improved by three orders of magnitude by increases in the content of coarse YSZ. The conductivity of the $z=23$ sample either became constant or slightly decreased with increases in the coarse YSZ content up to 30%, and then decreased gradually thereafter, although the conductivity of the $z=0$ and $z=9$ samples exhibited abrupt decreases at the 50-60% level. This difference in the conductivity curves can be attributed to the fact that there is a dependency on both the size of the YSZ particles and the content of both kinds of YSZ, which is related to the level of Ni. Such size effects have been observed in other cermet anodes, for example, by Dees et al. (13). Malliaris et al. (14) and Aharoni (15) have also investigated the effect of particle size on the conductivity of composites made with conductive and insulative powders. The suitable range for SOFC anodes is also shown in Fig. 6, which is more than 100 S/cm. This value was determined from the initial conductivity of our previous anode when treated under the same conditions, where cell performance deteriorated immediately.

**Characteristics of Anodes with and without the Fine YSZ**

The relation between polarization behavior and microstructure has been investigated by electrochemical techniques (15,16). In this study, we focus on the influence of content levels of fine YSZ, which was examined by means of ac impedance spectroscopy under non-zero, stepwise direct current densities and EPMA analysis. The microstructures and the element distributions of Ni and Zr in the samples 4-6-0 and 4-6-2 are shown in Figs. 7 and 8, respectively. From the secondary electron image, the thickness of the anode layer was confirmed to be about $80 \mu m$. In the Zr element

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Fig. 7 The microstructure of and Ni and Zr distributions in the 4-6-0 sample.
distribution map for the 4-6-2 sample, the fine YSZ is seen as dark or white gray parts, which are extended around the coarse YSZ to cover the Ni particles and to form bridges connecting the coarse YSZ particles. Comparison with the 4-6-0 sample indicates that the coarse YSZ contact becomes more solid when fine YSZ is used, and the dispersion and connection of the Ni is also subtly changed in the presence of the fine YSZ.

With respect to the current density-cell voltage characteristics of the respective single cells with anodes, the measurements indicate that cell performance was better for the 4-6-2 sample than that for the 4-6-0 sample, with the current density of the 4-6-2 sample cell reaching approximately 0.40 A/cm² when the potential between the reference and anode was 0.4 V, although this was limited to about 0.28 A/cm² for the 4-6-0 sample. The results of the spectroscopy were applied to compensate for IR and the analysis of electrode reaction (16,17). Figure 9 shows the polarization curves after excluding the IR for each polarized value. The over-potential of the 4-6-0 sample becomes higher and shifts to a lower current density than the 4-6-2 sample. It is thought to depend on the distribution of the electrochemically active sites, electrodes with firm YSZ networks have been found to exhibit smaller over-potentials.

**Optimal Mixture Ratios**

An optimal mixture of the three powders was determined from the present results, as shown in Fig. 10. Although some of the x-y-0 samples exhibited excellent characteristics and are applicable for SOFC anodes in terms of dimensional stability and electrical conductivity, these were not included because the performance of the anode without fine YSZ was low.
CONCLUSIONS

The present investigation of YSZ-supported anodes suggests that coarse and fine YSZ grains form a solid structure and prevent damage due to reduction of the NiO or Ni agglomeration. However, coarse YSZ alone is not a suitable material for long-term stability, since slight changes in volume and porosity were observed. The addition of fine YSZ is effective in achieving a more stable anode, without any substantial decreases in electrical conductivity and alterations to the microstructure. The present results indicate that conductivity depends not only on the Ni content but also on the particle sizes of the YSZ grains and suggest an optimal mixture ratio for the coarse YSZ and fine YSZ. The present investigation has shown that the microstructure of YSZ-supported anodes is highly correlated with the characteristics of the electrode. Electrode polarization phenomena were strongly affected by the fine YSZ content of the powder. These results indicate a suitable range for the mixture ratios of the three powders for SOFCs.

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