Anodic performance of bilayer Ni-YSZ SOFC anodes formed by electrophoretic deposition

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Bilayer Ni-YSZ anode films for SOFCs were prepared by electrophoretic deposition (EPD). The thickness of each layer of the bilayer anode films, which consist of 50 wt % Ni-YSZ as the active layer and 70 wt % Ni-YSZ as the current collecting layer (50Ni-YSZ/70Ni-YSZ), were controlled by the deposition time of the EPD process. For the monolayer anodes, 70Ni-YSZ showed a better performance than 50Ni-YSZ. The bilayer film, 50Ni-YSZ/70Ni-YSZ, showed an even better performance than the 70Ni-YSZ monolayer film. Probably, 50Ni-YSZ anode has more reaction sites compared to 70Ni-YSZ; on the other hand, 70Ni-YSZ has higher porosity to be a gas diffusion (or current collecting) layer. The anodic performance of the bilayer film significantly depended on the film thickness of the 50Ni-YSZ layer, and 3 µm was found to be the optimized thickness as the active layer, which suggests that the charge transfer reaction site extended up to a 3-µm thickness from the anode/electrolyte interface.

Key-words : SOFC, Anode, Double layer, Electrophoretic deposition, Ni-YSZ

1. Introduction

Solid oxide fuel cells (SOFCs) are the next-gen hydrogen fueled power generator, because of their high energy conversion efficiency and fuel adjustability. Ni cermets are currently used as the anode material of the SOFCs. The most typical material is Ni-8 mol % YSZ (Ni-YSZ), which contains 40–70 vol % metallic Ni dispersed into the YSZ.1 Ni particles possess a good catalytic activity for the hydrogen oxidation reaction, and YSZ is known as an oxide ion conductor with a good conductivity and stability.2,3) Since YSZ has a poor electronic conduction, Ni should moderately aggregate in the cermet anode to ensure current collecting paths. Although the Ni aggregation enhances the current collection property, it simultaneously decreases the number of reaction sites or length of the three phase boundary (TPB). In particular, propagation of the Ni aggregation during cell operation frequently increases the anodic overpotential. Another problem of the Ni condensed YSZ anode is the mismatch of thermal expansion coefficient (TEC) between the anode layer and the YSZ electrolyte layer. The TEC of the Ni-YSZ cermet significantly increases with an increase in the Ni content; 10.5 × 10⁻⁶ K⁻¹ for YSZ and 12 × 10⁻⁶ K⁻¹ for 60 vol % Ni-YSZ.4) One solution of the above-mentioned trade-off is to divide the Ni-YSZ anode into an active layer and current collecting layer, which is known as a functionally graded structure. Many researchers have already reported SOFC electrodes with functionally graded structures.5–15) Functionally graded structures have been prepared by screen-printing,6–7) spray drying,8,9) and PVD.10,11) We previously succeeded in forming double layer cathodes consisting of LSM-YSZ as the active layer and LSM (La₀.₈Sr₀.₂MnO₃) as the current collecting layer (LSM-YSZ/LSM) by electrophoretic deposition (EPD).12) The LSM-YSZ/LSM bilayer cathodes exhibited significantly better performances compared to the monolayer LSM and LSM-YSZ cathodes. EPD is a colloidal ceramic process in which a ceramic particle in a stable suspension migrates to an electrode in a dc electric field to form a deposit.13,14) The amount of the deposit is controlled by adjusting the EPD conditions such as the deposition time and applied voltage. The one of the characteristics of EPD is the relatively high density of the deposit film. Uchikoshi et al.15) reported that the YSZ compact prepared by EPD tended to have a high sinterability enough to be comparable to that prepared by the 200 MPa cold isostatic pressing (CIP). This characteristic may cause a good adhesion between the electrode and electrolyte, compared to the other deposition process described above.

For an anode film, Wang et al.14) prepared a continuously graded anode functional layer on the surface of an anode substrate by the EPD technique in which the Ni and YSZ composition linearly change along the depth direction of the layer. They concluded that 9.8 µm was the optimal thickness for the anodic function. In order to understand the effect of the thickness of the active layer, we adopted the EPD technique to form anodic bilayers in which the 50 wt % Ni-YSZ and 70 wt % Ni-YSZ layers were deposited as the active and current collecting layers with controlled film thicknesses, respectively.

2. Experimental

2.1 Preparations of Ni-YSZ powders

The Ni-YSZ powders were prepared by the impregnation method using the Ni(NO₃)₂·6H₂O (Wako, >99% pure). The Ni(NO₃)₂·6H₂O aqueous solution contained the prescribed amount of YSZ powder (HSY-8; Daiichi kigenso, mean particle size = 0.4 µm) for the weight ratios of 50 and 70 wt % in the Ni metallic form. The mixed suspension was slowly evaporated on a hot plate at 150°C to yield the precursor. The obtained precursor was pressed into a pellet and calcined in air at 1300°C for 2 h. The calcinated pellet was pulverized by wet ball milling in methanol to yield a fine NiO-YSZ powder.

2.2 Film preparation by EPD

The monolayer and bilayer anode films were formed by the
EPD method. A 0.24 g sample of the NiO-YSZ powders was added to 30 mL of acetylacetone containing 0.005 g of I2 as the charging agent, and then the mixtures were sonicated for 20 min to yield a suspension. An 8 mol % YSZ sheet with a 0.5 mm thickness (Tosoh) was used as the electrolyte substrate. One surface of the YSZ sheet was painted with a graphite rod to yield a conductive surface. The graphite-treated YSZ sheet and a stainless sheet separated by a distance of 1 cm were immersed in the suspension regulated at 30°C, and a 22 V constant dc voltage was applied. The bilayer anode films were prepared as follows. First, 50Ni-YSZ was deposited on the graphite surface in the 50Ni-YSZ suspension. After drying the deposit at room temperature, 70Ni-YSZ was deposited in the similar manner in the 70Ni-YSZ suspension. The film thickness of each layer was adjusted by the deposition time. The deposited films were finally sintered at 1300°C in air for 2h.

2.3 Measurements of electrochemical performance
After the anode formation, the cathode and reference electrodes were formed using Pt-paste on the other side (anode) of the YSZ sheet, then sintered at 600°C for 1 h. The areas of the cathode, anode and reference electrodes were 0.25, 0.25, and 0.1 cm², respectively. The Pt cathode was wired with Pt-lead using Pt-paste (Tanaka Kikinzoku Kogyo TR-7907). The surface of cathode was attached to Ni-mesh (200 mesh, aperture 0.075 mm) as the terminal current collector using Pt-paste. The three-terminal cell configuration and the setup used for the cell test are shown in Fig. 1. For the cell tests, the anode and counter sides were exposed to humidified H₂ and compressed air, respectively. The gas flow rates were 50 ml/min. The voltage between the anode and the reference, \( \Delta V_{C-R} \), was measured for different constant current between the cathode and anode. All the fuel cell tests were conducted at 700°C. The current was controlled by an electronic load (Takasago; FK-160LZ).

3. Results and discussion
3.1 Preparation of mono- and bilayer Ni-YSZ anode films
As shown in Fig. 2, the thickness of the anode films was controlled by the deposition time of the EPD process. The thickness was almost linear relative to the deposition time, and the deposition rate was nearly the same between the 50 and 70Ni-YSZ films. Figure 3 shows cross-sectional views of the 50 and 70Ni-YSZ monolayer films after sintering at 1300°C and reduction under hydrogen at 600°C. Both anode films are about 30 μm in thickness, and they are porous and homogeneous. Based on the result in Fig. 2, bilayer anodes consisting of 50Ni-YSZ/70Ni-YSZ were prepared by EPD. Figure 4 shows SEM-EDX images of the double layer anode in the cross-sectional view observed after the hydrogen reduction. From the Ni and Zr elemental mappings, the formation of the double layer with a 6.9/8.7 μm thickness was confirmed. Furthermore, it seems that the 70Ni-YSZ layer is more porous than the 50Ni-YSZ layer. This is because the hydrogen reduction eliminates oxygen from NiO and the oxygen deficits propagates into the pores. In this sense, the 50Ni-YSZ/70Ni-YSZ double layer is considered as a...

![Fig. 1. The cell configuration used in the measurements for the anodic properties.](image1)

![Fig. 2. Calibration curve of the film thickness adjustment by the electrophoretic deposition.](image2)

![Fig. 3. Fractured surfaces of the 50 and 70Ni-YSZ anode films sintered at 1300°C in air followed by H₂ reduction at 600°C.](image3)

![Fig. 4. SEM-EDX analysis of the fractured surface of the 50Ni-YSZ/70Ni-YSZ bilayer anode.](image4)
porosity-graded structure as well as concentration-graded structure. The porosity-graded structure is favorable for promoting gas diffusion.19)

3.2 The electrochemical properties of the anode films

Figure 5 shows the i-v characteristics of the cells with 50Ni-YSZ and 70Ni-YSZ anodes. The film thickness was 13 and 16 μm, respectively. Apparently, the 70Ni-YSZ anode exhibited a higher performance compared to the 50Ni-YSZ anode. Figure 6 shows the results of the four-terminal dc conductivity measurements for the 50Ni-YSZ and 70Ni-YSZ compacts prepared by the uni-axial pressing at 20 MPa. Both cermets exhibited the sufficiently high conductivity, and the 70Ni-YSZ exhibited a higher conductivity compared to 50Ni-YSZ due to the higher Ni concentration. The observed negative temperature dependence means that metallic conduction of the Ni is predominant. It is widely accepted that conductivity of a Ni-YSZ cermet is controlled by the percolation effect and the conductivity threshold occurs around 33 vol%.20) Both the 50Ni-YSZ (40 vol %) and 70Ni-YSZ (60 vol %) are beyond the threshold, and therefore, their conductivities should be high enough to have a sufficient current collecting effect. Therefore, the difference of the conductivity is not likely to be a reason for the difference of the anodic property. Since the H2 oxidation reaction mainly takes place at the three phase boundary (TPB) of H2 (or H), Ni and YSZ, the 70Ni-YSZ anode with the higher concentration of Ni seems to have a longer TPB length. However, this is not necessarily true, because the high concentration of Ni simultaneously induces Ni particle aggregation, which results in a reduced TPB length. We next examined the anodic performance of the double layers with different layer thicknesses. Figure 5 also shows the i-v characteristic of the cell with the 50Ni-YSZ/70Ni-YSZ bilayer anode (3μm/14μm). A remarkable enhancement in the i-v characteristic was observed for the double layer anode. This result suggests that the 50Ni-YSZ and the 70Ni-YSZ layers act as active and current collecting layers, respectively, and the 50Ni-YSZ provides a longer TPB length than the 70Ni-YSZ. Figure 7 shows the anodic overpotential of the monolayer and the bilayer anodes. By using the bilayer structure, the anodic overpotential dramatically decreased compared to the monolayer anodes. Figure 8 shows the anodic overpotential at different current densities. It is clear that the anodic property depends more on the thickness of the first layer. By increasing the thickness of the first layer from 3 to 6μm, a significant increase in the overpotential was observed. This result suggests that about 3μm 50Ni-YSZ layer practically acts as the active layer, and the residual part of the layer is only considered as a low conductive layer. Therefore it should be effective to replace the resistive layer by the high conductive 70Ni-YSZ layer. Antunes et al.21) investigated the thickness
The effect of the bilayer cathodes, i.e., LSM-YSZ/LSM. In their study, the critical thickness of the LSM-YSZ layer was 8 μm. The critical thickness of the active layer cannot be unambiguously determined, because it is also a function of the microstructure (grain size) and porosity.\textsuperscript{23} Therefore, a further investigation will be required for the bilayer anode in terms of the relationship between the critical thickness and morphology of the active layer. We are also curious about the active layer with thickness smaller than 3 μm. Unfortunately, in this study, the thinner films with a homogeneous thickness were not reproducible in our EPD experiment. It seems that the anodic property does not significantly depend on the thickness of the 70Ni-YSZ layer in the range of 9–20 μm. Generally, the current collecting effect is governed by the in-plane resistance of the electrode film and the effect increases with the electrode thickness.\textsuperscript{23,24}

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R_{\text{in-plane}} = (\rho_0/4d) \times r^2
\]

where $\rho_0$ = resistivity of electrode, $d$ = thickness of electrode, and $r$ = spacing of the metal mesh. The $R_{\text{in-plane}}$ value of the 70Ni-YSZ at 70°C was evaluated as follows. The $\rho_0$-value at 70°C was cited from the result in Fig. 6, i.e., 7.5 $\times$ 10$^{-4}$ Ω cm. The $r$-value was used as an aperture of the Ni-mesh (0.075 mm). When the $d$-value is 9 μm, the $R_{\text{in-plane}}$ value of the 70Ni-YSZ at 70°C was evaluated to be 1.2 $\times$ 10$^{-5}$ Ω cm$^2$. Assuming the current collecting effect is saturated above the thickness of 9 μm, the $R_{\text{in-plane}}$ value of 1.2 $\times$ 10$^{-5}$ Ω cm$^2$ is low enough to give the sufficient current collecting effect. We also evaluated the $R_{\text{in-plane}}$ values of the 50Ni-YSZ with 13 μm thickness, and obtained the value of 1.3 $\times$ 10$^{-6}$ Ω cm$^2$. This value is very close to the evaluated value of the 70Ni-YSZ with 9 μm thickness, which suggests that the 50Ni-YSZ with 13 μm thickness also possesses a sufficiently large current collection effect. This result supports that the difference of the anodic properties between the 50Ni-YSZ and 70Ni-YSZ shown in Fig. 7 is not due to the difference of the conductivities. Thus, in this study, the EPD method provided the relatively dense 50Ni-YSZ anode films. This tendency is one of the characteristics of the ceramic film produced by the EPD method, and might be a positive factor for preparing the thin active layer with a few micrometer thickness. However, the dense morphology may cause a high gas diffusion barrier, which can be a negative factor for the current collecting layer with more than 10 μm thicknesses. Further study will be required for optimizing the EPD conditions to achieve a moderately porous morphology of the anodic films.

4. Conclusion

The bilayer anode films consisting of 50 wt %Ni-YSZ (50Ni-YSZ) and 70 wt %Ni-YSZ (70Ni-YSZ) were formed using the electrophoretic deposition (EPD) technique. In the anode films, 50 and 70Ni-YSZ were deposited as the bottom and top layers, respectively. The thickness of the layers was successfully controlled by the deposition time of the EPD process. For the monolayer anode, the 70Ni-YSZ was superior to the 50Ni-YSZ in its anodic property. However, the formation of the 50Ni-YSZ/70Ni-YSZ bilayer gave a significantly higher anodic property compared to the monolayer anodes. This result suggests that the 50Ni-YSZ, which has a lower Ni content, possesses a greater number of reaction sites due to its higher Ni dispersion compared to the 70Ni-YSZ, and the addition of the 70Ni-YSZ layer effectively enhanced the anodic property. Since the 70Ni-YSZ layer has a porous structure, it functions as a good gas diffusion and current collecting layer. The critical thickness of the 50Ni-YSZ as an active layer was 3 μm in the present anode structure.

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