Preparation and Characteristics of Ni/YSZ Cermet Anodes by Vapor-phase Deposition

Tsutomu IOROI*, Yoshiharu UCHIMOTO, Zempachi OGUMI and Zen-ichiro TAKEHARA

Received December 20, 1995 ; Accepted February 7, 1996

High performance nickel/yttria-stabilized zirconia (Ni/YSZ) anodes were prepared by a novel vapor-phase method. The vapor-deposited Ni/YSZ cermets were prepared by reacting surface-oxidized nickel with zirconium and yttrium chlorides using nickel oxide as an oxygen source. After the vapor-phase reaction, it was found that nickel grains of the cermets are covered with porous YSZ layer. In the present work, the morphology and polarization behaviors of the vapor-deposited Ni/YSZ cermet anodes were compared with those of the conventional slurry-coated Ni/YSZ cermets. The steady-state polarization and AC complex impedance measurements indicated that the vapor-deposited Ni/YSZ cermets show lower anodic polarization than the cermets prepared by the conventional slurry method. This decrease in the polarization was attributed to an increase of electrochemical active sites, three-phase-boundary, in the vapor-deposited Ni/YSZ cermet anodes.

1 INTRODUCTION

Solid oxide fuel cells have high power-generation efficiency with little NO_x emissions. Stabilized-zirconia, especially yttria-stabilized zirconia (YSZ), is used as an electrolyte in solid oxide fuel cell, because the YSZ has relatively high oxide-ion conductivity as well as high chemical stability both in oxidizing and reducing atmospheres^{1,2}.

A porous nickel/yttria-stabilized-zirconia (Ni/YSZ) cermet is a currently used anode material in solid oxide fuel cells (SOFCs)^{2,3}. At a metal anode of SOFC (nickel, platinum etc.), fuel gas such as hydrogen is electrochemically oxidized at a YSZ electrolyte/metal anode/fuel gas interface, what is called a triple-phase-boundary (TPB) region^{4,5}. Not only Ni/YSZ cermet prevents the nickel particles from sintering which causes degradation of the anode, but also the cermet expands the TPB region, leading to improved anode performance. Conventionally, the Ni/YSZ cermet anodes have been prepared by a slurry method⁶⁻⁸. In order to prepare highly stable and electrochemically active Ni/YSZ cermet

anodes, it is necessary to control the YSZ content and its distribution in the cermet. The electric conductivity of the Ni/YSZ cermet containing more than 60 volume % of YSZ is decreased rapidly, corresponding to a break of the path of electric conduction in the nickel, leading to high anode overpotential⁶⁻⁸. This decrease in electric conductivity is inevitable for the cermet prepared by the slurry method. In contrast, a Ni/YSZ cermet prepared by the vapor-phase method which we have developed is able to cover the surface of the nickel oxide selectively with a porous or dense YSZ⁹.

In the present work, we have produced Ni/YSZ cermets on dense YSZ electrolytes by the vapor-phase method and examine their morphology and polarization characteristics in comparison with that of the conventional Ni/YSZ cermet anodes.

2 EXPERIMENTAL

2.1 Preparation of Ni/YSZ cermet anodes by a slurry method

Nickel oxide powder was prepared by oxidizing nickel powder (Type 255, >99.7% purity, Inco Co., Ltd.) in air at 1473 K for 5h. This nickel oxide powder and 8 mol% Y₂O₃ doped ZrO₂ powder (TZ-8Y, >99.9% purity, Tosoh Co., Ltd., Japan) were mixed at an appropriate

Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, (Sakyo-ku, Kyoto, 606-01, Japan)

Key Words : Fuel cell, Ni/YSZ cermet, Vapor-phase deposition

ratio by using an agate mortar yielding NiO/YSZ mixture. Nickel oxide/YSZ slurries were made by mixing NiO/YSZ powder, solvent (i-propanol; reagent-grade, Wako Pure Chemical Industries Ltd., Japan) and binder (polyvinylbutyral resin; reagent-grade, Wako Pure Chemical Industries Ltd., Japan). The nickel oxide/YSZ slurry was painted on a surface of YSZ electrolyte disks (pre-prepared TZ-8Y at 1773 K for 5h). After drying for a day, the disks were heated at 1573 K for 3h to remove the binder and to proceed the sintering of the nickel oxide and the YSZ powder.

2.2 Preparation of Ni/YSZ cermet anodes by the vapor-phase method

Substrates used for the vapor-phase reaction were surface-oxidized Ni/YSZ cermet mounted on YSZ electrolytes. This surface-oxidized Ni/YSZ cermet was made by reduction of NiO/YSZ cermet in hydrogen at 1273 K for 2h, and succeeding re-oxidation of the surface of the nickel grains in air at 873 K for 30 min. Figure 1 shows a schematic diagram of a reactor used to produce YSZ films on the nickel oxide (nickel) surface. The reactor was made of a silica-glass tube, and the reaction zone was heated at 1273 K in an electric furnace. The substrates were set in a substrate holder which was located in the reaction zone. Ar gas was flowed in the substrate holder to keep off the metal chlorides vapor before and after the vapor-phase reaction. The silica-glass tube was equipped for source-chloride sublimation two side arms, one for zirconium tetrachloride ($ZrCl_4$) (>99% purity, Wako Pure Chemical Industries Ltd., Osaka, Japan) and the other for yttrium trichloride (YCl_3) (>99.9% purity, Aldrich Chemical Company, Milwaukee, WI). The $ZrCl_4$ was heated at 443 K and the YCl_3 at 1008 K. Each vaporized chloride was supplied to the substrate using Ar gas at a rate of 100 cm^3 (STP) min^{-1} as a carrier. The pressure in the silica-glass reactor

Fig. 1 Schematic diagram of an apparatus for preparation of Ni/YSZ cermets by a vapor-phase method.

was maintained at 1.3×10^2 Pa during the reaction.

The morphologies and elemental distribution of the treated substrate were observed by a scanning electron microscope (SEM) (model S-510, Hitachi, Tokyo, Japan) and a electron-probe microanalyzer (EPMA) (model EMAX-1770, Horiba Instruments, Kyoto, Japan) respectively.

2.3 Cell arrangements

Figure 2 shows a schematic diagram of a three electrodes cell used for the polarization measurements. A YSZ pellet (22 mm diam., 1 mm thick.) coated with electrodes was placed between mullite tubes (21 mm outer diam.). The fuel gas side of the disk was sealed with a glass (Pyrex) ring packing. The working electrode was Ni/YSZ cermet as described above and an electrical contact was made by nickel mesh and nickel wires. At the opposite side of the YSZ disk, the counter and reference electrodes were coated with using platinum paste and the electrical contacts were made by platinum mesh and platinum wires. The gas was supplied to the electrodes through inner mullite tubes. For the working electrode side, hydrogen gas saturated with water vapor at room temperature (10°C) was supplied, and air was supplied to the counter and the reference electrodes.

2.4 Electrochemical measurements

The two measuring methods were used to investigate

Fig. 2 Schematic diagram of a single SOFC used for measurement of Ni/YSZ cermet electrode properties.

the electrochemical properties of the Ni/YSZ cermet anodes: (i) the steady-state polarization measurements combined with the current-interruption techniques¹⁰⁾, and (ii) the AC complex impedance measurements¹¹⁾. In the steady-state polarization measurements, loading current of the cells (Ni/YSZ anode | YSZ electrolyte | Pt cathode) was controlled with a galvanostat (model HA-301, Hokuto Denko Ltd., Tokyo, Japan) and the potential difference between the working electrodes and the reference electrodes was recorded by a potentiometer. The internal resistance of the cell was estimated by the current-interruption measurements; the potential decay of the working electrodes was observed with a signal analyzer (model SM-2100A, Iwatsu Electric Co., Ltd., Tokyo, Japan) and the instantaneous voltage drop was measured. The AC complex impedance of the cell was studied over the frequency range of 100 kHz - 0.1 Hz. The AC amplitude between the electrodes was kept below 10 mV. All of the AC complex impedance measurements were performed with a frequency response

analyzer (solartron 1255, Schlumberger Technologies, Hampshire, England) and a potentiostat (PARC model 273A, EG&G Instruments Co., Princeton, NJ).

3 RESULTS AND DISCUSSION

3.1 Morphological studies

Figure 3 (a) shows a scanning electron micrograph of cross-section of the NiO/YSZ cermet anode prepared by the slurry method (containing 10 weight % YSZ); the nickel oxide and the YSZ grains sintered each other and the contact between the grains were thick. Rather small content of the YSZ (10 w%) was aimed to clarify the effects of the vapor-phase deposited YSZ on the nickel grains as described below. In order to prepare the surface-reduced Ni/YSZ cermets, the NiO/YSZ cermet anodes were reduced in hydrogen atmosphere to Ni/YSZ cermets. After the reduction, as shown in Fig. 3 (b), the nickel grains were sintered to construct a framework of a porous structure, and the YSZ particles (smaller ones) were dispersed on the nickel surface. Figure 3 (c) shows

Fig.3 Scanning electron micrographs of Ni(NiO)/YSZ cermets:

- (a) NiO/YSZ cermet prepared by slurry method;
- (b) Ni/YSZ cermet after reduction of (a) in hydrogen at 1273 K for 2h;
- (c) Ni/YSZ cermet after oxidation of (b) in air at 873 K for 30 min;
- (d) Ni/YSZ cermet after the vapor-phase reaction with $ZrCl_4$ and YCl_3 at 1273 K for 30 min.

Fig. 4 (a) Current density vs. potential plot (■) of Ni/YSZ cermet anode prepared by the slurry method. The symbol (□) show the IR drop compensated potential.

Fig. 4 (b) Current density vs. potential plot (■) of Ni/YSZ cermet anode prepared by the vapor phase method. The symbol (□) show the IR drop compensated potential.

a cross-section of the surface-re-oxidized Ni/YSZ cermet in air at 873 K for 30 min. From the SEM observations of a fractured cross-section of the surface-re-oxidized nickel, the surface oxide layer was estimated as about 0.5 μm thick. This surface-re-oxidized substrate was served to the vapor-phase processes described at the

experimental section. After the vapor-phase reaction at 1273 K for 10 min, a YSZ layer was deposited on the surface of the nickel grains as shown in Fig. 3 (d). This deposited YSZ layer was considerably porous and composed of fine grains. Moreover it was found from XRD analyses that the nickel oxide layer on nickel grains is completely consumed after the vapor-phase reaction. As we have reported before, the YSZ deposition reactions between nickel-oxide and metal chloride vapors include chemical vapor deposition (CVD) and electrochemical vapor deposition (EVD) processes⁹⁾. In the initial stage of the vapor-phase reactions, the CVD reactions predominantly occurred to produce porous YSZ layer. Allowing further CVD reactions to proceed, the YSZ film became denser, and the reaction process was changed to the EVD, leading the dense YSZ film growth. In the present case, the surface-oxidized Ni/YSZ cermet contained too little amount of the nickel oxide to proceed the following EVD step. Thus it was concluded that most of the YSZ layer on the nickel grains is deposited by the CVD reactions between nickel oxide and the metal chloride vapors.

3.2 Electrochemical studies

The anodic polarization characteristics of the Ni/YSZ cermet anodes were evaluated in a fuel cell condition. Figure 4 (a) shows a typical steady-state current-voltage curve of the slurry-coated Ni/YSZ cermet anode (containing 10 weight % YSZ); the voltage drop was separated into ohmic (resistance of a part of YSZ electrolyte, anode, nickel lead wire, and contact resistance) and nonohmic (η) components (anodic overvoltage). This separation of the voltage drop was conducted with the current-interruption method. The observed open-circuit voltages between the working and the reference electrode at 1273 K were about 1.09 V that is close to the theoretical value, 1.10 V. Under the current-loading conditions, potential of the Ni/YSZ cermet anode deviated from the open-circuit voltage with increasing the cell current. From the current-interruption measurements, the main component of the overvoltage was ohmic resistances, in particular, resistance of the nickel lead wire (which is estimated at 0.57 Ω using the conductivity data of nickel). Thus, ohmic resistance of the cell except for that of nickel wire was not so large. Figure 4 (b) shows a current-voltage curve of the vapor-deposited Ni/YSZ cermet anodes. This anode shows smaller nonohmic overvoltage than that of the slurry-coated one, while the ohmic resistances were still larger. Since the ohmic resistances of the electrolyte, nickel wire

and cathode were the same in the both case, this increase of ohmic resistances must be attributed to that of the anode or the contact resistance between the anodes and the current collectors. As mentioned above, the surface of the nickel grains of the vapor-deposited Ni/YSZ cermet was covered with porous YSZ layer, thus it inhibit electrical contacts between the nickel grains and the current collectors.

From these polarization measurements, the IR-free anodic overvoltage of the Ni/YSZ cermet anodes was plotted as a function of the current density in Fig. 5; closed squares (■) represent the anodic overvoltage of the Ni/YSZ cermet anodes prepared by the slurry method, and open squares (□) represent that of the vapor-phase

Fig. 5 Current density vs. IR free anodic overpotential plots (Tafel plot) of Ni/YSZ cermet anode prepared by slurry method (■) and vapor phase method (□). The Solid lines are fitting results by using eq. [1].

Fig. 6 AC impedance plots of Ni/YSZ cermet anode prepared by the slurry method (■) and vapor phase method (□).

method. This indicated that the anodic overvoltage of the vapor-deposited Ni/YSZ cermet anodes was much lower than that of the slurry-coated ones. In particular, the anodic overvoltage decreased about 50 mV in the high current density region ($>200 \text{ mA cm}^{-2}$).

Kawada et al.⁷⁾ reported that the current density (j)-overvoltage (η) curve of a Ni/YSZ cermet anode is represented by the following experimental equation;

$$j = j_0 [\exp(2F\eta/RT) - \exp(-F\eta/RT)] \quad [1]$$

and by differentiating eq. [1] with respect to η ,

$$j_0 = \sigma_e RT/3F = S_e RT/3FR_e \quad [2]$$

where j_0 is apparent exchange current density, $\sigma_e (=dj/d\eta|_{\eta=0})$ is electrode interface conductivity, S_e is electrode area, and R_e is electrode interface resistance. The solid lines shown in Fig. 5 were the fitted results for the anodic overvoltage-current density curves by using eq. [1]. The fitting analyses showed that j_0 value for the slurry-coated and the vapor-deposited Ni/YSZ cermet anodes are 40 mA cm^{-2} and 150 mA cm^{-2} respectively. It was noted that j_0 value for the vapor-deposited Ni/YSZ cermet is larger than that of the Ni/YSZ cermet reported by Kawada et al.⁷⁾, 118 mA cm^{-2} .

Figure 6 shows the AC complex impedance spectra of the Ni/YSZ cermet; Closed squares (■) represent a spectrum of the Ni/YSZ cermet anode prepared by the slurry method, and open squares (□) represent that by the vapor-phase method. The electrode interface resistance σ_e of the vapor-deposited Ni/YSZ cermet was much smaller than that of the slurry-coated Ni/YSZ cermet. This result agreed with that of the steady-state polarization measurements described above. For the spectrum of the slurry-coated cermet, an additional small arc appeared at the low frequency side. Mogensen et al.¹²⁾ reported that the AC complex impedance spectra for Ni/YSZ cermet consist of three arcs; The two arcs at the higher frequency side ($\sim 1 \text{ kHz}$ and $1 \text{ k-}10 \text{ Hz}$) were due to adsorbed proton transfer from nickel to YSZ, and the arc at the lowest frequency side (10 Hz -) was due to coupling of hydroxide ions on YSZ. Thus for the slurry-coated Ni/YSZ cermet, it seems that the larger arc at the high frequency side ($\sim 10 \text{ Hz}$) was due to the proton transfer, and the additional small arc (10 Hz -) was due to the coupling of the hydroxide ions. Since the proton transfer reaction can take place only at the electrochemically active sites, this reaction rate for the slurry-coated cermet was slower than that for the vapor-deposited one. Therefore, the arc at the high frequency side became smaller in the vapor-deposited Ni/YSZ cermet than that of the slurry-coated Ni/YSZ cermet.

In the spectrum of the vapor-deposited cermets, the arc at the low frequency side also shrunk and became obscure. As described above section, nickel grains were covered with the porous YSZ layer (high surface area), thus the coupling reaction of the hydroxide ions were enhanced. From these results, both the proton transfer and the hydroxide coupling reactions were enhanced in the vapor-phase deposited Ni/YSZ cermets.

The electrode interface conductivity σ_e for the slurry-coated and the vapor-deposited Ni/YSZ cermets, which was determined from the AC complex impedance measurements, were 1.1 S cm^{-2} and 4.9 S cm^{-2} . Substitutions of these values in eq. [2] gave j_o value, 40 mA cm^{-2} and 175 mA cm^{-2} , which were close to the fitted j_o as mentioned above. This indicated that eq. [1] is valid for the both Ni/YSZ cermet anodes regardless of the preparation methods. Thus, for the two type of Ni/YSZ cermet electrodes the reaction mechanism seemed to be the same, but the only reaction rate was different. The vapor-deposited Ni/YSZ cermet had larger number of the active sites (TPB region) for the hydrogen oxidation, because the nickel grains were covered more effectively with the porous YSZ layer. Thus, the vapor-deposited Ni/YSZ cermet anodes showed higher reaction rate (lower anodic polarization).

4 CONCLUSIONS

We have prepared the Ni/YSZ cermet anodes by the vapor-phase method and found that the cermet anodes showed the lower anodic polarization than the cermets prepared by the slurry method. The nickel grains of the vapor-deposited Ni/YSZ cermets were covered with porous YSZ layer, causing an increase of the electrochemical active sites for the hydrogen oxidation. It is thought that the vapor-deposition process using

nickel oxide as an oxygen source is useful for preparation of active Ni/YSZ cermet anodes.

References

- 1) N. Q. Minh, T. Takahashi, Science and Technology of Ceramic Fuel Cell, Elsevier, Amsterdam (1995).
- 2) A. J. Appleby and F. R. Faulkes, Fuel Cell Handbook, Van Nostrand Reinhold, New York (1989).
- 3) N. Q. Minh, *J. Am. Ceram. Soc.*, **76**, 563 (1993).
- 4) J. Mizusaki, H. Tagawa, T. Saito, K. Kamitani, T. Yamamura, K. Hirano, S. Ehara, T. Takagi, T. Hikita, M. Ippommatsu, S. Nakagawa and K. Hashimoto, *J. Electrochem. Soc.*, **141**, 2129 (1994).
- 5) J. Mizusaki, H. Tagawa, K. Isobe, M. Tajika, I. Koshiro, H. Maruyama and K. Hirano, *J. Electrochem. Soc.*, **141**, 1674 (1994).
- 6) D. W. Dees, T. D. Claar, T. E. Easler, D. C. Fee and F. C. Mrazek, *J. Electrochem. Soc.*, **134**, 2141 (1987).
- 7) T. Kawada, N. Sakai, H. Yokokawa, M. Dokiya, M. Mori and T. Iwata, *J. Electrochem. Soc.*, **137**, 3042 (1990).
- 8) S. Murakami, Y. Akiyama, N. Ishida, Y. Miyake, M. Nishida, Y. Itoh, T. Saito and N. Furukawa, *Denki Kagaku*, **59**, 320 (1991).
- 9) Z. Ogumi, T. Ioroi, Y. Uchimoto, Z. Takehara, T. Ogawa and K. Toyama, *J. Am. Ceram. Soc.*, **78**, 593 (1995).
- 10) D. Y. Wang and A. S. Nowick, *J. Electrochem. Soc.*, **126**, 1155 (1979).
- 11) J. E. Bauerle, *J. Phys. Chem. Solids*, **30**, 2657 (1969).
- 12) M. Mogensen, S. Primdahl, J. T. Rheinlander, S. Gormsen, S. Linderroth and M. Brown, *Proc. of 4th Intern. Symp. on SOFC*, ed. by M. Dokiya, pp. 657, The Electrochem. Soc., Inc. (1995).