A HIGH-PERFORMANCE ELECTRODE FOR MEDIUM-TEMPERATURE SOFC: MIXED CONDUCTING CERIA-BASED ANODE WITH HIGHLY-DISPERSED Ni ELECTROCATALYSTS

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ABSTRACT

We have developed a high-performance anode for medium-temperature SOFCs. Mixed conducting samaria-doped ceria (SDC) particles were employed in combination with highly dispersed metal electrocatalysts on their surfaces. Fairly small amounts of Ni nanoparticles (6 to 8 vol%) were found to enhance the anode performance significantly at 700° to 800°C in humidified H2. It is shown that the dispersion of nm-sized Ni increased the reaction area (contact portion with SDC) more effectively than μm-sized Ni in the cermet-type anode.

INTRODUCTION

It is desirable to operate solid oxide fuel cells (SOFCs) at a medium temperature (~800°C) to overcome many serious problems such as degradation of materials and a limited choice of materials. Besides a reduction of ohmic loss in the solid electrolytes, development of high-performance electrodes is essential because the electrode reaction rates slow down at such temperatures.

It is very important for a high-performance electrode to have both a highly active electrocatalytic reaction zone and a sufficient gas-supplying network in the microstructure. The anode performance of conventional Ni-YSZ cermet (typical Ni content = 50 vol%) at medium temperatures was improved by means of optimization of the microstructure (1-4). Because reactants (fuel gas, electrons, and oxygen ions) must meet at reaction sites, the three-phase boundary zone (hatched zone in Figure 1A) is essential for this anode due to the pure electronic and ionic conductivity of Ni and YSZ, respectively. For such a cermet-type anode, however, it is intrinsically difficult to increase the effective reaction zone (ERZ) dramatically, because the contacting portions between the μm-sized particles of components are limited.

Therefore, we have proposed a new design concept of the catalyzed-reaction layers, which realizes high-performance anode and cathode for medium-temperature operating SOFCs (5). As shown in Figure 1B, mixed conducting oxide particles and samaria-doped ceria, (CeO2)0.8(SmO1.5)0.2 (SDC), were employed as the anode materials in combination with highly dispersed metal electrocatalysts on the surface. Using the mixed conducting oxide anode results in an enlarged ERZ over the whole surface. Nanometer-sized
electrocatalysts loaded on the surface certainly activate the anodic process at the boundary. We found that Ru-dispersed SDC exhibited fairly high performances at 800°C (5,6). A large depolarizing effect was also seen on La(Sr)MnO₃ (LSM) or La(Sr)CoO₃ (LSC) cathodes with highly dispersed Pt (or Pt-Rh) microcatalysts (5,7-10). Both the overpotential and the ohmic resistance of SDC anodes and LSM (or LSC) cathodes were appreciably lowered by controlling their microstructures (10-12). The performances of SDC anode and LSM or LSC cathode with optimized microstructures were enhanced further with nm-sized Ru and Pt electrocatalysts, respectively.

The next target is to enhance anode performance by dispersing inexpensive metal catalysts on the SDC. In our previous study (5), however, the SDC was not sufficiently activated by nm-sized Ni catalysts with 0.1 mg cm⁻² (ca. 1 vol%). However, higher Ni loading can be accepted to enhance the performance because Ni is much cheaper than Ru by ca. 1/40. In this paper, we show that 6 to 8 vol% of Ni nanoparticles enhanced the SDC anode performance significantly at 700° to 800°C in humidified H₂. We also compared this Ni-dispersed SDC with Ni-SDC cermet anodes (μm-sized Ni with >50 vol%), which were recently employed in medium-temperature SOFCs (13-17). The polarization properties, the ohmic resistances, and the microstructures (pore-size distribution and Ni-mapping) of two types of anodes were examined as a function of the amount of Ni. It is shown that the dispersion of nm-sized Ni enhanced the effective reaction area (contact portion with SDC) more effectively.

**EXPERIMENTAL**

An 8 mol% yttria-stabilized zirconia disk (YSZ, diameter 13 mm, thickness 1 mm) was used as the solid electrolyte. Samaria-doped ceria (CeO₂)₀.₈(SmO₁.₅)₀.₂ with Ni particle (nm or μm-sized) loading was used as the anode material. The mean diameter of SDC particles d_SDC used in this work was found to be 0.6 μm.

SDC anodes with highly dispersed nm-size Ni catalysts were prepared as follows. An SDC paste was prepared from SDC powder, a thickener (Hi-Metlose 65), a mixed aqueous solution of cerium and samarium nitrates (the same composition as the SDC), and fine polymer beads as a pore-former (d = 1.2 μm, 0.5 wt% in the paste) by mixing in a ball mill (12). Onto the YSZ surface, porous SDC anodes were prepared by screen-printing the SDC paste, followed by firing at 1150°C for 4 h. During this heat treatment, the fine polymer beads and the added nitrates decomposed to form μm-sized pores and fine SDC particles, respectively. The projected surface area of the SDC anode was 0.25 cm², and the specific mass of the SDC attached to the YSZ disk was ~6 mg/cm². Nickel particles were highly dispersed onto the SDC anode surface as in our previous work (5). The SDC anode was impregnated with Ni(NO₃)₂ solution, followed by heating in air (up to 900°C) to decompose the Ni compound. The resulting NiO particles were then reduced to Ni microcrystals in the fuel stream of the test cell at 1000°C for 1 h. The amount of Ni microcrystals thus loaded was 0.5 to 1.0 mg/cm² (about 6 to 12 vol%). Hereinafter, Ni-dispersed SDC anodes thus prepared will be denoted as dispersion-type.

For comparison, Ni-SDC cermet anodes (denoted as cermet-type) were prepared by screen-printing a mixture of NiO powder (particle size = ~1.4 μm, reagent grade, Kanto Chemicals Co.) and the SDC paste described above, followed by firing at 1150°C for 4 h.
The specific mass of (NiO + SDC) attached to the YSZ disk was ~6 mg/cm², and the projected area was 0.25 cm². The NiO particles in the layer were then reduced in the fuel stream of the test cell at 1000°C for 1 h. The amount of Ni in the cermet was 8–70 vol%.

Scanning electron microscopy (SEM) was performed to observe the microstructure and the Ni/Ce elemental distributions in the anode cross sections by an electron probe microanalysis (EPMA) using Nikon ESEM-2700 equipped with energy dispersive X-ray analyzer (EDAX CDU LEAP detector). The pore-size distribution and the pore volume in the layers were measured by a mercury pore sizer (Shimadzu, Auto-Pore 9220) (12).

Construction of the test cell was the same as in our previous work (5). A porous Pt cathode was used. Two Au wires for current supply and potential probe were contacted to an Au-mesh current collector attached to each electrode. Hydrogen gas saturated with water vapor at 30°C (P[H2O] = 0.042 atm) was introduced to the anode compartment (flow rate = 30 cm³/min, the fuel utilization = 6.5% at 1 A/cm²) and oxygen gas at atmospheric pressure was supplied to the cathode compartment at a flow rate of 30 cm³/min. The infrared (IR)-free polarization characteristics (I - E curves) of various anodes were measured by a current-interruption method using a Pt/air reference electrode at 700°C to 900°C. All the I - E curves were obtained under the steady state.

RESULTS AND DISCUSSION

Polarization Properties of Ni-Dispersed SDC and Ni-SDC Cermet Anodes

Figure 2 shows the IR-free polarization curves for the Ni-dispersed SDC anodes measured in humidified H₂ at a cell temperature of 800°C compared with the Ru-dispersed SDC anode (dashed line) (12). In our previous study, Ru showed the highest activation effect among various metal catalysts examined with the loading amount of 0.1 mg cm⁻² on the SDC (5). However, by increasing the amount of Ni catalysts to 0.50 or 0.75 mg cm⁻² in the present research, the anode showed very high performance. At an overpotential (η) of 0.1 V operated at 800°C, the current density on the Ni-dispersed SDC (0.75 mg-Ni cm⁻², 8 vol%) was 0.8 A cm⁻², which is higher than that obtained earlier at Ru-dispersed SDC anode (12). On the other hand, Ni-SDC cermet with the same 8 vol% Ni content exhibited a poor performance. In the next section we discuss why the dispersion-type and cermet-type anodes show such different performances from various viewpoints.

Microstructures of Ni-Dispersed SDC and Ni-SDC Cermet Anodes

The pore-size distribution and the pore volume in the SDC, Ni-dispersed SDC and Ni-SDC cermet were measured by a mercury pore sizer. Two different types of micropores were found in the SDC anode without Ni catalysts, i.e., primary-pore (0.1 <d <1 μm) and secondary-pore (d >10 μm). It is considered that the primary pores and the secondary pores correspond to a space within the SDC aggregates and a space between the aggregates, respectively (12). The pore-size distribution and the pore volume were scarcely changed by loading Ni particles with 8 vol% in the SDC layer, irrespective of the preparation protocols. Therefore, the gas-diffusion rates (supply of hydrogen and removal of water vapor) are not the reason for the distinct difference in the polarization...
performances between the dispersion-type and the cermet-type in Figure 2.

Figure 3 shows typical SEM images (A, B) and elemental distributions of Ni (C, D) in the cross sections of Ni-dispersed SDC (A, C) and Ni-SDC cermet (B, D), respectively. The thickness of both anodes was found to be almost the same (ca. 20 μm). Although both anodes contained the same amount of Ni (8 vol%), the distribution was different. In the dispersion-type, fairly uniform elemental distributions of Ni (Figure 3C) and Ce (not shown) were observed. The particle diameter of Ni \(d_{Ni}\) estimated from XRD was \(\approx 20\) nm. The interparticle distance \(d_{Ni-Ni}\) based on an equation using \(d_{SDC} = 0.6\) μm and densities of Ni and SDC was 22 nm (18). Thus SEM and XRD observations clearly demonstrated that Ni nanoparticles were highly dispersed over SDC particle surfaces as expected in Figure 1B. On the other hand, the \(d_{Ni}\) in the cermet-type was found to be \(\approx 0.6\) μm, and several submicron to micron-size Ni particles were segregated in the cermet (Figure 3D).

**Effect of Content and Particle Size of Ni on the Anode Performance**

The Ni content in Ni-SDC (or GDC) cermet anodes, as employed in literature (13-16), ranged from 50 vol% to 90 vol%. Then, we examine an effect of the Ni content on the properties of both the dispersion-type and the cermet-type with respect to the ohmic resistance and the output current density.

We recently clarified that the high conductivities of both oxide ions \(\sigma_{\text{ion}}\) and electrons \(\sigma_{\text{el}}\) in the SDC anode layer are very important in reducing not only the ohmic loss but also the polarization loss (6,11,12). The area-specific ohmic resistance \(R\) of the anode layer is a good measure to evaluate the effective reaction area (11,12). The value of \(R\) was estimated by measuring the ohmic resistances of two types of cells that had anodes of either \((\text{Ni} + \text{SDC})\) or Pt layers together with the same YSZ electrolyte and the same Pt cathode, i.e., \((\text{Ni}+\text{SDC})/\text{YSZ}/\text{Pt}\) and \(\text{Pt}/\text{YSZ}/\text{Pt}\), under the cell operating condition. Because the ohmic resistance of the latter cell agreed approximately with that calculated from the ionic conductivity of the YSZ itself, the ohmic resistance of Pt electrodes could be ignored. We therefore subtracted this value from the ohmic resistance of the former cell to obtain that of the \((\text{Ni} + \text{SDC})\) anode layer, which may consist of a resistance in the \((\text{Ni} + \text{SDC})\) layer and one at the interfaces of both \(\text{YSZ}/(\text{Ni} + \text{SDC})\) and \((\text{Ni} + \text{SDC})/\text{Au}\) current collector. An error in the calculation of \(R\) was less than 0.1 Ω cm\(^2\) due to a small difference in the resistances of the YSZ disks from sample to sample.

Figure 4 shows the values of \(R\) and the current densities at \(\eta = 0.1\) V as a function of the Ni content for two types of anodes. In the cermet-type with μm-sized Ni (closed symbols), the current density increased steeply at Ni content >50 vol% and the value of \(R\) decreased with increasing Ni, reaching nearly zero at Ni content >60 vol% at the cell temperature of 700° to 900°C. Thus, both the ohmic loss and the polarization loss decrease with increasing the amount of Ni in the cermet, although such a high loading may increase a possibility of sintering of Ni particles (reduction of effective reaction area) during a long-term operation.

The dispersion-type anodes (open symbols in Figure 4) with nm-sized Ni of only 6 to 8 vol% exhibited much higher current densities than those of any cermet-type anodes (even with 70 vol%) at every temperature examined. The values of \(R\) decreased with a small
amount of Ni loading and reached nearly zero with 8 vol% Ni at 800° to 900°C and with 12 vol% Ni at all temperatures. The current density showed the maximum at 8 vol% and decreased at 12 vol% at 700° to 900°C. Thus the dependence of the anode performance on the Ni content in the dispersion-type is not so simple as in the cermet-type.

These results can be explained as follows. The improvement of the anode performance by Ni dispersion indicates that the less active sites on SDC for the anodic reaction are modified by nm-sized Ni particles to form more active sites at the boundary between Ni, SDC and H₂. Hence, we presume that the predominant reaction occurs at the SDC surfaces (Figure 1B). Then the anode reaction can be envisaged to consist of two elementary steps (12):

\[ O^2-(YSZ) \rightarrow O^2-(SDC) : \text{ion transfer through the interface} \]  \[ O^2-[SDC] + H_2[SDC] \rightarrow H_2O(g) + 2 e-[SDC] : \text{electron transfer at active surface sites of SDC} \]

where \([SDC] \) represents a limited active site on SDC particle surface. \( O^2-[SDC] \), \( H_2[SDC] \), and \( e-[SDC] \) stand for the oxide ion, the adsorbed hydrogen, and the electron transferred at the active site, respectively. This is a simplified scheme as the adsorbed species of hydrogen (molecular or atomic) and the reaction intermediates are not known. When Ni catalysts are loaded, step [2] is enhanced as follows.

\[ O^2-[Ni-SDC] + H_2[Ni-SDC] \rightarrow H_2O(g) + 2 e[Ni-SDC] \]  \[ \text{where the active site, [Ni-SDC], is formed at the boundary of Ni and SDC particle surface. The circumference length } L, \text{ the part of Ni catalyst domes contacting with the SDC surface, is a measure of the number of such active sites. Because } L \text{ is proportional to } d_{Ni}^{-2}, \text{ nm-sized Ni must promote the step [3] more effectively than the } \mu \text{-m-sized one.} \]

In the cermet-type anode with high Ni content, e.g., >50 vol%, a contribution of a reaction step at Ni/YSZ electrolyte interface may increase besides steps [2] and [3]:

\[ O^2-[YSZ] + H_2[Ni-YSZ] \rightarrow H_2O(g) + 2 e[Ni-YSZ] \]

As shown in Figure 4, however, the cermet-type anode with \( \mu \)-m-sized Ni requires a larger Ni content than in the dispersion-type with nm-sized one to reduce both the ohmic loss and the polarization loss. This is because the contacting portions between the \( \mu \)-m-sized particles of Ni and SDC (or YSZ) are limited. Indeed, it was reported that the performances of Ni-SDC or Ni-GDC cermet anodes were improved by using fine Ni particles (14,16,17).

In the dispersion-type anodes with Ni-particle size of \( d_{Ni} = 20 \) nm on the SDC, the interparticle distances \( d_{Ni-Ni} \) were calculated to be 27, 22, and 19 nm for 6, 8, and 12 vol% Ni, respectively. The increase in output current density with increasing Ni content from 6 to 8 vol% certainly reflects the increase in \( L \). The experimental result of \( R = 0 \) at 12 vol% Ni loading indicates that Ni particles on the SDC surface can contact with each other at \( d_{Ni-Ni} \). Because \( \sigma_{on} \) and \( \sigma_{e} \) in the SDC are sufficiently high at high temperatures (800° to 900°C) in humidified H₂, negligibly small \( R \) could be obtained at 8 vol% (see Figure 4B) even if Ni nanoparticles cannot directly contact in the layer. However, the
number of electroactive sites [Ni-SDC] at the boundary of Ni particles and the SDC surface might rather decrease by increasing Ni content further even though the electronic network becomes perfect.

CONCLUSIONS

The present study showed that the performance of a mixed conducting samaria-doped ceria (SDC) anode was significantly enhanced with highly dispersed nm-sized Ni catalysts of only 8 vol% loading at low operating temperature around 800°C. The current density on the Ni-dispersed SDC anode at an overpotential of 0.1 V was 0.8 A/cm² at 800°C in humidified H₂. Highly dispersed nm-sized Ni catalysts enhanced the reaction area (contact portion with SDC) more effectively than μm-sized Ni in the cermet-type anode, resulting in noticeable reduction of the Ni content required for lowering both the ohmic loss and the polarization loss.

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Figure 1. Schematic concepts of anode reaction in SOFCs using conventional Ni-YSZ anode (A) and catalyzed-anode layer (B).
Figure 2. Polarization curves (IR-free, measured in humidified H₂) of Ni-dispersed SDC, Ru-dispersed SDC (0.1 mg-Ru cm⁻², dashed line) (12), and 8 vol% Ni-SDC cermet anodes at 800°C. The dispersions of Ni catalysts with 0.50 mg cm⁻² and 0.75 mg cm⁻² correspond to 6 and 8 vol%, respectively.

Figure 3. SEM images (A, B) and elemental distributions of Ni (C, D) in the cross sections of Ni-dispersed SDC (A, C) and Ni-SDC cermet (B, D).
Figure 4. Changes of current densities at $\eta = 0.1$ V (IR-free) (A) and area-specific ohmic resistances, $R$ (B) as a function of Ni content at Ni-dispersed SDC (open symbols) and Ni-SDC cermet anodes (closed symbols).