HIGH-PERFORMANCE ELECTRODE FOR MEDIUM-TEMPERATURE SOLID OXIDE FUEL CELLS
ACTIVATION OF YTTRIA-DOPED CERIA ANODE
WITH HIGHLY DISPERSED Ru ELECTROCATALYST

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ABSTRACT

Yttria-doped ceria (YDC), which shows a high electronic conductivity
and a moderate ionic conductivity, was examined as an anode material for
medium-temperature SOFCs. In order to enhance gas-diffusion rates in the
YDC anode, additional μm-sized pores were introduced by sintering a
YDC paste containing fine polymer beads (d = 1.2 μm), coated on an
yttria-stabilized zirconia electrolyte. Sintering of the YDC anode at
1250°C remarkably lowered both the IR-free overpotential and the ohmic
resistance. The performance of the YDC anode was appreciably enhanced
by highly dispersed Ru catalyst, especially at low operating temperature.
The current density on the Ru (0.1 mg/cm²)-YDC anode at an
overpotential of 0.1 V was 0.4 A/cm² at 800°C in humidified H₂.

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. However, two major obstacles must be solved to operate
medium-temperature SOFCs. The first is to reduce ohmic loss in the solid electrolyte (1-7). Secondly, it is essential to develop high performance electrodes because the electrode reaction rates slow down at such temperatures.

We have developed a porous catalyzed-reaction layer for medium-temperature
SOFCs (8). Mixed conducting oxide particles, samaria-doped ceria [(CeO₂)₀.₈(SmO₁₅)₀.₂,
denoted as SDC] for the anode and La(Sr)MnO₃ (LSM) for the cathode, were employed
in combination with highly dispersed (nanometer-sized) metal electrocatalysts on their
surfaces. Ru-dispersed SDC and Pt- (or Pt-Rh-) dispersed LSM exhibited fairly high
performances at 800°C (8-10). Both the overpotential and the ohmic resistance of SDC
anodes and LSM cathodes were appreciably lowered by controlling their microstructures
(11-14). The performances of SDC anode and LSM cathode with optimized
microstructures were enhanced further with nm-sized Ru and Pt electrocatalysts,
respectively. We expect to achieve still higher performance by using catalyzed-reaction
layer of other mixed-conducting materials with higher activity than LSM or SDC.

For example, La(Sr)CoO₃ (LSC) is known to exhibit a higher cathodic performance
than LSM (2, 15, 16). However, LSC tends to react easier with yttria-stabilized zirconia
(YSZ) electrolyte than LSM at high temperatures (>1000°C) (2, 16). We have recently reported that a thin and dense SDC interlayer was effective to avoid unfavorable solid-state reactions between LSC and YSZ (17, 18). Control of the microstructure of LSC cathode appreciably lowered the IR-free overpotential without an increase of the ohmic resistance (19). The cathode performance was enhanced further with highly dispersed Pt catalysts at 3 wt% loading, especially at low operating temperatures. The current density on the Pt-LSC cathode at an overpotential of -0.05 V was 1 A/cm² at 800°C in air.

The next target is to enhance the anode performance by employing other mixed-conducting materials with higher activity than SDC. The mixed conduction in doped ceria depends on the kind and the concentration of dopant. As shown in Fig. 1, in SDC at 800°C, the ionic conductivity (σ_{ion}) is dominant in a high oxygen partial pressure region P[O₂] > 10¹⁰ atm, and n-type electronic conductivity (σ_e) increases with decreasing P[O₂] (20). Indeed, the good anode performance of the SDC was ascribed to high σ_{ion} and σ_e at low P[O₂] region (9, 11). Yttria-doped ceria (YDC) exhibits about 3 times higher σ_e than that of SDC, while its σ_{ion} is moderate, i.e., it is lower than that of SDC but is comparable to that of 8 mol% YSZ (20). The high σ_e (> 10 S cm⁻¹ at 800°C) in the YDC anode is expected to reduce the ohmic loss and, probably, the overpotential even at high fuel utilization (e.g., 70 % or more) in SOFCs. Furthermore, Y₂O₃ is cheaper than Sm₂O₃. In this paper, we focus on the effects of σ_{ion} and σ_e in the mixed-conducting ceria (YDC and SDC) on the anode performance. It is shown that the porous YDC anode exhibited high performance even at 800°C and its performance was enhanced further by Ru-electrocatalysts loaded on the surface.

**EXPERIMENTAL**

An 8 mol% yttria-stabilized zirconia disk (YSZ, diameter: 13 mm, thickness: 1 mm) was used as the solid electrolyte. Yttria-doped ceria (CeO₂)₁₋ₓ(YO₁.₅)ₓ (X =0.2 or 0.3) compounds with and without Ru particle loading were used as the anode material. Raw YDC powder was synthesized by a solid-state reaction of reagent-grade CeCl₃ and Y₂O₃. The finely ground YDC powders were sieved and their particle size distribution was determined by a laser scattering particle-size analyzer. The mean diameter of YDC particles used in this work was found to be 0.4 μm. A YDC paste was prepared from YDC powder, a thickener (Hi-Metlose 65), a mixed aqueous solution of cerium and yttrium nitrates (the same composition as the YDC), and fine polymer beads as a pore-former (d = 1.2 μm, 0.5 wt% in the paste) by mixing in a ball mill. Onto the YSZ surface, porous YDC anodes were prepared by screen-printing the YDC paste, followed by firing at 1150°C or 1250°C for 4 h. During this heat treatment, the fine polymer beads and the added nitrates decomposed to form μm-sized pores and fine YDC particles (< 1 μm), respectively. The projected surface area of the YDC anode was 0.25 cm² and the specific mass of the YDC attached to the YSZ disk was about 3 mg/cm².

Scanning electron microscopy was performed to observe the microstructure of the YDC anode. The pore-size distribution and the pore volume in the YDC layer were measured by a mercury pore sizer (Shimadzu, Auto-Pore 9220) (12). Ruthenium particles were highly dispersed onto the YDC anode surface in the same manner as our previous work (12). The YDC anode was impregnated with RuCl₃ solution, followed by heating at
600°C for 0.5 h in air to decompose the Ru compound. The resulting RuOx particles were then reduced to Ru microcrystals in the fuel stream of the test cell. The amount of Ru microcrystals thus loaded was 0.1 mg/cm² (about 3 wt%).

Construction of test cell was the same as in our previous work (8). A porous Pt cathode was used. Two Au wires for current supply and potential probe were contacted to a 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 IR-free polarization characteristics (I - E curves) of YDC anodes were measured by a current-interruption method using a Pt/air reference electrode at 800 to 1000°C. All the I - E curves were obtained under the steady state.

RESULTS AND DISCUSSION

Microstructure and Pore-Size Distribution in YDC Layer

Ceria-based materials show a relatively high isothermal lattice expansion upon reduction (21). Because the lattice expansion decreases with increasing dopant concentration, we mainly examined properties of highly doped YDC (X=0.3) in this work. However, an application of a buffer layer with a ceria-zirconia composition gradient on the YSZ electrolyte surface may relax this problem. In such a case, the use of YDC as the anode material is favorable to control the composition of the buffer layer compared with the case of SDC.

First, we examined changes in the microstructure of YDC layers sintered at 1150°C (denoted as YDC1150) and 1250°C (denoted as YDC1250) by SEM. At YDC1150, a porous layer with a thickness of ca. 18 µm was formed. Micropores were uniformly formed in the layers by the pore-former, and a feature was very similar to that for SDC prepared under the same condition (12). At YDC1250, YDC particles were sintered well, giving a porous layer with a thickness of ca. 15 µm. Then, we characterized the pore-size distribution and pore volume of YDC layer. Figure 2 shows integration curves of pore volumes per unit weight of YDC and SDC layers as a function of pore diameter, d. Both layers were sintered at 1150°C for 4 h. Two different types of micropores were found in both YDC and SDC layers, i.e., primary pores with a pore diameter between 0.2 and 1 µm and secondary pores (d > 10 µm). It is believed that the primary pores and the secondary pores correspond to space within the oxide aggregates and space between the aggregates, respectively. The volume of the primary pores, Vprim (d ≤ 1 µm), and that of secondary pores, Vsec (d > 1 µm), were calculated for each layer. These values are summarized in Table I. It was found that the Vprim in YDC is about two-times larger than that of SDC. The value of Vsec in YDC also increased by 18% compared with that of SDC. Therefore, the sinterability of YDC is lower than that of SDC.

Polarization Properties of YDC Anodes

Figure 3 shows the IR-free polarization curves for the YDC anodes (YDC1150 and YDC1250) measured in humidified H₂ in comparison with that for the SDC anode.
(sintered at 1150°C, cited from ref. 12). At the cell temperature of 1000°C, both YDC1150 and YDC1250 showed smaller IR-free overpotential (η) than that on the SDC anode. By lowering the cell temperature, the overpotential on YDC1150 anode increased significantly. In contrast, YDC1250 anode still showed higher performance than that of SDC at 800 and 900°C. As a measure of an electrocatalytic activity of each anode at low cell temperature of 800°C, the current density at η = 0.1 V on each anode is shown in Fig. 4A. The difference in the anode activities is markedly seen in the order YDC1250 > SDC > YDC1150.

Next, we discuss why three anodes show such different activities at 1000 to 800°C. We have recently clarified that the high conductivities of both oxide ions (σion) and electrons (σe) in the SDC anode layer are very important in reducing not only the ohmic loss but also the polarization loss (9, 11). The area-specific ohmic resistance (R) of the anode layer is a good measure to evaluate the effective reaction area. The value of R was estimated by measuring the ohmic resistances of two types of cells, which had anodes of either doped-ceria or Pt layers together with the same YSZ electrolyte and the same Pt cathode, i.e., Ceria/YSZ/Pt and Pt/YSZ/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 ceria anode layer, which may consist of a resistance in the ceria layer and one at the interfaces of both YSZ/ceria and ceria/Au current collector. However, a small difference in the resistances of the YSZ disks from sample to sample caused an error (about 0.1 Ω cm²) in the calculation of R.

At the cell temperature of 1000°C, the values of R at all the anodes were found to be negligibly small (< 0.1 Ω cm²). However, as shown in Fig. 4B, the R of YDC1150 at 800°C is very large, whereas that of YDC1250 or SDC is negligibly small (calculation error level). As reported before (12), the area-specific ohmic resistance for a SDC layer with a thickness of 20 μm and 75 % porosity is calculated to be only 0.0025 Ω cm² at 800°C in humidified H2. The area-specific ohmic resistance for a porous YDC layer is also negligibly small because of its higher total conductivity than SDC. This indicates that a contact resistance between ceria particles and one at the interface of YSZ/ceria were dominant in the values of R. Hence, when sintered at 1150°C, the electrical contact between YDC particles was not sufficient, which results from low sinterability of YDC described in the previous section.

Polarization behaviors at YDC and SDC anodes shown in Fig. 3 can be explained as follows. As discussed earlier (12, 22), the hydrogen oxidation reaction at the doped-ceria anode can be envisaged to consist of two elementary steps;

\[ \text{O}_2(\text{zirconia}) \rightarrow \text{O}_2(\text{ceria}) : \text{ion transfer through the interface} \quad [1] \]

\[ \text{O}_2^{\ast}[\text{ceria}] + \text{H}_2^{\ast}[\text{ceria}] \rightarrow \text{H}_2\text{O}(g) + 2 e^{\ast}[\text{ceria}] : \text{electron transfer at active surface sites of doped-ceria} \quad [2] \]

In step [2], O2[ceria*], H2[ceria*], and e*[ceria*] stand for the oxide ion, the adsorbed hydrogen, and an electron transferred at an active site on the ceria (YDC or SDC) surface,
respectively. At the high temperature of 1000°C, a large fraction of the YDC and SDC particle surface in the anode can work effectively, because $\sigma_{\text{ion}}$ and $\sigma_e$ in these oxides under a hydrogen atmosphere are very high (20) and the $R$ values of the anode layers are indeed low enough. An increase in the ohmic resistance of the ceria layer presumably reduces the effective reaction area. Higher performance of YDC1250 than that of YDC1150, especially at 800 and 900°C, can be ascribed to larger effective reaction area, because of very small $R$ value at YDC1250. On the other hand, in spite of the similar $R$ values, the activity of YDC1250 is higher than that of SDC at 800 to 1000°C (see Fig. 3 and 4). It is noted that YDC1150 with very low $R$ at 1000°C also showed higher performance than SDC. As described above, the $\sigma_e$ of YDC is remarkably high compared with that of SDC, whereas YDC exhibits lower $\sigma_{\text{ion}}$ than that of SDC. Hence, it is clear that high electronic conductivity in the mixed conducting YDC plays an important role to enhance the anode reaction rate, probably in step [2].

**Activation of YDC Anode by Loading Highly Dispersed Ru Catalysts**

In order to activate YDC1250 anode, Ru catalysts were highly dispersed on its surface (0.1 mg/cm², 3wt%). In this case, step [2] is enhanced as follows.

$$\text{O}^2\text{[Ru-ceria]} + \text{H}_2\text{[Ru-ceria]} \rightarrow \text{H}_2\text{O(g)} + 2 \text{ e}^\text{[Ru-ceria]} [3]$$

where the active site, [Ru-ceria], is formed at the boundary of Ru catalyst and the doped ceria surface. Figure 5 shows IR-free polarization curves for the YDC1250 with and without Ru catalysts in comparison with that for Ru-SDC (cited from ref. 12). Ru loading appreciably enhances the performance of the YDC anode especially at a low operating temperature. The current density at $\eta = 0.1$ V was 0.4 A/cm² at 800°C, which is 1.6 times higher than that without Ru catalysts. The performance of Ru-YDC is almost comparable to that of Ru-SDC at 800°C. This is probably because the activity of Ru catalysts is much higher than that of the reaction sites on the ceria ([ceria*] in step [2], ceria = YDC or SDC) especially at low-temperature operation about 800°C.

The performance test of YDC anode under various fuel utilization conditions and a long-term stability test are in progress.

**CONCLUSIONS**

The porous YDC anode, which was sintered at 1250°C, exhibited higher performance than that of SDC at the operating temperature of 800°C to 1000°C. High electronic conductivity in the mixed conducting YDC appreciably contributes to enhancing the anode reaction rate. The microstructure control in the YDC anode layer is important in increasing the (electronic + ionic) conduction and the gas diffusion rate, resulting in an enlarged effective reaction area. Highly dispersed Ru catalysts effectively enhanced the performance of the YDC anode.
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Figure 1. Electrical conductivities of SDC ($\text{CeO}_2)_{0.8}(\text{SmO}_1.5)_{0.2}$ and YDC ($\text{CeO}_2)_{0.8}(\text{YO}_1.3)_{0.2}$ as a function of oxygen partial pressure $P[\text{O}_2]$ at 800°C. Equilibrium $P[\text{O}_2]$ values corresponding to H$_2$-fuel utilization ($U_F$) of 70% (in practical SOFCs) and 6.5% (experimental condition in this work) are shown by dotted lines.

Figure 2. Integration curves of pore volumes per unit weight of YDC (X=0.3) and SDC layers sintered at 1150°C as a function of pore diameter, $d$.

Table I. Pore volumes in YDC (X=0.3) and SDC layers sintered at 1150°C.

|          | $V_{\text{sec}}$ ($d > 1 \ \mu\text{m}$) | $V_{\text{prim}}$ ($d \leq 1 \ \mu\text{m}$) |
|----------|----------------------------------------|------------------------------------------|
| YDC      | 0.33                                   | 0.29                                     |
| SDC      | 0.28                                   | 0.13                                     |
Figure 3. Polarization curves (IR-free, measured in humidified H₂) for YDC1150, YDC1250, and SDC anodes. Data for SDC are cited from ref. 12.
Figure 4. (A) Comparison of current densities on YDC1150, YDC1250 and SDC anodes at $\eta = 0.1$ V (IR-free) operated at 800°C. (B) Area-specific ohmic resistance, $R$, of three anode layers at 800°C.

Figure 5. Polarization curves (IR-free, measured in humidified H$_2$) for YDC1250, Ru-catalyzed YDC1250, and Ru-SDC anodes. Data for Ru-SDC are cited from ref. 12.