HIGH PERFORMANCE CATALYZED-REACTION LAYER FOR MEDIUM TEMPERATURE OPERATING SOLID OXIDE FUEL CELLS

III. EFFECTS OF COMPOSITION AND MORPHOLOGY ON PERFORMANCE OF ANODE AND CATHODE LAYERS

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ABSTRACT

Polarization properties of catalyzed-reaction layers, which we developed for medium temperature operating SOFC, were greatly improved by controlling their compositions and microstructures. The amount of Pt catalysts loaded on Sr–doped LaMnO$_3$ (LSM) cathode was reduced down to 1/5 by decreasing size of Pt particles. A large depolarizing effect was observed on the Pt-catalyzed LSM cathode, especially at high current densities. The anodic overpotential for the samaria-doped ceria (SDC) layer was appreciably lowered by applying both highly dispersed Ru microcrystals and 0.1µm-sized SDC particles onto the SDC layer.

INTRODUCTION

It is desirable to operate solid oxide fuel cells (SOFCs) at a medium temperature around 800°C, since the operation at lower temperature has many advantages such as a decrease in degradation of the constructing materials, shorter start-up, and wide choice of materials including metals rather than ceramics, etc. Preparation of thin film zirconia electrolyte or novel solid electrolytes with higher ionic conductivity is required to reduce the ohmic resistance. Besides these efforts, it is very important to develop high performance electrodes because the electrode reaction rates at both the anode and cathode must decrease in such temperature region.

We have proposed a new concept, "catalyzed-reaction layer", which realizes high performance anode and cathode for medium temperature operating SOFCs (1–4). As shown in Fig. 1 (c), mixed conducting oxide particles, samaria–doped ceria (SDC), were employed as the anode material in cooperation with highly dispersed noble metal catalysts on their surface. The use of mixed conducting anode results in an enlarged effective reaction zone beyond the physical triple phase boundary. Extremely electroactive catalysts loaded on the oxide surface certainly activate the anodic process at the boundary. We demonstrated that the anodic polarization resistance and its activation energy were greatly decreased by loading only a small amount of catalysts.
such as Ru, Rh, Ir, and Pt onto the SDC particles in SOFCs using H2 or gas mixture containing H2, CO2, and H2O (SG). Ru– or Ir–dispersed SDC exhibited high catalytic activities in steam reforming of methane (3), indicating their excellent potential for the application of internal reforming–type SOFC. Based on a similar concept as the anode, La(Sr)MnO3 cathode was catalyzed with Pt microcrystals as shown in Fig. 1 (d). A great depolarizing effect was also observed on Pt–catalyzed La(Sr)MnO3 cathode.

In this paper, we investigated effects of compositions and microstructures of the catalyzed–reaction layers on their performances. It is shown that the catalyzed reaction layers exhibit excellent performances by controlling such properties.

EXPERIMENTAL

A test fuel cell was constructed by using a sintered disk of 8 mol% yttria stabilized zirconia (YSZ, diameter: 13 mm, thickness: 1 mm) as the solid electrolyte (2);

Cell I : H2 + H2O (P[H2O] = 0.042 atm), catalyzed anode | YSZ | Pt, O2 (1 atm)

Cell II : Air, Pt | YSZ | catalyzed cathode, O2 (1 atm)

Samaria doped ceria (CeO2)1−x(SmO1.5)x (X = 0 ~ 0.4, denoted as SDC) with and without loading microcrystalline Ru catalyst was used as the anode in Cell I. The SDC was prepared from cerium and samarium nitrates by the same manner as in Ref. 3. The SDC powders with the mean diameter of 0.2 ~ 0.3 μm were used. A slurry of SDC was smeared on the surface of YSZ disk (projected area : 0.25 cm², thickness : 20 – 30 μm) and baked at 1050°C for 4 h, resulting in a sintered SDC layer of d = ca. 5 μm. On the SDC anode, microcrystalline Ru catalysts were dispersed by impregnating RuCl3 aqueous solution, followed by heating at 600°C in air. The cathode material used in Cell II was a perovskite–type oxide powder of (La0.85Sr0.15)0.9MnO3−δ (denoted as LSM), where δ is the number of oxygen deficiencies per unit cell, with and without loading microcrystalline Pt catalysts. A slurry of LSM (d = 3.8 μm) was smeared on the surface of YSZ disk (projected area : 0.25 cm², thickness : ca. 50 μm) and baked at 1000°C for 4 h. Microcrystalline Pt catalyst was dispersed on the LSM layer by impregnating either H2PtCl6 or [Pt(NH3)4]Cl2 aqueous solution, followed by heating at 1000°C for 1 h in air. Porous Pt electrode was attached as the counter electrode (cathode for Cell I, anode for Cell II). A gold wire was wound around the lateral of the disk as a reference electrode which indicated a reversible potential of oxygen in air. The anode and cathode compartments were separated by the YSZ electrolyte and each compartment was sealed by a glass ring gasket. The polarization characteristics of the electrodes (IR free) were measured by a current–interruption method at 800 ~ 1000°C.
RESULTS AND DISCUSSION

Effect of Microcrystalline Size of Pt Catalysts Loaded on LSM Cathode

We have reported that the electrocatalytic activity of LSM is remarkably enhanced by loading Pt catalysts with 0.5 mg/cm² (ca. 1.25 wt%) especially at high current density region, where the source of Pt catalysts was an impregnated H₂PtCl₆ (2). In order to clarify the size–effect of metal catalysts on the LSM, we evaluated the average diameter of Pt particles loaded on LSM from the full width at half maximum (FWHM) of the X–ray diffraction (XRD) peaks. The average diameter of Pt was ca. 40 nm; Pt particles were larger than we expected. With regard to the size–effect of metal catalysts dispersed on the mixed conducting support in the electrode reaction, we can expect as follows. Let us consider that the catalyst microcrystals with a mean diameter d are embedded in the hemispherical shape on the mixed conductor, i.e. ultra–fine domes on the support. When metal microcrystals exhibits extremely high electrocatalytic activity, they certainly activate the electrode reaction at the boundary. The circumference length per unit area, L, the part of catalyst domes contacting with the support, is a measure of such a highly activated boundary. Since L is proportional to $d^{-2}$, the size–effect of the catalyst must dramatically appear on the electrode reaction when the rate–determining step occurs in that boundary region.

Based on this consideration, we attempted to make the Pt particles smaller by using [Pt(NH₃)₄]Cl₂ (denoted as Pt–A) in place of H₂PtCl₆ (Pt–C) as the Pt source. The former Pt–complex (Pt–A) probably has a strong interaction with OH groups of oxide surfaces and, hence, is widely used in the preparation of conventional Pt–loaded oxide catalysts. Figure 2 shows polarization curves of LSM cathodes at 800°C without and with Pt catalysts (0.1 mg/cm² or 0.5 mg/cm²) prepared by impregnation of Pt–C or Pt–A. A significant overpotential was seen for LSM without catalysts. Platinum catalysts loaded on LSM exhibited no effect on the cathode performance in the low current density less than 0.1 A/cm², but exhibited a significant effect on the polarization in the high current region. It is seen that the performance of LSM is improved with increasing amount of Pt from 0.1 to 0.5 mg/cm², in the case of Pt–C. However, the LSM cathode loaded with 0.1 mg/cm² (0.25 wt%) of Pt, prepared from Pt–A, exhibited a comparable performance with that loaded with 0.5 mg/cm² Pt, prepared from Pt–C. It was found that the average diameter of Pt particles in the former was 30 nm, smaller than that of the latter (40 nm), indicating that use of [Pt(NH₃)₄]Cl₂ was effective to suppress aggregation of Pt particles on LSM. Although the particle size of Pt prepared from Pt–A is smaller than that of Pt–C by a factor of 3/4, the loading amount of Pt on LSM to obtain almost same performance is reduced down to as small as 1/5. This strongly supports our consideration on the size–effect of loaded catalysts that activate the cathodic reaction at the boundary between Pt and LSM. Judging from the extent of the activation effect, much smaller Pt particles, which were not detected by XRD, might be produced on LSM.
with the use of Pt-A. As the rate-determining step at a high current density region, it is possible to consider the dissociation of O₂ molecules (5) and/or the sequential reaction between oxygen atoms and oxygen vacancies in the LSM at the boundary, although such processes are in quasi-equilibrium at low current density where Pt catalysts showed no effect. Anyhow, the present results indicate that much higher performances can be expected by loading only a small amount of nm-sized ultra-fine Pt particles on LSM.

Since the cathodic performance of Pt-catalyzed LSM shown in Fig. 2 is still not a practically acceptable level, we are currently optimizing the morphology of LSM layer itself. In our preliminary experiments, the performance of uncatalyzed-LSM cathode was improved greatly by increasing the porosity to allow easier gas-diffusion through the layer.

**Activation of SDC Anode**

As reported previously (2), the polarization properties of SDC anodes with and without catalysts are greatly affected by the size (or morphology) of both particles of SDC-support and catalyst microcrystals. First, we examined effects of composition and morphology of the uncatalyzed-SDC on their polarization properties.

**Effect of Composition of SDC Powder.** The polarization properties of SDC anodes with a composition of (CeO₂)₁₋ₓ(SmO₁₅)ₓ were tested. Figure 3 shows current densities at the overpotential of 0.1 V as a function of the composition, X. The performance of the SDC anode depends strongly on the composition, and the maximum current density is obtained at X = 0.2, i.e. (CeO₂)₀.₈(SmO₁₅)₀.₂ at 800 ~ 1000°C. This dependency is ascribed to the conductivity of SDC; the SDC of X = 0.2 exhibits the highest conductivities of both oxide ion (σ_{ion}) and electron (σ_{e}) at 800~1000°C under hydrogen atmosphere (6). We have already reported that very high performance of the catalyzed-SDC anode can be obtained by using fuel gas with appropriate P[O₂] so as to give high values of both σ_{ion} and σ_{e} in SDC with X = 0.2 (4). The present result is consistent with this, and indicates that a good mixed conducting property (high σ_{ion} and σ_{e}) of the anode-layer is essential to achieve the high performance. Hereinafter, we adopted the SDC with this composition as the anode material.

**Effect of Microstructure of SDC Particles.** In order to reduce the ionic and electronic resistances both within the SDC layer and at the electrolyte interface, it may be effective to use a dense SDC layer. However, the gas-diffusion becomes worse in such a dense SDC-layer. Then, we examined to modify SDC surfaces. The SDC powders (d = 0.2~0.3 μm) were impregnated with aqueous solution of cerium and samarium nitrates having the same composition as stated above, followed by heat treatment at 400°C for 2 h. Thus, SDC microcrystals were dispersed on original SDC powders, the amount of which was 2.4 wt%. The modified SDC powders were sintered on YSZ as the anode.
Observations of SDC layers by scanning electron microscope showed that a lot of fine SDC particles smaller than 0.1 μm were dispersed on sintered SDC support (d = ca. 5 μm), while such fine particles were scarcely seen for unmodified-SDC layer. Figure 4 shows the polarization curves of SDC anodes with and without attaching fine SDC particles on the surface. The polarization loss obviously decreases by the surface modification. Two major factors contribute to this improvement. As observed by SEM, attached fine SDC particles enhanced the effective surface area of the anode layer. The second reason is that the contact resistance between the anode and the YSZ electrolyte was lowered, which was confirmed by an impedance measurement. Thus, as we expected, the performance of the SDC anode without metal catalysts was improved by controlling the surface structure.

Activation of SDC Anodes by Loading Ru Micro-catalysts. In order to improve the performance of the SDC anode with the surface modification, Ru microcrystals were dispersed on them. Figure 5 shows a comparison of current densities on SDC anodes with and without loading Ru microcrystalline catalysts in H₂ at the potential of −0.9 V vs the air reference electrode. This potential corresponds to a terminal voltage of 0.9 V for the SOFC in which both the ohmic loss of the cell and polarization loss at the air cathode are excluded. As described above, the SDC anode without catalysts exhibited a good performance at 1000°C, but the current density dramatically decreased below 900°C. In such a temperature range, a depolarizing effect given by Ru-catalysts became remarkable, indicating that the catalyzed-reaction zone is effective to improve the performance at medium temperatures. At 800°C, the current density on the SDC anode with Ru catalyst of 0.5 mg/cm² (1.25 wt%) was 5 times higher than that on uncatalyzed SDC. It is also expected that higher performance of the catalyzed-SDC anode can be obtained by using fuel gas with appropriate P(O₂) so as to give high σ_oh and σ_e in SDC (4); the optimum P(O₂) corresponds to hydrogen gas saturated with water at about 35°C. Hence, the catalyzed SDC is a very promising anode for SOFCs operating at medium temperatures. Furthermore, there is still some room for improvement in the performances. For example, as shown in Fig. 5, when the SDC powders prepared by the solid-state reaction (d = 1.6 μm) were used as the anode material and Ru catalysts were dispersed on the surface with 0.1 mg/cm², the current density even at 800°C (0.56 A/cm²) was higher than that obtained at 900°C for the Ru-SDC (0.5 mg/cm²) prepared from nitrates. So, the amount of Ru catalyst is decreased by changing a kind of SDC powders. We consider that this may be ascribed to a difference in the structures of the SDC layer or distribution states of Ru catalysts on the SDC, similar to that noted in the Pt-catalyzed LSM cathode. Optimization of the structure of the catalyzed-SDC anode layers are under progress.

CONCLUSIONS

Catalyzed-reaction layers worked effectively in the medium temperature operating
SOFC with YSZ solid electrolytes. Polarization properties of the catalyzed-anode and cathode were greatly improved by controlling their compositions and microstructures. The amount of Pt-catalysts loaded on Sr-doped LaMnO₃ (LSM) cathode was reduced down to 1/5 by decreasing size of Pt particles with the use of [Pt(NH₃)₄]Cl₂ as the Pt source in place of H₂PtCl₆. A large depolarizing effect was observed on the Pt-catalyzed LSM cathode (Pt loading = 0.1 mg/cm², 0.25 wt%), especially at high current densities. The anodic overpotential for the samaria-doped ceria (SDC) layer was appreciably lowered by applying both highly dispersed Ru microcrystals and 0.1µm-sized SDC fine particles onto the SDC layer. The amount of Ru-catalysts loaded on SDC anode was also reduced by changing a kind of SDC powders, which might have appropriate surface structures.

We have found that high ionic conductivity in the oxide electrolyte reduces not only the ohmic loss but also the polarization loss at Pt anode at 800 ~ 1000°C, at Pt cathode at 800°C, and at uncatalyzed-SDC anode at 800°C (7). Therefore, a combination of the solid electrolyte having high ionic conductivity with high performance catalyzed-reaction layers is effective to improve the performance of SOFC operating at medium temperature.

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Figure 1. Schematic illustrations of electrode reactions in SOFC using conventional type Ni-YSZ cermet anode (a), LSM cathode (b), and catalyzed reaction layers in our work (c) and (d).
Figure 2. Polarization curves (IR free) of LSM cathode without (○) and with (●, □, △) loading Pt micro-catalysts at 800°C in oxygen atmosphere (Cell II). LSM particle size = 3.8 μm. Amount of Pt catalyst; ●: 0.5 mg/cm² (from Pt–C), △: 0.1 mg/cm² (from Pt–C), □: 0.1 mg/cm² (from Pt–A).

Figure 3. Plots of current density at the overpotential of 0.1 V (IR free) for SDC anode, (CeO₂)₁₋ₓ(SmO₁.5)ₓ, as a function of composition X in wet H₂ (Cell I). Pure SDC without metal catalysts was used.
Figure 4. Polarization curves (IR free) of SDC (X = 0.2) anode without (○, △) and with (●, ▲) modifying the surface with fine SDC particles in H₂ (Cell I). ○, ● : 800°C, △, ▲ : 1000°C. The inset illustrates the surface modification of SDC schematically.

Figure 5. Comparison of current densities on surface-modified SDC anode with and without loading Ru microcrystalline catalysts in H₂ (Cell I) at the potential of -0.9 V vs air reference electrode (IR free). SDC(ss) was prepared from solid-state reaction, and others were from nitrates.