High-Performance Electrodes for Medium-Temperature Solid Oxide Fuel Cells – Mixed Conducting Ceria-Based Anode with Highly-Dispersed Ni Electrocatalysts

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

We have developed a porous catalyzed-reaction layer for medium-temperature SOFCs.[1-4] For the anode, mixed conducting samaria-doped ceria [$(CeO_2)_{0.8}(SmO_{1.5})_{0.2}$, denoted as SDC] was employed in combination with nanometer-sized Ru catalysts (< 1 vol%) on the surface.

In this paper, we show an activation of the SDC anode with highly dispersed (nm-sized, 6 to 8 vol%) nickel electrocatalyst, which is more practical than Ru used so far. We also compare the Ni-dispersed SDC with Ni-SDC cermet anodes (μm-sized Ni with > 50 vol%), which were recently employed in medium-temperature SOFCs.

Onto an 8 mol% YSZ electrolyte disk, porous SDC anodes were prepared by screen-printing a SDC paste, followed by firing at 1150°C for 4 h.[4] The SDC anode was impregnated with $Ni(NO_3)_2$ solution, followed by heating to 900°C in air. 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 thus loaded was 0.5 to 1.0 mg/cm^2 (about 6 to 12 vol%). Ni-SDC cermet-type anodes were prepared by screen-printing a mixture of NiO powder (d = 1.4 μm) and the SDC paste described above, followed by firing at 1150°C for 4 h. The NiO particles in the layer were then reduced in the same manner as described above. The Ni content in the cermet was 8 to 70 vol%. The steady state IR-free polarization characteristics of the anodes in humidified H_2 ($P[H_2O]$ = 0.042 atm) were measured by a current-interruption method in a three-electrode configuration (with Pt cathode and Pt/air reference electrode).

Figure 1 shows the IR-free polarization curves for the Ni-dispersed SDC anodes in humidified H_2 at the cell temperature of 800°C in comparison with that for the Ru-dispersed SDC anode (dashed line). 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.[1] However, by increasing the amount to 0.50 or 0.75 mg cm^{-2} in the present research, Ni catalysts 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}. On the other hand, Ni-SDC cermet exhibited a poor performance in spite of using the same Ni content as that in the dispersion-type. SEM, EDX, and XRD analyses indicated that Ni nanoparticles of 20 nm were highly dispersed over SDC particle surface in the dispersion-type, whereas submicron to micron-size Ni particles were segregated in the cermet.

The Ni content in Ni-SDC (or GDC) cermet anodes employed in literatures ranged from 50 vol% to 90 vol%. At our cermet anodes, indeed, the current density at η = 0.1 V increased steeply at Ni content > 50 vol% and the ohmic resistance (R) decreased with increasing Ni, reaching nearly zero at Ni content > 60 vol% at 700 to 900°C.

It is noted that the dispersion-type anodes with nm-sized Ni of only 6 to 8 vol% exhibited much higher current densities than those of any cermet-type at every temperature examined. The values of R reached nearly zero with 8 vol% Ni at 800 to 900°C and with 12 vol% at all temperatures. The current density, however, showed the maximum at 8 vol% and decreased at 12 vol% at 700 to 900°C.

These results can be explained as follows. The improvement of the anode performance by Ni dispersion indicates that very active site, [Ni-SDC], is formed at the boundary of Ni and the SDC surface.

$$O^{2-}[\text{Ni-SDC}]+H_2[\text{Ni-SDC}] \rightarrow H_2O(g) + 2\,e^-[\text{Ni-SDC}] \quad [1]$$

The circumference length L, the part of Ni catalyst domes contacting with the SDC surface, is a measure of the number of such active sites. Since L is proportional to d_{Ni}^{-2}, nm-sized Ni must promote the reaction [1] more effectively than the μm-sized one. In the dispersion-type anodes with Ni-particle size of d_{Ni} = 20 nm on the SDC, the interparticle distances $d_{Ni\text{-}Ni}$ were calculated to be 27 nm, 22 nm, and 19 nm for 6, 8, and 12 vol% Ni, respectively. There were no direct electric contacts among such separated Ni particles at < 8 vol%. The increase of the output current density with increasing Ni content from 6 to 8 vol% certainly reflects the increase of L. The experimental result of R = 0 at 12 vol% loading indicates that Ni nanoparticles on the SDC surface can contact with each other at $d_{Ni\text{-}Ni} < d_{Ni}$. However, the value of L might rather decrease by such an increase of Ni content even though the electronic network becomes perfect.

In conclusion, the present electrode has a distinct advantage, because the surface reaction on the mixed-conducting SDC anode can be activated by a small amount of nm-sized Ni electrocatalysts.

References

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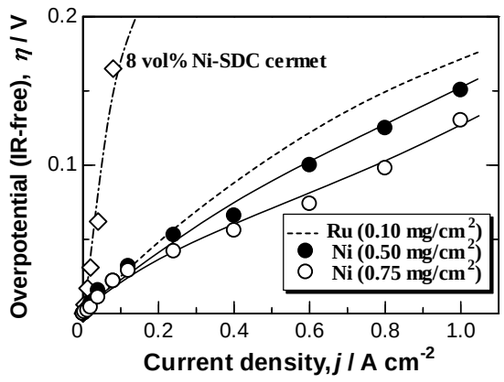

Figure 1. Polarization curves (IR-free, measured in humidified H_2) of Ni-dispersed SDC, Ru-dispersed SDC (0.1 mg-Ru cm^{-2}, dashed line), and 8 vol% Ni-SDC cermet anodes at 800°C. The dispersions of Ni with 0.50 and 0.75 mg cm^{-2} correspond to 6 and 8 vol%, respectively.