

Dispersion State of Ni Nanoparticles in Ceria-Based Anode for Medium-Temperature SOFCs

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We have developed high performance anode for medium-temperature SOFCs. Mixed conducting samaria-doped ceria [(CeO₂)_{0.8}(SmO_{1.5})_{0.2}, denoted as SDC] particles were employed in combination with highly dispersed metal electrocatalysts on their surfaces.^{1,2} Fairly small amount of Ni particles (8 vol.%) were found to enhance the anode performance significantly at 700-900°C.² This 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,

$$\text{O}^2[\text{Ni-SDC}] + \text{H}_2[\text{Ni-SDC}] \rightarrow \text{H}_2\text{O}(\text{g}) + 2 \text{e}[\text{Ni-SDC}]$$

where the active site, [Ni-SDC], is formed at the boundary of Ni and SDC particle surface.

In this paper, we demonstrate a stable performance of the Ni-dispersed SDC anode at 800°C for a long term over 1100 h. The dispersion state of Ni particles on SDC particles was observed by SEM before and after the test.

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. The SDC anode was impregnated with Ni(NO₃)₂ solution, followed by heating to 900°C in air.² 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 0.75 mg/cm² (about 8 vol.%).² The morphology of the anode layer was observed by a field-emission and in-lens-type SEM (Hitachi, S-5200).

Figure 1 shows the time course of the anodic overpotential η of 8 vol.% Ni-dispersed SDC operated at constant current density of 0.6 A cm⁻² at 800°C in a humidified H₂ ($P_{\text{H}_2\text{O}} = 0.042$ atm). A relatively rapid increase in the η was observed in the beginning 50 h. However, the anode has kept the high performance ($\eta = 0.17$ to 0.16 V at 0.6 A cm⁻²) over 1100 h; the η has rather been recovering toward the initial smallest value. Unfortunately, this run was terminated by a break in the electric power due to a lightning damage. However, we have clearly demonstrated that Ni-dispersed SDC anode is able to work stable without noticeable degradation for a long-term (> 1100 h). An increase of the η at the initial

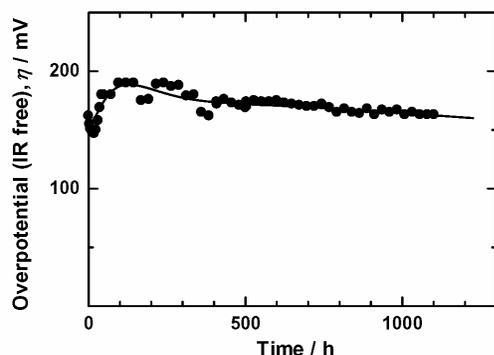


Fig. 1 Time course of the anodic overpotential η at 8 vol.% Ni-dispersed SDC operated under a constant current density of 0.6 A cm⁻² at 800°C in humidified H₂.

stage of the operation may be ascribed partly to an aggregation of Ni particles. The stable or improved performance after the prolonged operation suggests that the Ni particles were rather stabilized perhaps by changing the morphology at the contacting portion with SDC surfaces.

Figure 2 shows typical SEM images of Ni-dispersed SDC as-prepared (A) and after the long-term test (B). In order to observe the Ni particles on the SDC surface directly, the samples were observed at a low acceleration voltage of 1 kV without any pre-coating treatment. For the as-prepared one, Ni particles ranging from 20 to 100 nm are highly dispersed on the μm -sized SDC particles. Spherical or semispherical (dome-shape) Ni particles contact with the SDC. This is just the same image as that we illustrated the design concept of this catalyzed-anode.¹ The morphology changed dramatically after the long-term test. Fairly large and crystallized particles up to 170 nm are frequently seen while fine ones are still remaining. The circumference length L , the part of Ni catalyst domes contacting with the SDC surface, is a measure of the number of active sites [Ni-SDC]. The value of L is proportional to d_{Ni}^{-2} . If the average particle size grew during the test by 1.4 times, the value of L should decrease to about 1/2. Since the performance in Fig. 1 is inconsistent with this calculation, some factor(s) may contribute to keep the cell performance. One of the possibilities is that change in the shape of Ni particles as seen in Fig. 2B. This may be caused by a continuous redox reaction, *i.e.*, an oxidation of Ni by evolved water vapor in the anode reaction and a reduction by fresh H₂. Thus, the number of active sites may be increased by wetting of Ni with SDC substrate, compared with a point contact between spherical-shape Ni and SDC. However, we just observed the top surface of the sample (far from the interface SDC/YSZ). It is important to observe the cross-section to evaluate a depth profile of Ni. Such research is under progress.

- 1) M. Watanabe, H. Uchida, M. Shibata, N. Mochizuki, and K. Amikura, *J. Electrochem. Soc.*, **141**, 342 (1994).
- 2) H. Uchida, S. Suzuki, M. Watanabe, *Electrochem. Solid-State Lett.*, **6**, A174 (2003).

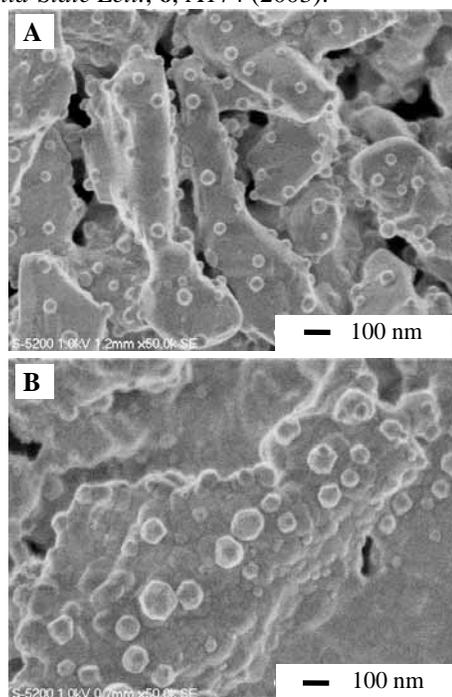


Fig. 2 SEM images of Ni-dispersed SDC as-prepared (A) and after the long-term test (B, top surface).