FULL PAPER

Depth-direction analysis of nickel depletion in a Ni–gadolinia-doped ceria hydrogen electrode after steam electrolysis operation

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We have examined the initial-stage degradation of a Ni–gadolinia-doped ceria (GDC) cermet hydrogen electrode prepared on a GDC buffer layer of a stabilized-zirconia electrolyte supported cell during steam electrolysis operation at 800 °C. With use of an air reference electrode, the IR-free electrode potential E and ohmic resistance of the hydrogen electrode side ($R_{\text{H}_2\text{-side}}$) were recorded. After a steam electrolysis operation at -1.0 A cm^{-2} for 211 h, the $R_{\text{H}_2\text{-side}}$ increased appreciably, by 36 %, while the value of E was nearly unchanged. It was found via a depth-direction analysis with use of focused ion beam-scanning ion microscopy that the remaining percentage of Ni decreased to ca. 60 % in the layer between 1 and 3 μm from the top of the GDC buffer layer, followed by a further decrease to 42 % at 0.5 μm . Since this suggests a significant cathodic polarization within the thin reaction zone, an enlargement of the reaction zone, together with a stabilization of Ni contacting with GDC, could be essential to mitigate such a degradation.

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1. Introduction

The electrolytic production of hydrogen, Power-to-Gas (P2G), has been attracting much attention worldwide as a large-scale, long-term, cost-effective storage of intermittent renewable electricity from solar and wind power. Compared with proton-exchange membrane type and alkaline-type electrolyzers, the conversion efficiency in a solid oxide electrolysis cell (SOEC) is the highest, in principle, due to favorable thermodynamic and kinetic conditions at high temperature. When SOECs are operated in reverse, they can work as solid oxide fuel cells (SOFCs) to generate electricity with high efficiency by consuming stored hydrogen or other fuels. Thus, the reversible solid oxide cell (R-SOC, operating as both SOEC and SOFC) is a promising direct energy converter between hydrogen and electricity.

Since the first concept was reported in the late 1960s,^{1,2)} the component materials commonly used in SOEC single cells are identical with those adopted in SOFCs: an yttria-stabilized zirconia (YSZ) electrolyte with a Ni–YSZ cermet hydrogen electrode and a perovskite-type oxygen electrode based on $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ (LSM), $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ (LSC)

or $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$ (LSCF).^{1)–20)} Typical particle size of Ni (d_{Ni}) in Ni–YSZ cermet ranges from 0.1 to 1 μm . It has been recognized that the degradation rates in the SOEC operation mode are much larger than those in the SOFC mode.^{8)–20)} The degradation mechanism of the Ni–YSZ cermet hydrogen electrode for the hydrogen evolution reaction (HER) in the SOEC mode has remained unclear,^{8,10)–20)} while that of the oxygen electrodes observed in both operation modes has been clarified extensively.^{9)–13)} For Ni–YSZ cermet electrodes, in addition to a segregation of impurities (such as Si) at the triple phase boundary (TPB) and/or agglomeration of Ni,^{8,10)–14)} a depletion of Ni close to the electrode/YSZ electrolyte interface has been reported, specifically, at high current densities (or high overpotentials).^{14)–17),19),20)}

In order to reduce the overpotential, the TPB should be enlarged. For the anodic hydrogen oxidation reaction (HOR) in SOFCs, the use of mixed ionic-electronic conduction (MIEC) in samaria-doped ceria (SDC) or gadolinia-doped ceria (GDC) with Ni or other metal catalysts has been effective in enlarging the TPB.^{21)–25)} We found that Ni-dispersed SDC H_2 electrodes exhibited high performances for both the HOR²⁵⁾ and HER,^{26),27)} where the d_{Ni} was ca. 50 nm. It has been reported that the infiltration of GDC or Mo-doped ceria in the Ni–YSZ H_2 electrode enhanced the performance and durability in the SOEC mode,^{28)–31)} but the mechanism is unclear. This is due to a difficulty of analysis of the interface between Ni (sub- μm size), ceria thin film or islands (nm size), and YSZ (sub- μm

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size) particles. Thus, the analysis of degradation of Ni–GDC or Ni–SDC cermet (sub- μm to μm particles) can provide valuable information for both Ni-dispersed SDC and GDC-infiltrated Ni–YSZ.

Here, we focus on the degradation of the Ni–GDC cermet hydrogen electrode in the initial stage of SOEC operation. Long-term tests ($\geq 1,000$ h) have been usually performed to clarify the degradation factors in coin-cells or practical cell/stacks. However, we often observed a domino-effect: a serious degradation of the O_2 electrode accelerated the degradation of the H_2 electrode, and vice versa. One of the possible reasons for such a phenomenon is that the distribution of current density became non-uniform, resulting in local damage at high current density spots, triggering the degradation of the counter electrode material. A short-term test, followed by an analysis of the microstructure, is expected to provide essential information on the areas where the degradation commences and how to mitigate it.

In the present work, we examined the initial-stage degradation of a Ni–GDC $[(\text{CeO}_2)_{0.9}(\text{GdO}_{1.5})_{0.1}]$ cermet hydrogen electrode prepared on a GDC buffer layer/stabilized zirconia electrolyte during SOEC operation. It was found by a depth-direction analysis of Ni that the remaining percentage of Ni decreased to 60 % in the interfacial layer between 1 and 3 μm from the buffer layer, followed by a decrease to 40 % at 0.5 μm . This suggests the importance of enlarging the TPB to mitigate the depletion of Ni.

2. Experimental

A commercial coin-type single cell with a scandia-stabilized zirconia (ScSZ) electrolyte support (2.0 cm in diameter, 0.15 mm in thickness) was employed:

O_2 electrode|GDC buffer layer|ScSZ|GDC buffer layer| H_2 electrode

The hydrogen electrode consisted of a Ni–GDC (50 vol.% Ni) catalyst layer (CL) and Ni–YSZ (50 vol.% Ni) current collection layer (CCL). The porosity of the Ni–GDC CL was ca. 30 %. The overall thickness of the hydrogen electrode was ca. 50 μm . The oxygen electrode consisted of an LSM–GDC (52 vol.% LSM) CL and LSM CCL. The projected area of each electrode was 1.23 cm^2 . The GDC buffer layers are expected to reduce the contact resistance between the ScSZ electrolyte and the electrodes (Ni–GDC and LSM–GDC): in previous work, we found that a thin SDC interlayer between an SDC-based electrode and a YSZ electrolyte reduced not only the contact resistance but also the IR-free polarization loss.³²⁾ As a platinum/air reference electrode (ARE), a Pt wire was wrapped along the periphery of the ScSZ electrolyte disk and fixed with Pt paste to form a porous Pt electrode.

The set-up for the test cell for SOEC operation was described in our previous report.²⁷⁾ The test cell was sealed with a gold ring. The H_2 electrode was reduced in humidified hydrogen ($p[\text{H}_2\text{O}] = 0.04$ atm) at $T_{\text{cell}} = 800^\circ\text{C}$ for 30 min prior to the performance evaluation. The SOEC was operated at $T_{\text{cell}} = 800^\circ\text{C}$ and a constant current den-

Fig. 1. Schematic representation of (a) a conventional cross-sectional view of a Ni–GDC CL prepared on a GDC buffer layer and (b) a layer-by-layer view parallel to the interface at a distance L from the interface.

sity of -1.0 A cm^{-2} with humidified hydrogen ($p[\text{H}_2\text{O}] = 0.8$ atm, H_2 flow rate = $300 \text{ cm}^3 \text{ min}^{-1}$) while supplying dry O_2 at $200 \text{ cm}^3 \text{ min}^{-1}$ to the O_2 electrode. The conversion of water vapor was maintained at a low level, ca. 0.7 % for -1.0 A cm^{-2} . The time course of the potential of each electrode and the ohmic resistances were measured by the current-interruption method in a three-electrode configuration. A current-off pulse (100 μs -width) was applied to the cell from a current-pulse generator (NPGS101-2A, Nikko Keisoku Ltd., Japan), and the resulting potential responses with reference to the ARE were recorded with a storage oscilloscope (VC-6045, Hitachi Ltd., Tokyo, Japan).

After 211 h of operation, the test cell was carefully cooled down while supplying 5 % H_2 gas (N_2 -balance) to the H_2 electrode in order to minimize the re-oxidation of Ni. Test samples of the H_2 electrodes were embedded in epoxy resin.

As shown schematically in **Fig. 1(b)**, the area fraction of Ni, corresponding to the Ni volume fraction, for a thin layer of Ni–GDC CL, was analyzed by scanning ion microscopy (SIM) in a focused-ion beam system (FIB, FB-2200, operated at an acceleration voltage of 40 kV, Hitachi High-Tech Corp. Tokyo, Japan) in the depth direction, from 5 to 0.5 μm from the CL/buffer layer interface. An advantage of SIM is the superiority of the secondary electron image of the top surface, due to the much shallower penetration depth of the Ga-ion beam in comparison with that of the electron beam in conventional SEM. In contrast to the conventional cross-sectional view of the CL [perpendicular to the interface, **Fig. 1(a)**], we observed several layer-by-layer images parallel to the interface. The size of each original, representative, two-dimensional image observed was $36 \mu\text{m} \times 36 \mu\text{m}$, which was then cropped to $23 \mu\text{m} \times 23 \mu\text{m}$ to discard the edge contrast effect. The image was processed by ImageJ 1.52a (NIH, USA public domain software). A pristine sample (obtained just after the reduction) was also analyzed in the same manner. Because the initial Ni content in the Ni–GDC cermet was provided by Ni vol.%, $V(\text{Ni})/[V(\text{Ni})+V(\text{GDC})]$, we defined the area fraction of Ni in a similar manner, $A(\text{Ni})/[A(\text{Ni})+A(\text{GDC})]$, which corresponds to Ni volume fraction in the slice with a differential thickness dL .

Fig. 2. Time course of (a) IR-free potential E (vs. ARE) and (b) ohmic resistance R_{ohm} during operation of the Ni-GDC H_2 electrode ($p[H_2O] = 0.8 \text{ atm}$, H_2 balance) and LSM-GDC O_2 electrode (pure O_2) at 800°C with a constant current density of -1.0 A cm^{-2} (SOEC mode). Reliable values of ohmic resistance of the O_2 electrode side, $R_{O2-side}$, were not obtained from 25 to 74 h (shown by a dashed line), probably due to electrical noise.

3. Results and discussion

3.1 Changes in performances of Ni-GDC cermet hydrogen electrode

Figure 2 shows the time course of the IR-free potential E of each electrode and the ohmic resistances R_{ohm} of the oxygen and hydrogen electrode sides ($R_{O2-side}$ and $R_{H2-side}$) during SOEC-mode operation at -1.0 A cm^{-2} and $T_{cell} = 800^\circ\text{C}$. The value of E at the Ni-GDC H_2 electrode shifted in the positive direction during the initial 30 h (improvement in the HER performance), and gradually shifted to the negative direction (slight degradation). The value of E returned to the initial value after 211 h, i.e., the improvement in the HER performance was counterbalanced by the degradation. The value of $R_{H2-side}$ increased with time appreciably (36 % after 211 h, with a linear fitting). The degradation of the LSM-GDC O_2 electrode was quite marked with respect to the positive shift in E and a large increase in $R_{O2-side}$ (nearly 3 times), consistent with those reported so far.^{9)–13)} As seen in IR-free polarization curves (I - E curves, **Fig. 3**), the polarization characteristics of the LSM-GDC O_2 electrode degraded over the whole current-density range examined, although this is out of the scope of the present work. In contrast, it is very interesting that the polarization performance itself of the H_2 electrode in **Fig. 3** was nearly unchanged (or rather improved from -0.2 to -0.9 A cm^{-2}) after 211 h of operation, in spite of the increase in the ohmic resistance $R_{H2-side}$.

3.2 Change in microstructure of Ni-GDC cermet hydrogen electrode

Then, the microstructure of the Ni-GDC H_2 electrode was observed with FIB-SIM. **Figure 4** shows a series of SIM images of the Ni-GDC CL at various distances L from the top of the GDC buffer layer in the pristine state and after the SOEC operation. In these images, Ni is

Fig. 3. Polarization curves (IR-free I - E curves) of the Ni-GDC H_2 electrode and LSM-GDC O_2 electrode at $T_{cell} = 800^\circ\text{C}$ (open black symbols, initial performance; solid red symbols, after SOEC operation for 221 h).

observed as light gray, GDC as dark gray, and pores as black. In the pristine state, Ni particles ranging from 0.5 to $2 \mu\text{m}$ were distributed in the CL with $L = 0.5$ to $5 \mu\text{m}$, and the particle size decreased with decreasing L . Based on the image analysis, values of area fraction of Ni are shown as a function of L in **Fig. 5(a)**. The area fraction of Ni also decreased from 62.4 % ($L = 5 \mu\text{m}$) to 40.4 % ($L = 1 \mu\text{m}$), but the average value of 49.7 % over the $5\text{-}\mu\text{m}$ thickness was consistent with the catalogue value of 50 vol.% Ni in the cermet. We suppose that the manufacturer of the coin-type cells might intentionally prepare such gradients of particle size and fraction of Ni within the CL. Smaller size Ni particles can enhance the effective reaction zone (ERZ), even with a relatively low Ni fraction at $L = 0.5$ to $1 \mu\text{m}$, while a high Ni fraction at $L = 4$ to $5 \mu\text{m}$ can provide an increased electronic conductance toward the Ni-YSZ CCL. Relatively large size Ni particles in the upper layer could be formed via agglomeration due to the high Ni fraction.

After SOEC operation for 211 h, some of the GDC and Ni particles were seen to be agglomerated in SIM images, but the Ni content at $L = 4$ and $5 \mu\text{m}$ was virtually unchanged compared with the pristine state, as seen in the Ni remaining percentage in **Fig. 5(b)**. The Ni remaining percentage with reference to the pristine state decreased obviously to 60 % at $L = 1$ to $3 \mu\text{m}$. Although the flatness of the sample decreased in the upper part at $L = 0.5 \mu\text{m}$ (very close to the GDC buffer layer), the image analysis for the limited area ($23 \mu\text{m} \times 23 \mu\text{m}$, similar to the other images to avoid artifacts) provided the Ni remaining percentage as low as 42 %. Thus, even during a relatively short-term operation of SOEC, we confirmed a depletion of Ni close to the interface of the Ni-GDC/GDC buffer layer. Such a local change in the microstructure near the interface suggests a large overpotential applied in the thin layer.

The depletion of Ni close to the Ni-YSZ/YSZ electrolyte interface has been observed in SOEC operation, resulting in increases in both the ohmic resistance (R_{ohm}) and the polarization resistance (R_p)/capacitance in the electrochemical impedance spectroscopy.^{14)–17),19),20)} It has

Fig. 4. A series of SIM images of the Ni-GDC CL at various distances L from the top of GDC buffer layer in the pristine state and after the SOEC operation. Ni is observed as light gray, GDC as dark gray, and pores as black.

Fig. 5. (a) Area fraction of Ni as a function of distance L in the pristine state and after SOEC operation for 211 h; (b) Ni remaining percentage (with reference to the pristine value).

been clearly understood that such increases in R_{ohm} and R_p can be ascribed to a disruption of percolation among Ni particles (leaving isolated Ni with increased porosity in the layer). However, the mechanism for the Ni depletion is still unclear. While a hypothesis of Ni transport via formation of volatile species such as $Ni(OH)_x$ ^{14),33),34)} could explain an acceleration of Ni depletion with temperature and $p[H_2O]$, this is inconsistent with an observation of almost no change in Ni distribution under the open circuit condition at $p[H_2O] = 0.8$ atm and 800 °C for 1000 h.¹⁵⁾ We estimated the amount of Ni vaporized from the Ni-GDC electrode based on the total equilibrium partial pressure of gaseous Ni species, $p[Ni(g)]$, calculated thermodynamically, i.e., $p[Ni(g)] = 1 \times 10^{-10}$ atm at 800 °C and 5×10^{-10} atm at 850 °C in H_2 with $p[H_2O] = 0.8$ atm.³⁴⁾ Assuming that the Ni-GDC was completely equilibrated with $(H_2 + H_2O)$ gas flow, the amount of Ni loss was calculated to be about $20 \mu g cm^{-2}$ after 211 h even at 850 °C (considering local heating due to the overpotential). This value corresponds to only 3 % of the mass of Ni loaded in the interfacial layer with $3 \mu m$ thickness, in which a significant Ni depletion was observed in Fig. 5(b). Hence, the transport of Ni via the formation of volatile species was, if at all, not predominant in our test cell operated for 211 h.

On the other hand, it has been recently reported as an alternative mechanism that the wettability of Ni on YSZ at the interface by the cathodic polarization in the SOEC mode might become less than that in the inactive support layer, leading to the migration of Ni from the active zone outward (e.g., support layer).^{19),20)} Indeed, by using a patterned Ni film electrode/YSZ, Jia et al. have observed a delamination of Ni from the YSZ in the SOEC mode due to the decrease in the wettability of Ni, together with an

Fig. 6. Schematic representation of Ni-YSZ (a, c) and Ni-GDC electrodes for the H_2 evolution reaction in the pristine state (a, b) and after the degradation by Ni-depletion (c, d). Both electrodes were prepared on YSZ electrolyte for simplicity. The ERZ around the physical TPB is shown by the red hatched region. By MIEC, the ERZ can be enlarged over the whole surface of the GDC (red dotted mesh), together with isolated Ni particles operating as electrocatalysts.

inverse phenomenon of increased Ni wettability in the SOFC mode.³⁴⁾ We found for a Ni-dispersed SDC electrode that Ni nanoparticles were stabilized by the increased wettability with SDC during continuous operation of the SOFC at 800 °C for over 1100 h.³⁶⁾ In the SOEC operation in the present work, however, such an interaction between Ni and GDC might be weakened, similar to the case of Ni-YSZ, resulting in the Ni depletion in the interfacial region.

3.3 Impact of Ni depletion on the electrode performances

We consider that the impact of Ni depletion on the electrode performance of Ni-GDC should be distinct from that for the case of Ni-YSZ. Considering pathways for the HER and HOR at Ni-YSZ electrodes, including the surface diffusion (or spillover) of hydrogen- and oxygen-species,^{37)–39)} the ERZ is limited to the vicinity of the Ni/YSZ interface (slightly beyond the physical TPB line), as schematically shown in Fig. 6(a):

where $e^- [Ni]$ and $O^{2-} [YSZ]$ denote an electron transferred from Ni within the electronically percolated network and an oxide ion in YSZ network, respectively. The upper and lower arrows in reaction (1) represent the HER and HOR. When some fraction of Ni particles is lost (or migrated) to disrupt the percolation, R_{ohm} increases, and, simultaneously, R_p increases, due to the decrease in the ERZ, as reported in the literature.^{15),19),20)} The isolated Ni particles can no longer contribute to either the electronic conduction path or the ERZ.

Next, we consider the Ni-GDC electrode prepared on a YSZ electrolyte (not GDC buffer layer) for simplicity. As shown in Fig. 6(b), the most active zone is also located at the vicinity of the Ni/GDC interface:^{21)–27)}

where $\text{O}^{2-}[\text{GDC}]$ denotes an oxide ion in the GDC network. Since the ionic conductivity σ_{ion} of GDC or SDC at 800 °C is about 3 times higher than that of YSZ,^{(40),(41)} the ERZ in reaction (2a) should be enhanced compared with the case of Ni–YSZ. Additionally, due to the MIEC in GDC with high electronic conductivity (ca. 0.2 S cm^{-1} in H_2 at $p[\text{H}_2\text{O}] = 0.8 \text{ atm}$ ⁽⁴¹⁾) and σ_{ion} stated above, the ERZ is enlarged over the GDC surface:^{(22),(42),(43)}

where $\text{e}^-[\text{GDC}]$ and $\text{e}^-[\text{Ni}/\text{GDC}]$ stand for an electron transferred from mixed-conducting GDC. The notation of $[\text{Ni}/\text{GDC}]$ in reaction (2c) designates an isolated Ni (out of percolation) but in contact with GDC, so that it can still operate as an electrocatalyst^{(22),(25)–(27)} [see Fig. 6(d)]. The increase in $R_{\text{H}_2\text{-side}}$ shown in Fig. 2(b) can be ascribed to a loss of Ni that disrupts the percolation among Ni particles. However, the nearly unchanged IR-free polarization performance of Ni–GDC in Figs. 2(a) and 3, in spite of the Ni depletion, suggests that the HER proceeded via reactions (2b) and (2c) to supplement a decrease in the rate via reaction (2a), as expected. Thus, the detrimental impact of Ni depletion on the Ni–GDC electrode performance was mitigated by MIEC.

However, to minimize the increase in the R_{ohm} and R_{p} , the Ni depletion itself in H_2 electrodes must be suppressed. If the Ni depletion at Ni–GDC were triggered by a large cathodic overpotential for the HER, similar to the case of Ni–YSZ,^{(19),(20),(35)} further enlargement in the ERZ, together with a stabilization of Ni in contact with GDC, is essential. Very recently, we found that the durability of a double-layer H_2 electrode, consisting of a SDC scaffold with highly dispersed Ni–Co nanoparticles as the CL and a thin current collecting layer of Ni–YSZ cermet, was improved greatly by reversible cycling operation between the SOEC and SOFC modes.⁽⁴⁴⁾ Further analysis of the Ni–Co nanoparticle/SDC interface is in progress in our laboratory.

4. Conclusions

We examined the initial-stage degradation of a Ni–GDC cermet hydrogen electrode under SOEC operation at -1.0 A cm^{-2} and 800 °C for 211 h. The IR-free potential was found to be nearly unchanged, while the ohmic resistance $R_{\text{H}_2\text{-side}}$ increased appreciably. A depth-direction analysis by FIB–SIM demonstrated a depletion of Ni in the interfacial layer, up to a thickness of 3 μm . The degradation of IR-free polarization performance was mitigated due to the mixed ionic and electronic conduction in GDC, compared with the case of Ni–YSZ electrodes. However, it is essential to enlarge the reaction area, together with a stabilization of Ni in contact with GDC (or other materials), to increase the durability.

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