HIGH PERFORMANCE ELECTRODES FOR REVERSIBLE SOLID OXIDE FUEL CELLS

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ABSTRACT

We have developed high performance electrodes for reversible SOFCs. In an SOFC mode, mixed conducting samaria-doped ceria (SDC) anode was activated effectively by highly dispersed Ni electrocatalysts. A porous LaCoO3-based cathode prepared on a thin and dense SDC interlayer exhibited a low overpotential of -0.05 V at 0.4 A cm⁻² and 800°C in air. A solid oxide electrolysis cell (SOEC) using the same component materials as the SOFC produced hydrogen with a small IR-free cell voltage = 1.15 V at 0.5 A cm⁻² and 900°C under the atmosphere of H₂ + H₂O (p[H₂O] = 0.6 atm, p[H₂] = 0.4 atm) and O₂ (1 atm).

INTRODUCTION

Solid oxide electrolysis cells (SOECs) are expected, in principle, to provide the highest efficiency for electrolytic production of pure hydrogen. An advantage of the SOECs is the reduction of applied voltage due to favorable thermodynamic and kinetic conditions. For example, the thermodynamic decomposition voltage of water vapor is only 0.95 V at 900°C. When the SOECs are operated reversely, they can work as solid oxide fuel cells (SOFCs) to generate electricity with a high efficiency by consuming natural gas, coal gas, or stored hydrogen. Thus, so-called reversible SOFC is regarded as a reciprocal direct energy converter between hydrogen and electricity.

The operating temperature of SOECs is, so far, restricted to about 1000°C (1-3) because of insufficient performance of the electrolyte and electrodes at low temperatures. Lowering the operating temperature is a good option to overcome a limited choice of the component materials. The SOEC can utilize waste heat from various sources, e.g., steel-making or coal-gasification, for its endothermic operation. However, it is essential to develop high performance electrodes for both SOECs and SOFCs operated at reduced temperatures, besides the reduction of ohmic losses in solid electrolytes.

We have proposed a new design concept of catalyzed-reaction layers, which realizes high performance anode and cathode for medium temperature SOFCs (4). Mixed conducting oxide particles, samaria-doped ceria [(CeO₂)₀.₈(SmO₁.₅)₀.₂, denoted as SDC] for the anode (4-9) and LaCoO₃-based material with SDC interlayer for the cathode (10-12), were employed in combination with highly dispersed metal electrocatalysts on their surface. Use of the mixed conducting oxides results in an enlarged effective reaction zone (ERZ) over the whole oxide surface. Nanometer-sized metal electrocatalysts loaded on the
surface certainly activate the electrode reaction at the boundary. Recently, we found that several vol% of Ni nanoparticles enhanced the SDC anode performance significantly at 700-900°C in humidified H₂ (8, 9). This Ni-dispersed SDC has been applied to the SOEC cathode to produce H₂ from water vapor (13).

In the present research, we report the performances of these electrodes in both SOFC and SOEC operation modes. It is demonstrated that an SOEC, comprised of Ni-dispersed SDC cathode, La(Sr)CoO₃ anode (with SDC interlayer) and YSZ electrolyte, produced hydrogen with a small IR-free cell voltage = 1.15 V at 0.50 A cm⁻² and 900°C.

**EXPERIMENTAL**

An 8 mol% yttria-stabilized zirconia disk (YSZ, diameter: 13 mm, thickness: 1 mm) was used as the solid electrolyte. Samaria-doped ceria (CeO₂)₀.₈(SmO₁.₅)₀.₂ electrodes (cathode for SOEC, anode for SOFC) with highly dispersed nanometer-sized Ni catalysts were prepared in the same manner as in our previous works (8, 9, 13). To reduce the contact resistance between the SDC electrode and YSZ electrolyte, a thin film of SDC (thickness = ca. 1 μm) was attached on one side of YSZ surface (6-9). Onto the SDC thin film, porous SDC electrode was prepared by screen-printing an SDC paste (containing SDC powder, mixed aqueous solution of Ce and Sm nitrates, and fine polymer beads as pore-former), followed by firing at 1150°C for 4 h. During this heat-treatment, the fine polymer beads and the added nitrates decomposed to form μm-sized pores and fine SDC particles, respectively. The projected surface area of the SDC electrode was 0.25 cm². Nickel particles were highly dispersed onto the SDC surface in the same manner as our previous work (8, 9, 13). The SDC electrode was impregnated with Ni(NO₃)₂ solution, followed by heating in air (up to 900°C) to decompose the Ni compound. The resulting NiO particles were then reduced to Ni microcrystals in H₂ stream of the test cell at 1000°C for 1 h. The amount of Ni microcrystals thus loaded was 0.75 mg cm⁻² and 1.50 mg cm⁻², corresponding to about 8 vol% and 17 vol%, respectively. The particle diameter of Ni, estimated from XRD, was 20 to 30 nm.

A porous La₀.₆Sr₀.₄CoO₃ (LSC, Praxair Specialty Ceramics Co.), La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃ (LSCF, Praxair Specialty Ceramics Co.), or Pt counter electrode was formed on the backside of the YSZ electrolyte. A thin dense film of SDC (thickness = ca. 1 μm) was attached on one side of YSZ surface before coating the LSC or LSCF electrode. This SDC interlayer prevents unfavorable solid-state reactions between the YSZ and LSC (or LSCF) (10-12). Ono the SDC interlayer, porous LSC or LSCF electrodes were prepared by screen-printing the paste containing the pore-former, followed by firing at 1050°C for 1 h.

The steady state IR-free polarization characteristics (I - E curves) of the electrodes were measured by a current-interruption method by using the Pt/air reference electrode. The ohmic resistance of the cell was obtained from the slope of the linear relationship between the IR loss and the current density. A local heating of the electrode by current passing must be avoided, because it reduces not only the ohmic resistance but also the electrode polarization. We carefully inspected the absence of the local heating by checking the constant ohmic resistance of the cell at the all current densities examined (9, 12, 13).
RESULTS AND DISCUSSION

Polarization Properties of SDC Anodes and LSC Cathodes in SOFC

Figure 1 shows the IR-free polarization curves for the mixed-conducting electrodes with and without metal electrocatalysts at the cell temperature $T_{\text{cell}}$ of 800°C (7-9). The microstructure of these electrodes was controlled by using polymer beads as the pore former. Highly dispersed Ni catalysts of only 8 vol% (0.75 mg-Ni cm$^{-2}$) significantly enhanced the performance of the SDC anode in humidified H$_2$ ($p[H_2O] = 0.04$ atm). The current density $j$ on the Ni-dispersed SDC anode at an overpotential ($\eta$) of 0.10 V was 0.80 A cm$^{-2}$, which is about 4 times higher than that without Ni catalysts. Microstructural analyses of Ni-dispersed SDC (9) indicated that nanometer-sized Ni catalysts enhanced the anodic reaction rate by increasing the active reaction sites [Ni-SDC] and lowering the electronic resistance in the anode effectively.

\[ O_2^{[\text{Ni-SDC}]} + H_2[\text{Ni-SDC}] \rightarrow H_2O(\text{gas}) + 2e[\text{Ni-SDC}] \quad [1] \]

It was also found that the Ni-dispersed SDC anode exhibited a stable performance at 800°C and 0.60 A cm$^{-2}$ in humidified H$_2$ for a long term over 1100 h (9).

The LSC cathode prepared on the SDC interlayer exhibited very high performance in air at $T_{\text{cell}} = 800°C$, i.e., $j = 0.40$ A cm$^{-2}$ at $\eta = 0.05$ V (12). The performance was enhanced further by dispersing a small amount of nm-sized Pt catalysts (0.10 mg cm$^{-2}$, 1 vol%) on the LSC surface; $j = 1.0$ A cm$^{-2}$ at $\eta = 0.05$ V. In this case, the following reaction steps are expected to be activated greatly by Pt-loading in the LSC layer,

\[ O_2(\text{gas}) \rightarrow 2 O_{\text{ad}}(\text{Pt-LSC}) \quad [2] \]

\[ O_{\text{ad}}(\text{Pt-LSC}) + 2 e^- (\text{Pt-LSC}) \rightarrow O_2^2(\text{LSC}) \quad [3] \]

Figure 1. IR-free polarization curves of anodes (measured in humidified H$_2$, $p[H_2O] = 0.04$ atm) and cathodes (measured in air) in SOFC at $T_{\text{cell}} = 800°C$. 

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where the active site, (Pt-LSC), is formed at the boundary of the Pt catalysts and the LSC surface (12).

Based on these data, the IR-free terminal voltage ($E_{\text{cell}}$) for the SOFC with the Ni-SDC anode and Pt-LSC cathode was calculated to be 0.96 V at $j = 0.50$ A cm$^{-2}$ and $T_{\text{cell}} = 800^\circ$C, operated with humidified H$_2$ and air. The value of $E_{\text{cell}}$ can still be as high as 0.93 V when using the LSC cathode without any metal catalyst. Since the ohmic resistances of Ni-SDC, LSC and Pt-LSC layers were found to be sufficiently low under the operating condition (8, 9, 12), we can subtract 0.03 V as an IR-loss from the $E_{\text{cell}}$ if a thin YSZ electrolyte with the thickness of 25 $\mu$m were employed in our cell. Such performances evaluated for a small test cell under low fuel utilization (3.2% at 0.5 A cm$^{-2}$) are important, because they give us a clear ultimate target.

**Performances of SOEC with Ni-dispersed SDC Cathode and LSC (or LSCF) Anode**

Figure 2 shows the hydrogen evolution rate $v$(H$_2$) as a function of the current density in an SOEC using Ni-dispersed SDC cathode and Pt counter anode at $T_{\text{cell}} = 900^\circ$C. The value of $v$(H$_2$) accords well with Faraday’s law. Therefore, the current efficiency ($\eta_{\text{eff}}$) for the H$_2$ evolution at the Ni-dispersed SDC cathode was confirmed to be unity in the current density region examined.

![Figure 2](image)

**Figure 2. Hydrogen evolution rate at Ni(8 vol.%)-dispersed SDC cathode at $T_{\text{cell}} = 900^\circ$C and $p$(H$_2$O) = 0.4 atm. Solid line shows Faraday’s law.**

Figure 3 shows the IR-free polarization curves for LSC anode, (LSCF + SDC) anode (in O$_2$) and Ni(8 vol%)-dispersed SDC cathode (in H$_2$ + H$_2$O, $p$(H$_2$O) = 0.4 atm, $p$(H$_2$) = 0.6 atm) at $T_{\text{cell}} = 900^\circ$C. While the thermal expansion coefficient (TEC) of LSCF is more compatible to the SDC interlayer than that of LSC, the oxide ionic conductivity is somewhat lower than the LSC (14, 15). We have recently clarified that the high conductivities of both oxide ions ($\sigma_{\text{ion}}$) and electrons ($\sigma_e$) in the mixed-conducting electrode layer (SDC anode and LSC cathode) are very important in reducing not only the ohmic loss but also the polarization loss (6-8, 12). Then, SDC powder (50 wt%) was added in the LSCF cathode layer in order to enhance the $\sigma_{\text{ion}}$ and to match the TEC with that of SDC interlayer further. It is seen that the performance of LSC and (LSCF + SDC)
anodes were almost the same. For example, at \( j = 0.50 \text{ A cm}^{-2} \), the IR-free potential at both LSC and (LSCF + SDC) anodes was only 0.14 V vs. air reference electrode. Thus, the IR-free applied cell voltage \( (E_{\text{cel}}) \) was just 1.20 V at \( j = 0.50 \text{ A cm}^{-2} \). However, a somewhat larger ohmic resistance of the cell with (LSCF + SDC) anode should be reduced by optimizing the composition (LSCF/SDC) and the microstructure.

Figure 3. IR-free polarization curves for LSC anode (O), [LSCF+SDC] anode (△), and Ni(8 vol%)-dispersed SDC cathode (■) in SOEC at \( T_{\text{cell}} = 900^\circ\text{C} \). Cathode gas: \( \text{H}_2+\text{H}_2\text{O} \) (\( p[\text{H}_2\text{O}] = 0.4 \text{ atm}, p[\text{H}_2] = 0.6 \text{ atm} \)), anode gas: \( \text{O}_2 \) (1 atm).

**Improvement of Cathode Performance by Increasing Ni Loading**

For the SOEC with Ni (8 vo.%) dispersed SDC cathode, the applied voltage including the IR-loss, \( E_{\text{app}} = E_{\text{cel}} + E_{\text{IR}} \), was found to be almost constant at \( p[\text{H}_2\text{O}] > 0.4 \text{ atm} \), due to a trade-off effect between a decrease in the IR-free overpotential (\( \eta_{\text{c}} \)) and an increase in the IR-loss (\( E_{\text{IR}} \)) of the SDC (13). The decrease in \( \eta_{\text{c}} \) with \( p[\text{H}_2\text{O}] \) is certainly ascribed to an increased transfer rate of water vapor to the reaction sites, whereas the increase in \( E_{\text{IR}} \) is due to the reduction in n-type electronic conductivity in the mixed-conducting SDC with increasing \( p[\text{H}_2\text{O}] \) (increase in the equilibrated \( p[\text{O}_2] \) in \( \text{H}_2\text{O} \) and \( \text{H}_2 \)). Such a reduction in \( \sigma_{\text{e}} \) may also induce a detrimental effect to reduce the ERZ at the Ni/SDC interface. Then, the Ni-loading was doubled (17 vol%).

Figure 4 shows changes in the cathode performances by increasing Ni-loading on the SDC in \( \text{H}_2 + \text{H}_2\text{O} \) (\( p[\text{H}_2\text{O}] = 0.6 \text{ atm}, p[\text{H}_2] = 0.4 \text{ atm} \)) at \( T_{\text{cell}} = 900^\circ\text{C} \) and \( 800^\circ\text{C} \). Platinum counter anode was employed to determine the area specific ohmic resistance of Ni-dispersed SDC cathode layer \( (R_{\text{Ni-SDC}}) \) in the similar manner as in ref. (7-12); the ohmic resistance of YSZ disk \( (R_{\text{YSZ}} = \text{the resistance of the cell, Pt/YSZ/Pt}) \) was subtracted from that of the cell Ni-SDC/YSZ/Pt. The values of \( R_{\text{Ni-SDC}} \) thus calculated are tabulated in Fig. 4. The IR-free cathodic overpotential decreases markedly by increasing Ni-loading, especially at low \( T_{\text{cell}} \) of \( 800^\circ\text{C} \). The value of \( R_{\text{Ni-SDC}} \) also decreases with increasing Ni-loading. Hence, additional Ni catalysts effectively enhance both the reaction rate and electronic conductance.
Figure 4. IR-free polarization curves for the Ni-dispersed SDC cathode in H₂ + H₂O (p[H₂O] = 0.6 atm, p[H₂] = 0.4 atm). Ni loading = 17 vol.% (♦), 8 vol% (●).

Then, we estimate the energy conversion efficiency ($\varepsilon$) of our SOEC, which is defined by

$$\varepsilon = \left[ \frac{\Delta H^0}{2F E_{app}} \right] \times j_{eff} = \left[ \frac{\Delta H^0}{2F (E_{ele} + E_{IR})} \right] \times j_{eff}$$

where $\Delta H^0$ and $F$ are the standard enthalpy change of the reaction and Faraday’s constant, respectively. As described above, the current efficiency $j_{eff}$ for the H₂ evolution was experimentally determined to be unity. By using the Ni (17 vol%)-dispersed SDC and the LSC anode, the value of $E_{ele}$ can be reduced to 1.15 V at $j = 0.50$ A cm⁻² and $T_{cell} = 900^\circ$C. The area-specific ohmic resistance ($R_{cell}$) of the present cell was 1.28 Ω cm⁻², which is smaller than that with Ni (8 vol%)-dispersed SDC (13). A large fraction of $R_{cell}$ was ascribed to that of 1 mm-thick YSZ electrolyte, $R_{YSZ} = 1.01$ Ω cm⁻². The remaining part ($R_{cell} - R_{YSZ} = 0.27$ Ω cm⁻²) was found to be ascribed to a contact resistance between oxide (SDC or LSC) particles and one at the interface of YSZ or (YSZ/SDC interlayer). Also, some fraction of the contact resistance was found to be due to an insufficient contacting pressure to the current collector at the LSC anode side. Although such a contact resistance should be minimized, here we employed this large contact resistance in the following calculation. Assuming that the YSZ electrolyte with the thickness of 50 μm is employed in our cell, the $R_{YSZ}$ may be reduced to 0.05 Ω cm⁻². Then, we may obtain $E_{IR} = 0.16$ V and $E_{app} = 1.31$ V at $j = 0.50$ A cm⁻² and $T_{cell} = 900^\circ$C. Based on $\Delta H^0_{HHV} = 285.8$ kJ mol⁻¹ (higher heat value) for H₂O(l) = H₂(g) + 1/2O₂(g) at 298 K, the efficiency $\varepsilon$ is estimated to be 113%. Since the value of $E_{app} = 1.31$ V is somewhat larger than the thermoneutral voltage of 1.29 V (= $\Delta H^0_{HHV}(900^\circ$C)/2F), the cell can be operated in an autothermal mode. The estimated efficiency for our cell at $T_{cell} = 900^\circ$C is comparable to the Dornier’s result at $T_{cell} = 1000^\circ$C; $E_{app} = 1.33$ V at 0.50 A cm⁻² ($\varepsilon = 111\%$) for a single cell without interconnection (1). The polarization performances of our Ni-dispersed SDC cathode and LSC or (LSCF + SDC) anode (with SDC interlayer) at $T_{cell} = 900^\circ$C are much higher than those of conventional electrodes (2, 3) at $T_{cell} = 1000^\circ$C. Hence, our next target is to reduce the contact resistance by optimizing the electrode microstructure, which is also a key technology to enhance the electrode performances.
CONCLUSIONS

The present study showed that mixed conducting samaria-doped ceria (SDC) dispersed with nm-sized Ni catalysts and LaCoO$_3$-based oxides (LSC or LSCF) with SDC interlayer are promising candidates for electrodes in a reversible SOFC. In SOFC mode, Ni-dispersed anode was confirmed to maintain a stable performance at $T_{\text{cell}} = 800^\circ$C and 0.6 A cm$^{-2}$ in humidified H$_2$ for a long term over 1100 h. An SOEC, comprised of Ni (17 vol%)-dispersed SDC cathode, La(Sr)CoO$_3$ anode (with SDC interlayer) and YSZ electrolyte, exhibited fairly high performance at least for the short term (a few days) test; IR-free cell voltage = 1.15 V at 0.5 A cm$^{-2}$ and $T_{\text{cell}} = 900^\circ$C under the atmosphere of H$_2$ + H$_2$O ($p[H_2O] = 0.6$ atm, $p[H_2] = 0.4$ atm) and O$_2$ (1 atm). For lowering the operating temperature of the SOEC further, the electrode performance must be improved further.

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