

Enhancement of Methane Oxidation at the Cermet Anode Consisting of Nickel-Cobalt and Samaria-Doped Ceria in Solid Oxide Fuel Cells

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The partial substitution of Co atoms for Ni atoms in the Ni-based cermet anode resulted in a decrease in the anodic overvoltage and interfacial resistance between the anode and electrolyte. This effect has been confirmed for single solid oxide fuel cells using a samaria-doped ceria (SDC) electrolyte. The results of electrochemical measurements and a product analysis by gas chromatography revealed that the direct oxidation of CH₄ is enhanced by the modification of the microstructure in the cermet anode, the effect of which is combined with a sufficient oxide ion supply through the electrolyte.

1. Introduction

Solid oxide fuel cells (SOFCs) have recently attracted much attention as a promising on-site power generation system owing to their high efficiency. The most attractive advantage of SOFCs is their adaptability to the existing infrastructure of the municipal gas power supply system. In particular, the electrode activity of the SOFC anode is important for its high performance.^(1–5) The nickel and yttria-stabilized zirconia (Ni-YSZ) cermet anode is most commonly used for the generation of a H₂-rich gas by the steam reforming of CH₄. This cermet anode is used as a porous layer in order to provide reaction paths at the interface between nickel particles and the YSZ electrolyte. However, the Ni-YSZ cermet anode generally shows a low activity for the direct electrochemical oxidation of CH₄. The development of a proper metal or alloy catalyst with the combination of a high-oxide-ion conductor is required for the electrochemical oxidation of hydrocarbon fuels.

We therefore investigated the electrochemical performance of an anode consisting of Ni-Co solid-solution alloy particles combined with a samaria-doped ceria (SDC) electrolyte. The anodic polarization resistance of the Ni_{1-x}Co_x-SDC anode was

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investigated for CH₄. The microstructure of these cermet anodes was characterized to reveal the origin of the enhancement effect on the electrochemical oxidation of CH₄.

2. Materials and Methods

A Ni_{1-x}Co_xO solid solution was prepared by heating a mixture of reagent-grade NiO and Co₃O₄ powders in an alumina crucible at 1273 K for 10 h in air. Phase identification of the prepared powders was made by X-ray diffraction (XRD). Pulverized Ni_{1-x}Co_xO powders were mixed with the Ce_{0.8}Sm_{0.2}O_{1.9} (SDC, NexTech) powder at a ratio of 40 mass% to form a slurry in glycerol. The slurry was painted as the anode on one face of the electrolyte. An SDC electrolyte disk (Shinko Electric Industries) 15 mm in diameter and 0.3 mm thick and an ScSZ (10 mol%Sc₂O₃-1 mol%CeO₂-ZrO₂, Daiichi Kigenso Kagaku Kogyo) disk 15 mm in diameter and 0.2 mm thick were used as the electrolytes. The painted disks were heated at 1573 K for 5 h. (La_{0.85}Sr_{0.15})_{0.9}Mn_{0.1}O₃ (LSM) powder and Sm_{0.5}Sr_{0.5}Co₃ (SSC) powder were used as the cathode for the ScSZ and SDC electrolyte disks, respectively. Cathode powders were mixed with glycerol to form a slurry. This slurry was painted on the other face of the electrolyte disk, and the disk was heated at 1473 K for 4 h. The anode was reduced in a H₂ atmosphere at 973 K to obtain a Ni-based SDC cermet before the cell measurements were recorded.

The fuel cell test assembly with the two-electrode configuration was used to evaluate the current-voltage (*I-V*) characteristics. Oxygen gas was supplied to the cathode at a flow rate of 2×10^{-5} m³/min. Methane gas was also used as the fuel. The CH₄ gas diluted with He in a volume ratio of 1:9 was used as the fuel gas at a total flow rate of 2×10^{-5} m³/min. The *I-V* curves of the cells were measured at 923–1023 K. The anodic overvoltage was measured by the current interruption method. The outlet gas from the anode was analyzed by gas chromatography (Shimadzu-GC8A). Impedance spectra were recorded with an impedance meter (Yokogawa WT1600).

3. Results and Discussion

Figure 1 shows the *I-V* and current–power curves (*I-P*) for a cell using a Ni-SDC cermet (cell 1) and one using a Ni_{0.5}Co_{0.5}-SDC cermet (cell 2) as the anode, both combined with the ScSZ electrolyte. The maximum power density for cell 2 was 89 mW cm⁻², which is higher than that for cell 1 (70 mA cm⁻²) when CH₄ was supplied as the fuel.

Figure 2 shows the voltage drop across the anode and cathode with respect to the reference electrode for the Ni-SDC anode (cell 1) and the Ni_{0.5}Co_{0.5}-SDC anode (cell 2) for CH₄. The increase in the anodic overvoltage with the discharge current is more evident for cell 1 than for cell 2 with CH₄ feeding.

Figure 3 shows SEM images of the interfacial region between the cermet anode and the electrolyte after cell testing. A comparison of the microstructures between cell 1 and cell 2 shows a significant increase in the grain size of the cermet anode in cell 2. Figure 4 shows SEM images of the mixtures of NiO and Co₃O₄ starting powders at different ratios after heating at 1273 K for 10 h. Increasing the ratio of Co to Ni resulted in a grain growth in Ni_{1-x}Co_xO, which is not expected considering the melting points of NiO (2257 K) and CoO (2206 K). Since Co₃O₄ decomposes into CoO at 1168 K, the phase transformation of Co₃O₄ to CoO can affect the grain growth during the solid-

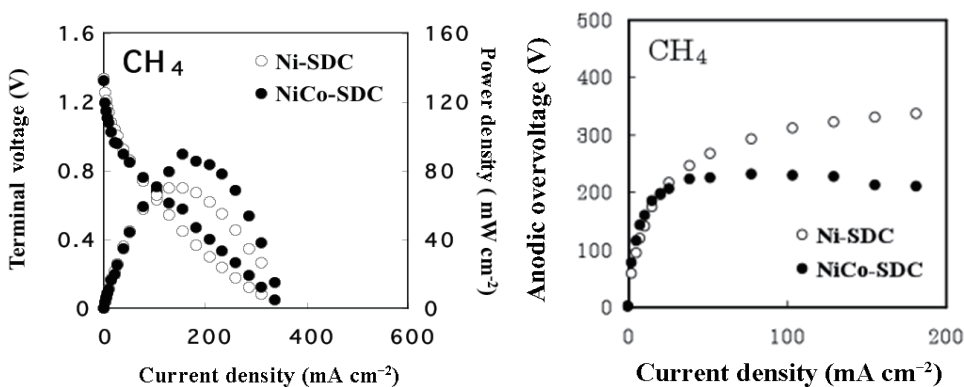


Fig. 1 (left). I - V and I - P curves for cell 1 and cell 2 at 1023 K.

Fig. 2 (right). Anodic overvoltages for cell 1 and cell 2 at 1023 K.

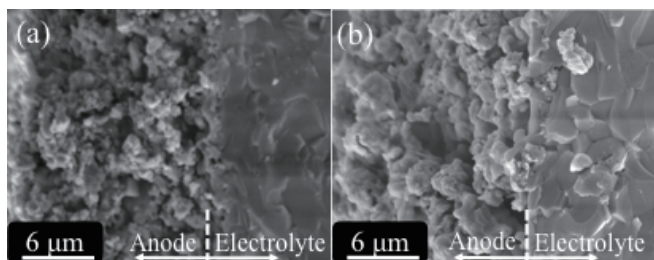


Fig. 3. Microstructures of the interfacial region of (a) cell 1 and (b) cell 2.

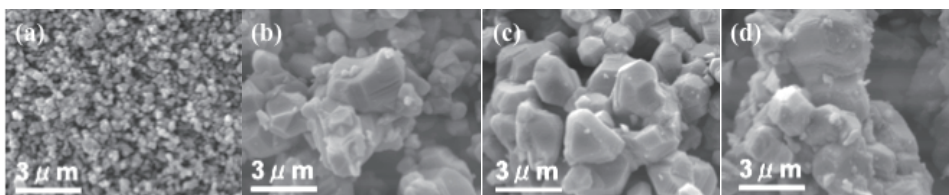


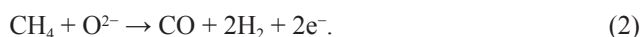
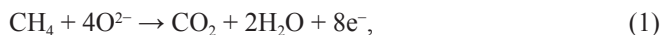
Fig. 4. Microstructures of the $\text{NiO-Co}_3\text{O}_4$ mixed powders heated at 1273 K for 10 h, which form the $\text{Ni}_{1-X}\text{Co}_X\text{O}$ solid solution particles with $X =$ (a) 0, (b) 0.25, (c) 0.5, and (d) 0.75.

state reaction between NiO and CoO. Furthermore, Co_3O_4 was found to be a sintering promoter of SDC at 1773 K.⁽⁶⁾ The ionic radius of Co^{2+} ions (78 pm) is much smaller than that of Ce^{4+} ions (101 pm) in the SDC lattice. This difference most likely causes the enhancement of the grain boundary mobility owing to a large distortion in the surrounding lattice that facilitates the defect migration in ceria.⁽⁶⁾ Figure 4 also reveals that the grain size was almost uniform in the $\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}$. These results suggest that the decrease in the anodic overvoltage for the $\text{Ni}_{0.5}\text{Co}_{0.5}$ -SDC anode (cell 2) was caused by a

decrease in the resistance to fuel gas diffusion to reaction sites at the interface between the electrolyte and the anode.

Figure 5 shows the production rates of H₂, CO, and CO₂ with the current density at 973 K in the outlet gas from the Ni_{0.5}Co_{0.5}-SDC cermet anode of a cell using SDC as the electrolyte (cell 3). The formation of H₂ or CO was detected at the open-circuit voltage (OCV), that is, 0 mA cm⁻². However, we found that the production of H₂, CO, and CO₂ was not detected at the open-circuit voltage when a zirconia-based electrolyte was used.⁽⁷⁾

The direct oxidation of methane at the SOFC anode is expressed as



Molecules of CH₄ adsorb at active sites on the metal surface of the anode, and they can decompose into the elements at temperatures lower than the thermodynamic decomposition temperature of 1058 K.⁽⁸⁾ The CH₄ decomposition depends on the chemical bond formed with the metal surface and other nearby adsorbed species. The decomposition of CH₄ into carbon and hydrogen can lead to reactions with oxide ions transported through the electrolyte. Nickel has a strong affinity for CH₄ and CO molecules, which results in coking and/or a CO poisoning effect on the metal catalyst. The addition of Ni atoms to Co atoms can impede this effect during the electrochemical oxidation of CH₄ at the cermet anode. Hydrogen is electrochemically converted to H₂O much faster than CO to CO₂ at low oxygen potentials. Although the production rate of H₂O could not be measured, the stoichiometric ratio of H₂ to CO, particularly for dry CH₄ feeding, implied the partial oxidation of CH₄ with the oxide ions. Figure 5 shows the partial oxidation of CH₄ under OCV conditions. This result indicates that the oxide-ion supply can occur through the electrolyte. This is probably specific to the electrochemical properties of SDC electrolytes. Ceria-based electrolytes show electronic conductivity at low oxygen partial pressures, which leads to an electronic current flow through the electrolyte of a cell

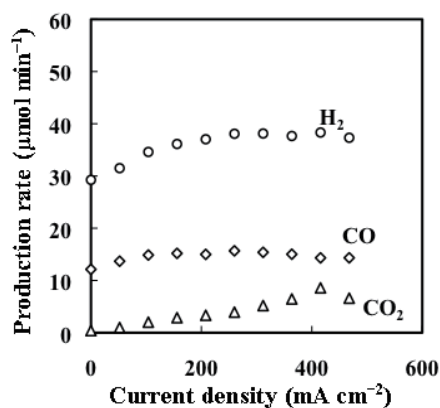


Fig. 5. Production rates of H₂, CO, and CO₂ formed by the electrochemical oxidation of CH₄ at 973 K for cell 3.

even at 0 mA cm^{-2} .⁽⁹⁾ When a cell is constructed with a CeO_2 -based electrolyte, the CeO_2 electrolyte is partially reduced at the anode side.⁽¹⁰⁾ The SDC electrolyte surface of cell 3 exposed to CH_4 produced H_2 and CO with the consumption of the lattice oxygen at low current densities according to eq. (2). The mixed ionic-electronic conduction in SDC can cause a short-circuit current flow at low current densities, which contributes to the electrochemical stability of cell 3 due to a concurrent supply of oxide ions and electrons to the anode side of the SDC electrolyte. The production rates of H_2 and CO showed a gradual decrease with an increase in that of CO_2 above approximately 200 mA cm^{-2} . At higher current densities, CO_2 is more favorable as a product than H_2 and CO according to eq. (1); oxide ion conduction is more dominant at higher current densities.⁽⁹⁾ It seems that the reduction of Ce^{4+} ions to Ce^{3+} ions, which is caused by the adsorption of methane onto the surface of a Sm_2O_3 -doped cerium oxide and the association with oxygen surface species in the oxide, enhances the electrochemical oxidation of methane.⁽¹¹⁾

Our results show that the electrochemical oxidation and activation of methane can be enhanced by suitable alloying in the metal catalysts of the cermet anode. The formation of surface active sites on the nickel-based catalyst plays an important role in the electrochemical oxidation of adsorbed CH_4 molecules; the partial oxidation of CH_4 takes place at these active surface sites, and they contribute to the production of H_2 , CO , and CO_2 depending on the amount of oxide ions supplied through the electrolyte. Molecules of CO adsorb strongly to the nickel surface owing to the back donation of electrons into the vacant orbital from the 3d electrons of nickel. This strong adsorption of CO molecules retards the further partial oxidation of CH_4 molecules on the nickel surface. Replacement of Co atoms with Ni atoms can weaken the adsorption of CO molecules since the electron density of the 3d orbitals of Co atoms is lower than that of Ni atoms.

Figure 6 shows the relationship of the cell stability for cell 3 between the maximum power density and the impedance spectra as a function of time for CH_4 feeding. The anodic polarization resistance for the electrochemical oxidation of CH_4 did not appreciably increase after 20 h, which corresponds to the stability of the maximum power density. This result indicates that the cell using the $\text{Ni}_{0.5}\text{Co}_{0.5}$ -SDC anode combined with the SDC electrolyte showed good performance for the direct oxidation of CH_4 .

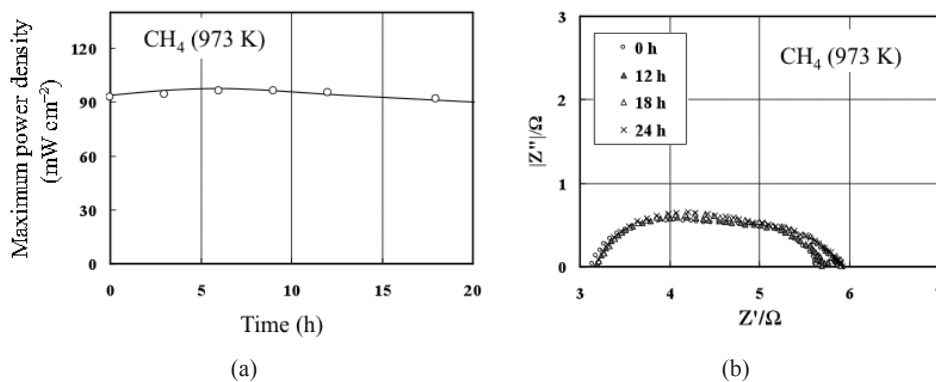


Fig. 6. (a) Maximum power density of cell 3 as a function of time and (b) impedance spectra of cell 2 corresponding to the times shown in (a).

4. Conclusions

The Ni_{1-x}Co_x-SDC cermet anode showed an increase in cell performance at a Co content of 0.5. A decrease in the anodic overvoltage and interfacial resistance contributed to the enhancement of cell performance. Grain growth of Ni_{1-x}Co_x particles and SDC particles became prominent with increasing amounts of the Co substitution in the binary Ni-Co alloy system in the cermet anode. The enhancement of the cell performance for the direct oxidation of CH₄ is most likely caused by the weak adsorption of CO molecules, which is a product of the partial oxidation of CH₄ with the O²⁻ ions transported through the electrolyte, on the surface of Ni_{1-x}Co_x particles and the decrease in the interfacial resistance.

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