ENHANCEMENT OF THE ELECTROCHEMICAL OXIDATION OF METHANE IN THE NICKEL-COBALT SDC CERMET ANODE

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ABSTRACT

Substitutional replacement of Co atoms for Ni atoms in the Ni-based samaria-doped ceria (SDC) cermet anode resulted in decreases in the anodic overpotential and interfacial resistance between the anode and electrolyte. The morphological observation, X-ray diffraction analysis, and temperature-programmed desorption (TPD) analysis have been made for the Ni_{1-x}Co_x-SDC cermet particles in order to discuss the mechanism for the enhancement of the direct oxidation of methane.

INTRODUCTION

Catalytic activity of solid oxide fuel cell (SOFC) anodes is important when hydrocarbon fuels are directly fed into an operating cell (1-5). The nickel and yttria-stabilized zirconia (Ni-YSZ) cermet anode is currently used for the generation of a hydrogen-rich gas by the steam reforming of methane in the internal configuration. However, the Ni-YSZ cermet anode shows a low activity for the direct electrochemical oxidation of methane. The development of a proper catalyst in combination with a high oxide-ion conductor is therefore required for the direct oxidation of hydrocarbon fuels.

We therefore have investigated the performance of anodes which consist of the Ni-Co alloy (6) and samaria-doped ceria (SDC). The anodic polarization resistance of the Ni_{1-x}Co_x-SDC anode was separately examined for hydrogen and methane. Microstructural characterization of the Ni_{1-x}Co_x-SDC cermet anode was made in order to reveal an enhancement effect on the direct oxidation of methane.

EXPERIMENTAL

The Ni_{1-x}Co_xO solid solution was prepared by heating a mixture of reagent-grade NiO and CoO powders in an alumina crucible at 1273 K for 10 h in air, and this process was repeated again to obtain solid solution powders. Phase identification of the prepared powders was made by X-ray diffraction analysis (XRD). Contamination from the alumina crucible was not detected for the prepared powders within the detection limit of the electron microprobe analyzer (EPMA). Pulverized Ni_{1-x}Co_xO powders were mixed with...
the SDC (Ce0.8Sm0.2O1.9) powder in a mass ratio of 30% to form a slurry using ethylcellulose binder (STD-100, Dow Chemical). The slurry was painted as the anode on one face of an SDC electrolyte disk, whose relative density was 98%. The disk was 15 mm in diameter and 0.3 mm thick. The painted disk was heated at 1573 K for 5 h. Sm0.5Sr0.5CoO3 (SSC) was used as the cathode. SSC powders were mixed with the ethylcellulose binder to form a slurry. This slurry was painted on the other face of the SDC disk, and the disk was heated at 1473 K for 5 h. The thickness of the anode and cathode was approximately 50 μm. Two 0.3 mm diameter platinum lead wires were attached to each electrode with a platinum mesh (#100 mesh) 3 mm x 3 mm in size. Following this fabrication procedure, the cell was fired at 1323 K for 1 h. The anode was reduced in a hydrogen atmosphere at 1023 K to obtain a Ni-based SDC cermet before the cell measurements.

The fuel cell test assembly with the two-electrode configuration was used to evaluate the current-voltage (I-V) characteristics. Anodic overpotential measurements were conducted using a cell configuration described elsewhere. The reference electrode was bonded as a small circle on the anode face separated by a 2-3 mm gap from the circular working electrode. Glass ring gaskets were used to fix and seal the peripheral areas of the anode and cathode faces of the cell to the ends of alumina tubes with a 2 mm thickness and a 15 mm outer diameter. In order to keep the same experimental condition, the prepared cells were kept at 1023 K for 6 h in air for sealing with the glass ring gaskets and subsequently kept at 973 K for 1 h in a dry hydrogen atmosphere to reduce the Ni1-xCoxO particles. Oxygen gas was supplied to the cathode at a flow rate of 2 x 10⁻⁵ m³/min. I-V curves of the cells were measured at 973-873 K for hydrogen humidified with 3 vol% water vapor whose total flow rate was 2 x 10⁻⁵ m³/min. Methane (CH₄) was also used as the fuel. Methane diluted with helium in a volume ratio of 1:9 was used as the fuel gas at a total flow rate of 2 x 10⁻⁵ m³/min. I-V curves of the cells for methane were measured at 973-873 K. Reproducibility of these I-V curves on increasing and decreasing the temperature was confirmed for each experiment. The anodic overpotential was measured by the current interruption method. The outlet gas from the anode was analyzed by gas chromatography. Impedance spectra were measured with an impedance analyzer (HP-4192A). Temperature-programmed desorption (TPD) analysis was applied to Ni1-xCox-SDC powders in order to characterize the adsorptive property for methane, carbon monoxide, and hydrogen.

RESULTS AND DISCUSSION

Fig. 1 shows voltage-current density curves and anodic overvoltage curves for the cells using the Ni1-xCox-SDC (X=0, 0.25, 0.50 and 0.75) anode for the humidified hydrogen. Increasing amount of Co resulted in an increase of the cell performance accompanying a decrease in the anodic overvoltage. However, we could not obtain these curves for the Co-SDC anode; preparation of this anode was difficult due to poor adhesive property to the SDC disk after firing. Almost the same tendency in the cell performance as that observed for hydrogen was identified for methane, as shown in Fig. 2. Fig. 3 shows a comparison of the Arrhenius plots of the reciprocal polarization resistance, $R_p^{-1}$, for the cell using the Ni-SDC anode and one using the Ni₀.₂₅Co₀.₇₅-SDC anode. The larger values in $R_p^{-1}$ thereby indicate a high activity for the oxidation of hydrogen or methane. The slope of the
Arrhenius plots remained almost constant, showing that the solid solutioning of cobalt into nickel in the fcc lattice does not change the apparent activation energy for the electrode reaction. The exhaust gas analysis for the methane introduced into the anode by gas chromatography revealed that the predominant products for the reaction occurring at the anode were hydrogen and carbon.

Fig. 4 shows a comparison of the surface morphology observed by scanning electron microscopy (SEM) for the prepared Ni$_{1-x}$Co$_x$O (X = 0 and 0.75) and their reduced states. The samples were prepared in the same manner as prepared for the Ni$_{1-x}$Co$_x$-SDC anode; Ni$_{1-x}$Co$_x$O powder slurries were painted on the face of SDC disks and heated at 1573 K for 5 h in air, followed by the reduction at 973 K for 2 h in a hydrogen atmosphere. Significant grain growth accompanying sintering of Ni$_{0.25}$Co$_{0.75}$ particles was identified, which reflects a formation of many open pores appearing at the surface of Ni$_{0.25}$Co$_{0.75}$ particles. Fig. 5 shows secondary electron images for the surface of the Ni-SDC anode and that of the Ni$_{0.25}$Co$_{0.75}$-SDC anode. Although the lateral resolution of elemental spot analysis by EPMA is low in the sub-micron range, both the elemental mapping and the contrast observed in the secondary electron image suggest that white small particles particularly identified for the Ni$_{0.25}$Co$_{0.75}$-SDC anode are probably SDC particles. This speculation is in good accordance with the morphology observed in Fig. 4. These results showed that concurrent grain growth takes place both in SDC and Ni$_{1-x}$Co$_x$ particles with increasing content of Co atoms. Impedance analysis of the cells suggested a decrease in the interfacial resistance between the anode and electrolyte.

Fig. 6 shows X-ray diffraction profiles for the prepared Ni$_{1-x}$Co$_x$O-SDC (X = 0, 0.25, 0.50, and 0.75) powders. Increasing amount of Co ions in Ni$_{1-x}$Co$_x$O shifted its reflection peaks to lower angles; this indicates an expansion of the unit cell by the substitution of Co ions for Ni ions in the fcc lattice. By contrast, SDC reflection peaks remained in the same positions regardless of the composition of Ni$_{1-x}$Co$_x$O. However, these reflection peaks from SDC became narrow and their intensities increased with increasing amount of the Co content. Fig. 7 shows the change of the full width at half maximum (FWHM) for the 422 reflection peaks. The decrease in FWHM indicates an occurrence of recrystallization of SDC particles, which corresponds to the morphological change observed in Fig. 5.

TPD analysis for the adsorption of methane to Ni$_{1-x}$Co$_x$O-SDC (X=0, 0.5, and 1.0) powders revealed that the amount of adsorbed methane molecules decreases by increasing the Co content, as shown in Fig. 8. The spectrum intensity of Ni$_{1-x}$Co$_x$O-SDC (X=0, 0.5, and 1.0) powders was normalized by the surface area, and the blank test for SDC powders did not affect the appearance of the TPD peaks in these spectra. These results indicate that cobalt atoms contribute to a weak adsorptive ability for methane molecules.

These results show that the alloying effect by adding Co atoms to the Ni-based SDC cermet anode contributes to an enhancement of the cell performance for methane. The decrease in the anodic overvoltage could be primarily caused by a decrease of the interfacial resistance between the anode and electrolyte. Since the melting temperature of Co is 1768 K and that of Ni is 1725 K, the addition of Co atoms to the Ni matrix cannot affect the morphology of the Ni$_{1-x}$Co$_x$-SDC cermet structure. We found that increasing amount of CoO in the starting Ni$_{1-x}$Co$_x$O phase significantly contributes to the grain growth of Ni$_{1-x}$Co$_x$O particles and SDC particles. The decrease in the polarization...
resistance and its temperature dependence imply that the increase of the reaction rate occurring at the triple phase boundary among the gas phase (methane), electrode (Ni$_{1-x}$Co$_x$), and electrolyte (SDC) is determined by the ability of oxide-ion transport to the reaction site. The activation for the direct electrochemical oxidation of methane is most likely to be caused by the supply of oxide ions through the electrolyte, whose ability is controlled by the crystalline state of the electrolyte near the interface region.

CONCLUSIONS

The Ni$_{1-x}$Co$_x$-SDC cermet anode showed an increase in the cell performance for hydrogen and methane with increasing amount of Co content up to 0.75. The decrease in the anodic overpotential and the interfacial resistance contributes to the enhancement of the cell performance. Grain growth of Ni$_{1-x}$Co$_x$ particles became prominent with increasing amount of the Co substitution in the Ni$_{1-x}$Co$_x$-SDC cermet anode. The decrease in the X-ray reflection peak width for SDC was observed with increasing amount of the Co substitution, which indicates an acceleration of sintering and recrystallization of the SDC particles coexisting with Ni$_{1-x}$Co$_x$ particles. The enhancement of the cell performance for the direct oxidation of methane is most likely to be caused by the weak adsorption of methane molecules on the surface of Ni$_{1-x}$Co$_x$ particles and the decrease in the interfacial resistance.

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Figure 1. The cell performance for the cells using the Ni$_{1-x}$Co$_x$-SDC anode and their anodic overvoltage for hydrogen added with 0.6 vol% water vapor at 973 K.

Figure 2. The cell performance for the cells using the Ni$_{1-x}$Co$_x$-SDC anode and their anodic overvoltage for methane at 973 K.

Figure 3. Arrhenius plots of $R_p^{-1}$ for (left) hydrogen, and (right) for methane.
Figure 4. SEM micrographs of Ni particles (left) and Ni_{0.25}Co_{0.75} particles (right).

Figure 5. SEM micrographs of Ni-SDC particles (left) and Ni_{0.25}Co_{0.75}-SDC particles (right).

Figure 6. X-ray diffraction profiles of Ni_{1-x}Co_{x}-SDC powders.
Figure 7. FWHM of the 422 reflection peak vs. x in Ni_{1-x}Co_x-SDC powders.

Figure 8. TPD spectra for Ni_{1-x}Co_x-SDC powders.