

Solid-solutioning effect of the Ni-based cermet on the electrochemical oxidation of methane

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Current solid oxide fuel cells (SOFCs) are designed to electrochemically oxidize a mixture of hydrogen and carbon monoxide, which is provided by the reforming of the natural gas (methane). The nickel and yttria stabilized zirconia (Ni/YSZ) cermet is most widely used as the anode for the steam reforming of methane. However, the endothermic nature of the steam reforming results in a deactivation of the anodic oxidation of methane mainly due to the carbon deposition over the nickel surface.

The direct oxidation of methane is possible in SOFCs using anodes which include oxide catalysts such as rare-earth-based perovskites and rare-earth-doped ceria. Several attempts have been made to promote the electrochemical oxidation of methane at the anode of SOFC using highly dispersed noble metal catalysts. However, the electrochemical oxidation and activation of methane has not been discussed in relation to the role of nickel-based catalysts. We have therefore examined electrocatalytic properties of the binary solid-solution system in nickel and cobalt as well as its microstructure.

The cermet anodes were prepared by mixing fine oxide powders prepared from metal oxalates in an appropriate molar ratio and heating at 1300-1400 °C in air. The volume ratio of the starting oxide powders and stabilized zirconia powders was fixed to 1:1. The fuel cell was composed of the yttria-stabilized zirconia (YSZ) or scandia-stabilized zirconia (ScSZ) disk, 15 mm in diameter and approximately 0.3 mm thick, and the electrodes. Methane added with water vapor and pure methane each diluted with helium were independently supplied to the anode as a fuel. Hydrogen was also used as a fuel for comparison. Anodic overpotential measurements were conducted using a three-electrode configuration by the current-interruption method. The exhaust gas from the anode was analyzed by the gas chromatography.

Figure 1 shows a comparison of the current-voltage (I - V) curves at 800°C for the cells using Ni-ScSZ and $\text{Co}_{0.5}\text{Ni}_{0.5}\text{-ScSZ}$ when methane added with water vapor approximately 0.6 vol.% was supplied. The cell using the $\text{Co}_{0.5}\text{Ni}_{0.5}\text{-ScSZ}$ showed a higher cell performance particularly for methane, indicating that solid solutioning of cobalt in the nickel-based cermet increased the maximum power density by approximately 50% only for methane due to a decrease in the anodic overvoltage. Linear relationships were observed between the anodic overvoltage and the current density at current densities less than approximately 30 mA/cm² in the temperature range examined. The anodic overvoltage in this range is caused by electrocatalytic (charge transfer) reactions at the interface between the electrode and electrolyte.

Arrhenius plots of the reciprocal polarization resistance, R_p^{-1} , were made for these cells in the temperature range between 750 to 850 °C. The Arrhenius plots showed that the cell using the $\text{Co}_{0.5}\text{Ni}_{0.5}\text{-ScSZ}$ cermet anode had a higher activity for the anodic oxidation of methane than the one using the Ni-YSZ cermet anode, but

the slope of both Arrhenius plots remained almost constant. This result indicates that the solid solutioning of cobalt in the Ni-based cermet does not change the apparent activation energy for the anode reaction but increases the amount of adsorbed species being involved in the reaction.

The formation of surface active sites on the nickel-based catalyst can play an important role in the electrochemical oxidation of adsorbed methane; the partial oxidation of methane takes place at these active surface sites and they contribute to the production of hydrogen and carbon monoxide. Carbon monoxide adsorbs strongly to the nickel surface due to the back donation of electrons into the vacant orbital from the 3d electrons of nickel. This strong adsorption of carbon monoxide retards the further partial oxidation of forthcoming methane molecules onto the nickel surface. Replacement of cobalt atoms for nickel atoms in the cubic lattice most likely weakens the adsorption of carbon monoxide since the electron density of the 3d orbitals of cobalt is lower than those of nickel. We found that the $\text{Co}_{0.5}\text{Ni}_{0.5}$ particles have a crystallographically oriented microstructure perpendicular to the (111) crystal plane, which was not observed for the Ni particles. The exposure of the most densely packed plane in the face-centered cubic structure could therefore contribute the formation of surface active sites for the electrochemical oxidation of methane.

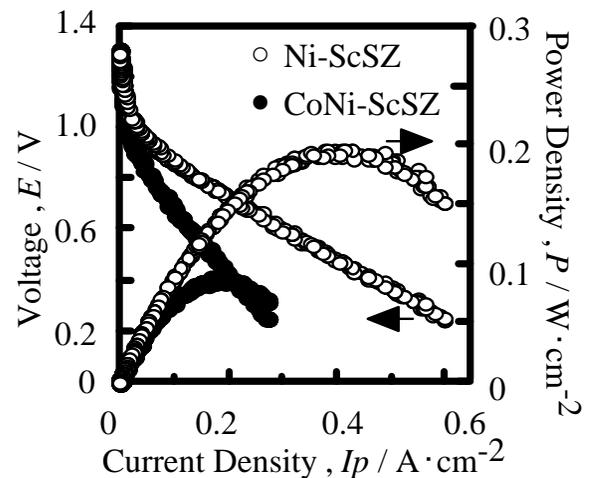


Figure 1. Comparison of the cell performance between the Ni-ScSZ cermet and the $\text{Co}_{0.5}\text{Ni}_{0.5}\text{-ScSZ}$ cermet at 800°C.