

# Electrochemical Oxidation Properties of Metal and Oxide Catalysts for Methane in Solid Oxide Fuel Cells

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Catalytic activity of solid oxide fuel cell (SOFC) anodes is important when natural gas (methane) is directly used as the fuel gas. The nickel and yttria stabilized zirconia (Ni/YSZ) cermet anode is currently used for the generation of a hydrogen-rich gas based on the steam reforming of methane in internal configuration. However, the endothermic nature of the steam reforming reaction results in a deactivation of the anodic oxidation reaction when the reaction temperature is decreased; the deactivation of the electrode reaction is mainly caused by the carbon deposition over the surface of nickel. The development of a proper catalyst, therefore, is required for the direct oxidation of methane.

Several studies have shown that the direct oxidation of methane is possible using anodes which include oxide catalysts such as rare-earth-based perovskites and rare-earth-doped ceria. Furthermore, several attempts have been made to promote the electrochemical oxidation of methane at the anode of SOFC using highly dispersed noble metal catalysts. In earlier studies, we found that the specific valence states of transition metal oxide particles,  $\text{HCoO}_2$ ,  $\text{HCrO}_2$ , and  $\text{PdCoO}_2$  show high catalytic activities for the anodic oxidation of methane and hydrogen. These effects can be explained by the alternate reduction and oxidation on the surface of the oxide catalysts. Since the anode is exposed to various reducing atmospheres, it is important to investigate the role of both metal and oxide catalysts. In this study we measured the methane oxidation properties mainly for the Ni/YSZ, Ni-Co/YSZ, and Ni-MgO/YSZ anodes. The results were compared with those of the hydrogen oxidation properties in relation to the microstructure of the anodes and the chemical states of metals.

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 fine YSZ powders (TZ8Y, Tosoh) was fixed to 1:1. The fuel cell was composed of the YSZ disc, 13 mm in diameter and 0.3 mm thick, and the electrodes.  $\text{CH}_4$  gas added with water vapor  $\geq 0.6$  vol% and pure  $\text{CH}_4$  gas each diluted with an equal amount of helium were independently supplied to the anode as fuel. Anodic overpotential measurements were conducted using a three-electrode configuration by the current-interruption method. The exhaust gas from the anode compartment was analyzed with a gas chromatograph.

The starting oxide powders form solid solutions in the as-prepared condition. During the measurements, both nickel and cobalt oxides were reduced to metals but magnesium oxide was stable; catalytic activities of the Ni/YSZ, Ni-Co/YSZ, and Ni-MgO/YSZ anodes were compared for

methane and hydrogen in the temperature range at 650-850 °C. The Ni-Co solid solution resulted in a decrease of the anodic overpotential for methane but not for hydrogen, indicating a high activity for the electrochemical oxidation of methane. The presence of small amounts of MgO particles in the Ni-YSZ anode significantly reduced the anodic overpotential for methane without losing the porous microstructure of the Ni-YSZ cermet. The anodic overpotential of the Ni-MgO/YSZ anode for hydrogen shows the highest value among the anodes measured; this indicates that the presence of MgO particles impedes the charge transfer process between the adsorbed hydrogen and oxide ions transported through the electrolyte at the surface of nickel.

The exhaust gas composition analysis for methane added with 0.6%  $\text{H}_2\text{O}$  by gas chromatography revealed that the ratio of  $\text{CO}$  and  $\text{H}_2$  was approximately 2:1 at discharge currents up to about 250  $\text{mA}/\text{cm}^2$  at 800 °C. Small amounts of  $\text{CO}_2$  were detected with increasing the discharge current. These results show that the catalytic activity of Ni-MgO is predominantly for the partial oxidation of methane. The effect of water vapor ratio on the cell performance has been investigated. The enhancement of the cell performance is probably caused by the catalytic reforming of methane by the oxide ions and the water vapor. The metal support interaction plays an important role for the electrochemical oxidation of methane in SOFCs. The solid-solutioning effect of metal catalysts and the role of oxide supports are discussed.