SOLID-SOLUTIONING EFFECT OF THE Ni-BASED CERMET ON THE ELECTROCHEMICAL OXIDATION OF METHANE

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ABSTRACT

A new electrocatalyst which enhances the activity for methane oxidation at the anode was investigated. The solid solutioning of cobalt into nickel, whose starting oxide solid solution was prepared by co-precipitation from a mixed solution of oxalic acid and metal nitrates, resulted in an increase in the cell performance, particularly for the direct methane use. The partial oxidation of methane probably takes place at the active sites of the Co$_{0.5}$Ni$_{0.5}$ alloy surface. The enhancement of the anodic oxidation of methane depends on a crystallographically oriented microstructure along the (111) crystal planes, which was not observed for the nickel particles. The cell performance was evaluated by the anodic polarization resistance and the production rates of CO, CO$_2$ and H$_2$. The activation mechanism is discussed in terms of the formation of surface active sites for the electrochemical oxidation of methane.

INTRODUCTION

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 natural gas (methane). Methane is oxidized at a nickel-based cermet anode, which catalyzes the reforming reaction of methane with steam, and oxygen is reduced at a cathode based on the strontium-doped lanthanum manganites. Oxide ions are transported through a solid electrolyte disk. The present SOFC units operate at 900-1000°C to achieve their high performance. Although these high operating temperatures promote rapid reaction kinetics at the anode-electrolyte interface, decreasing the SOFC operating temperatures accompanied by the direct use of methane-containing fuel gases are desirable. However, the nickel-based cermet anode currently used in SOFCs is unsuitable due to deactivation of the nickel surface when methane is directly used as the fuel. Lowering the SOFC operating temperature thus requires alternative anode materials which show a high activity for the electrochemical oxidation of methane without deactivation of the anode.

The direct oxidation of methane is possible in SOFCs using anodes which include oxide catalysts such as La$_{0.8}$Ca$_{0.2}$CrO$_{3-δ}$ (1) and rare earth-doped ceria (2). It seems that the reduction of Ce$^{4+}$ to Ce$^{3+}$, which is caused by the adsorption of methane onto the surface of a doped cerium oxide and the association with oxygen surface species in the oxide,
enhances the electrochemical oxidation of methane (3,4). However, the electrochemical oxidation and activation of methane has not been discussed in terms of the solid-solutioning effect of the metal catalysts. We have therefore examined the direct oxidation of methane at the cermet anode prepared from a solid solution of CoO-NiO.

EXPERIMENTAL

The solid-solution oxides were prepared by a co-precipitation method using a solution of oxalic acid and metal nitrates. The oxide powders were obtained by heating the precipitates at 1100°C for 24 h in air. The conventional preparation method using a solid state reaction between CoO and NiO reagent powders under the same heating condition was employed for comparison. Phase identification for these powders by X-ray diffraction indicates a single phase formation. The anode powders were prepared by mixing commercially available 8 mol% yttria-stabilized zirconia (YSZ: TZ8Y, Tosoh) or 10 mol% scandia and 1 mol% ceria-stabilized zirconia (ScSZ, Rare-Earth Chemical) with the oxide starting powders in an appropriate molar ratio, which was followed by calcination at 1300°C for 10 h in air. The calcined powders were ground in an agate mortar with a pestle, and painted on one side of an YSZ disk or an ScSZ disk (Shinko Electric Industries) with glycerol, which was followed by heating at 1350°C for 10 h in air. These electrolyte disks were 15 mm in diameter and 0.28 mm thick. (La0.8Sr0.15)0.90MnO3 powder was mixed with glycerol and subsequently painted as the cathode. The calcination for the cathode was performed at 1300°C for 10 h in air. The thickness of each electrode was approximately 50 μm. Two 0.3 mm diameter platinum lead wires were attached to each electrode with a platinum mesh (#100 mesh) 2 mm x 2 mm in size. Following this fabrication procedure, the cell was fired at 1250°C for 1 h. The anode was reduced in a hydrogen atmosphere at 850°C to obtain a Ni-based YSZ (or ScSZ) 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 (5). A platinum reference electrode was bonded onto the small semicircular portion of the anode face separated by a 2 mm gap from the semicircular 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. Methane (CH4) gas was used as the fuel. The fuel gas diluted with an equal amount of He gas was introduced into the anode compartment at a total flow rate of 4 x 10⁻³ m³/min. Oxygen gas was supplied to the cathode at the same flow rate. The outlet gas from the anode was analyzed by the gas chromatography.

RESULTS AND DISCUSSION

Figure 1 shows comparisons of the current-voltage (I-V) and current-power curves (I-P) at 800°C between the cell using a Ni-YSZ cermet and one using a Co0.5Ni0.5-YSZ cermet as the anode when hydrogen and methane were independently supplied as the fuel. The cell
using the Co$_{0.5}$Ni$_{0.5}$-YSZ cermet showed a higher cell performance particularly for CH$_4$; the maximum power density for the Co$_{0.5}$Ni$_{0.5}$-YSZ cermet was approximately two times as high as that for the Ni-YSZ cermet. The significant enhancement in the cell performance for the methane feeding was observed for the Co$_{0.5}$Ni$_{0.5}$-YSZ cermet anode, whose starting material, Co$_{0.5}$Ni$_{0.5}$O, was prepared by co-precipitation from a solution of oxalic acid and metal nitrates. Figure 2 shows comparisons of the current-overvoltage at 800°C for hydrogen and methane between the Ni-YSZ and Co$_{0.5}$Ni$_{0.5}$-YSZ cermet anodes. The anodic overvoltage of the Co$_{0.5}$Ni$_{0.5}$-YSZ cermet was significantly lower than that of the Ni-YSZ cermet. Figure 3 shows the Arrhenius plots of the reciprocal polarization resistance, $R_p^{-1}$, for the cell using the Ni-YSZ cermet and one using the Co$_{0.5}$Ni$_{0.5}$-YSZ cermet as the anode in the temperature range between 700 to 800°C. The polarization resistance, $R_p$, was determined from the slope of the line showing a linear relationship between the anodic overpotential and current density at low current densities less than approximately 50 mA/cm$^2$. The larger values in $R_p^{-1}$ thereby mean a high activity of the anode for the methane feeding; the anodic activation overpotential, $\xi_{\text{act}} = a R_p \times i$, is caused by charge transfer reactions at the anode. The solid solutioning of cobalt into nickel increased the electrocatalytic activity of the anode by about two times for methane. However, the slope of the Arrhenius plots remained almost constant, indicating that the solid solutioning of cobalt does not change the apparent activation energy for the anode reaction but increases the amount of reactants, probably adsorbed methane onto the surface of the CoNi alloy, being involved in the reaction.

Figure 4 shows variations of the maximum power density for the cells using the Co$_x$Ni$_{1-x}$-YSZ cermet anode when hydrogen and methane were supplied as the fuel. The Co-YSZ cermet anode showed the lowest maximum power density both for hydrogen and methane, which agreed with the previous results obtained for the comparison of the hydrogen oxidation activity at the Co-YSZ and Ni-YSZ cermet anodes (6). Our results showed that increasing amount of cobalt in the Co$_x$Ni$_{1-x}$-YSZ cermet does not affect the cell performance for hydrogen up to approximately $x = 0.8$ but increases the cell performance for methane up to approximately $x = 0.5$, the Co$_{0.5}$Ni$_{0.5}$-YSZ cermet exhibited the highest activity for the anodic oxidation of methane.

The same activity for methane was also observed for the Co$_{0.3}$Ni$_{0.7}$-ScSZ cermet anode combined with the scandia-stabilized zirconia electrolyte, 10 mol%Sc$_2$O$_3$-1 mol%CeO$_2$-89 mol%ZrO$_2$, as shown in Fig. 5. Due to higher electrical conductivities in ScSZ, the cell performance was higher than that of the cell using the YSZ electrolyte, and the maximum power density for the Co$_{0.3}$Ni$_{0.7}$-ScSZ cermet was approximately two times as high as that for the Ni-ScSZ cermet when methane was supplied as the anode gas. The behavior of the anodic polarization resistance showed the same tendency as that observed for the Co$_{0.3}$Ni$_{0.7}$-YSZ cermet; the apparent activation energy remained constant but the methane oxidation activity significantly increased by the increase in the number of molecules for the reaction at the anode.

Figure 6 shows X-ray diffraction patterns for the Co$_{0.5}$Ni$_{0.5}$ alloy powder reduced at 850°C, the starting Co$_{0.5}$Ni$_{0.5}$O powders prepared by the co-precipitation route and a comparison of 111 and 200 reflections between the Co$_{0.5}$Ni$_{0.5}$ alloy powders prepared by the co-precipitation route and the conventional solid-state reaction. The relative intensity
ratio of the 111 reflection to the 200 reflection, $I_{111}/I_{200}$, for the Co$_{0.5}$Ni$_{0.5}$ alloy powder prepared by the co-precipitation route was 3.4. However, the Co$_{0.5}$Ni$_{0.5}$ alloy powder prepared by the conventional solid-state reaction between cobalt oxide (CoO) and nickel oxide (NiO) exhibited $I_{111}/I_{200} = 2.6$, which is almost close to the standard cobalt powder (JCPDS #15-0806), $I_{111}/I_{200} = 2.4$, and the standard nickel powder (JCPDS #04-850), $I_{111}/I_{200} = 2.5$. These results indicate that crystal orientation occurs for the Co$_{0.5}$Ni$_{0.5}$ alloy powder prepared by the co-precipitation route; the most densely packed planes with randomly occupied by cobalt and nickel atoms preferentially appeared at the alloy surface. Since we could not measure this crystallographically oriented structure for the Co$_{0.5}$Ni$_{0.5}$-YSZ (or -ScSZ) cermet by X-ray diffraction, the identical conditions for firing and reducing these cermets were used for the preparation of the alloy powder. The crystal orientation thus most likely occurred in the microstructure of metals in the cermet.

To understand the effect of solid solutioning of cobalt into nickel on the enhancement of the methane oxidation at the anode, we compared the production rates of H$_2$, CO and CO$_2$ at 800°C in the outlet gas between the cells using the Ni-YSZ and Co$_{0.5}$Ni$_{0.5}$-YSZ cermet anodes. Figure 7 shows the production rates of H$_2$, CO and CO$_2$ with current densities. Feeding a mixture of methane and 0.6 vol% water vapor as the anode fuel resulted in a production of H$_2$ and CO with the approximate ratio $H_2:CO=3:1$ at the open-circuit voltage. In contrast, feeding dry methane did not result in the formation of H$_2$ or CO at the open-circuit voltage. CO$_2$ was not detected at least up to the current density 0.6 A cm$^{-2}$ regardless of the water vapor addition to methane. The production rates of H$_2$ and CO linearly increased with increasing current density and the production ratio of H$_2$ to CO remained about 2 when the external current was observed. The relationship between the production rates of H$_2$ and CO and the current density was almost identical in the Ni-YSZ and Co$_{0.5}$Ni$_{0.5}$-YSZ cermet anodes. These results suggest that the Co$_{0.5}$Ni$_{0.5}$-YSZ cermet enhances the conversion of methane to H$_2$ and CO.

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

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\text{CH}_4 + 4\text{O}^2^- \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 8e^- \quad [1]
\]

\[
\text{CH}_4 + \text{O}^2^- \rightarrow \text{CO} + 2\text{H}_2 + 2e^- \quad [2]
\]

Methane molecules adsorb at active sites of the metal surface of the anode and they can decompose into carbon and hydrogen. The methane decomposition depends on the chemical bond formed with the metal surface and other nearby adsorbate species. The decomposition of methane into carbon and hydrogen can lead to reactions with oxide ions transported through the electrolyte. Hydrogen is electrochemically converted to H$_2$O much faster than CO to CO$_2$ at low oxygen potentials. Although we could not measure the production rate of H$_2$O, the stoichiometric ratio of H$_2$ to CO particularly for the dry methane feeding implies the partial oxidation of methane with the oxide ions. The production rates of H$_2$ and CO measured for the Co$_{0.5}$Ni$_{0.5}$-YSZ cermet anode were higher than those for Ni-YSZ cermet anode under the same voltage. The enhancement of the methane conversion to H$_2$ and CO resulting in low anodic overpotentials by the solid solutioning of cobalt into nickel well explains the behavior of the Arrhenius plots of the inverse polarization resistance shown in Fig. 3.
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 probably takes place at these active surface sites and they contribute to the production of H₂ and CO. CO strongly adsorbs 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 CO retards 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 CO since the electron density of the 3d orbitals of cobalt is lower than those of nickel. We found that the Co₀.₃Ni₀.₅ powder has a crystallographically oriented microstructure along the (111) crystal plane, which was not observed for the nickel powder. The exposure of the most densely packed plane in the face-centered cubic structure could therefore contribute to the formation of surface active sites for the electrochemical oxidation of methane.

CONCLUSIONS

Solid solutioning of cobalt into nickel in the cermet anode increased the electrocatalytic activity for the direct oxidation of methane in solid oxide fuel cells using stabilized zirconia disks as the electrolyte. The Co₀.₃Ni₀.₅-YSZ (or -ScSZ) cermet anode showed the lowest anodic polarization resistance. The partial oxidation of methane probably takes place at the active sites of the Co₀.₃Ni₀.₅ alloy surface. The enhancement of the anodic oxidation of methane depends on a crystallographically oriented microstructure along the (111) crystal planes, which was not observed for the single nickel particles. Arrhenius plots of the inverse polarization resistance and the production rates of CO, CO₂, and H₂ revealed that the increase in the cell performance is due to the formation of surface active sites for the partial oxidation of methane with the oxide ions.

ACKNOWLEDGMENTS

This work has been supported by Tokyo Electric Power Company. We gratefully acknowledge Shinko Electric Industries Co., Ltd. for the supply of zirconia disks.

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Figure 1. $I$-$V$ and $I$-$P$ relationships for the cells using the Co$_{0.5}$Ni$_{0.5}$-YSZ and Ni-YSZ cermet anodes for the fuel added with 0.6 vol% water vapor.

Figure 2. Anodic overvoltage for the cells shown in Fig. 1.
Figure 3. Arrhenius plots of the reciprocal polarization resistance for the Co$_x$Ni$_{1-x}$-YSZ and Ni-YSZ cermet anodes for methane added with 0.6 vol% water vapor.

Figure 4. Maximum power density for the Co$_x$Ni$_{1-x}$-YSZ cermet anode.
Figure 5. $I$-$V$ and $I$-$P$ relationships for the cells using the Co$_{0.6}$Ni$_{0.4}$-ScSZ and Ni-ScSZ cermet anodes for the fuel with 0.6 vol% water vapor.

Figure 6. X-ray diffraction profiles of the Co$_{0.6}$Ni$_{0.4}$ powders prepared by the co-precipitation route. Enlarged profiles show a comparison between the alloy powders prepared by the co-precipitation route and the conventional solid state reaction.
Figure 7. Production rates of CO, CO₂, and H₂ as a function of the current density.