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# Effect of precious metal addition to Ni-YSZ cermet on reforming of $CH_4$ and electrochemical activity as SOFC anode

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## Abstract

Various kinds of precious metals were added to the Ni-$Y_2O_3$-stabilized zirconia (Ni-YSZ) cermets, and the relation between steam reforming of $CH_4$ and the electrochemical activity as a solid oxide fuel cell (SOFC) anode was investigated. Ru and Pt additions promoted the reforming and suppressed the coke depositions. The electrochemical activity of the SOFC anode was enhanced by the addition of Ru and Pt, indicating that these precious metals effectively functioned as the anode catalysts. The impedance related to gas diffusion was greatly reduced, indicating that stability of the anode catalyst of SOFC was considerably improved since coke was hardly deposited.

*Keywords:* SOFC; Steam reforming; AC impedance; Ni-YSZ cermets; Carbon deposition; Precious metal

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## 1. Introduction

Power generation by solid oxide fuel cells (SOFCs) is one of the most attracting energy conversion systems because of high efficiency and low pollution. The high operating temperature enables to reform various kinds of hydrocarbon fuels with steam on the anode internally in a SOFC module. Such simplified internal reforming operation of SOFC system results not only in low costs owing to the elimination of pre-reformer, but also in efficient thermal heat recuperation by the endothermic steam reforming reaction.

Natural gas is regarded as a relatively cheap and popularly available fuel with a plenty of deposit; thus it is suitable for SOFC. The main component of natural gas is methane, and the Ni-$Y_2O_3$-stabilized zirconia (Ni-YSZ) anode material catalyzes the following reforming of methane:

Steam reforming of methane :

$$CH_4 + H_2O \rightarrow 3H_2 + CO \quad (1)$$

Water gas shift reaction :

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

However, internal reforming of methane often accompanies carbon deposition. The active sites of the anode are covered with deposited carbon, leading to the

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deactivation, loss of cell performance and lower SOFC reliability [1,2].

The majority of studies on Ni-YSZ-based cermet anodes have focused on kinetics of internal reforming of hydrocarbons [3–5], the effect of $CeO_2$ addition to the Ni-YSZ cermet [6], the influence of microstructure [7–9] and electrochemical performance as an electrode [10,11]. Only a few reports dealt with carbon deposition on the anode during catalysis for reforming of fuel. The reaction gas composed of high steam/carbon (S/C) ratios typically over 2 was used to suppress carbon deposition; however, it is unattractive for fuel cells since steam dilution of the fuel lowers the conversion efficiency. Steam reforming of methane on supported nickel catalysts has been studied by many workers [12–17]. Some additives such as alkaline earth oxides and ceria have been reported as effective in suppressing carbon deposition [18–21]. In the present investigation, precious metal components were added to Ni-YSZ cermets to avoid carbon deposition. The Ni-YSZ cermets were characterized by AC impedance analysis. The relation between electrochemical activity and the catalytic properties of promoted Ni-YSZ cermets for steam reforming of methane and carbon deposition was investigated.

## 2. Experimental

### 2.1. Preparation of modified Ni-YSZ cermets

8 mol% $Y_2O_3$-stabilized zirconia (abbreviated hereafter as YSZ, Tosoh Co., TZ-8YS) and NiO were milled for 24 h, the mixtures were impregnated with aqueous solution of $Ru(NO_3)_3$, $Rh(NO_3)_3$, $Pd(NO_2)_2(NH_3)_2$, and $Pd(NO_2)_2(NH_3)_2$ (Tanaka Kikinzoku). The weight ratio of Ni:YSZ:precious metal was set at 1:0.32:0.01. The sintered samples were then pulverized into powder or granular shape.

### 2.2. Methane decomposition and steam reforming of methane

An YSZ disk ($\phi$8 mm, 0.2 mm thick) was used as the support. One side of the disk was painted with the slurry of the mixture of polyethylene glycol (Wako Pure Chemical Industries, Average molecular weight = 300) and the cermet powder was prepared. The disk was then calcined at 1400 °C for 5 h in air, and the thickness of the resulting cermet film was 50 μm. Methane was decomposed at atmospheric pressure using thermogravimetric analyzer (Shimadzu, TGA-50), where the catalyst powder was loaded in the basket of the balance. Prior to the reaction, catalysts were reduced in the stream of 5% $H_2$/Ar from the room temperature to 1000 °C at a constant heating rate of 10 °C/min, and the temperature was held at 1000 °C for 10 min. Then $H_2$/Ar flow was changed to the flow of 67% methane and 33% $N_2$. The carbon deposition rate for first 1 min was defined as follows:

$$\text{carbon deposition rate} = \frac{\text{weight increase by deposited carbon}}{\text{cermet weight} \times \text{reaction period}}$$

A gaseous mixture composed of 20% $CH_4$, 40% $H_2O$ and 40% $N_2$ was fed at the total rate of 71.2 ml/min at STP for steam reforming reaction of methane. Catalytic activity was measured on decreasing reaction temperature from 1000 to 600 °C.

### 2.3. Electrochemical property of various Ni-YSZ cermets

A perovskite-type $La_{0.6}Sr_{0.4}MnO_3$ mixed oxide was prepared as a cathode according to the following procedure. Calculated amounts of $(CH_3COO)_3La\cdot nH_2O$, $(CH_3COO)_2Sr\cdot(1/2)H_2O$, and $(CH_3COO)_2Mn\cdot 4H_2O$ (Wako Pure Chemical Industries) were dissolved in water. Water was removed from the mixed solution at 100 °C and dried at 120 °C overnight. Resulting powders were milled for 24 h and calcined at 900 °C for 10 h. A YSZ disk ($\phi$20 mm, 0.5 mm thick) was used as the support. The slurry of the mixture of polyethylene glycol and the $La_{0.6}Sr_{0.4}MnO_3$ was applied on the other side of the disk, on the one side of which the Ni-YSZ cermet anode had been deposited. Then the disk was calcined at 1150 °C for 5 h in air. A gaseous mixture of 15% $CH_4$, 45% $H_2O$ and 40% $N_2$ was supplied as anode gas to the Ni-YSZ and precious metal-modified Ni-YSZ cermets at 150 ml/min at STP. Gaseous oxygen was fed to the $La_{0.6}Sr_{0.4}MnO_3$ cathode, and current–voltage characteristics were measured at 1000 °C on a Hokuto Denko HA-301 galvanostat. Impedance spectra of anode/electrolyte interface of the fuel cells with the various cermets were recorded over a frequency range of 0.01–$10^6$ Hz with an AC amplitude of 10 mV using frequency response analyzer (Solartron 1260) at the open circuit condition.

## 3. Results and discussion

### 3.1. Carbon deposition on various cermets

An effect of additive to the Ni-YSZ cermets on the rate of carbon deposition is summarized in Table 1. On Ni-YSZ, methane was decomposed to form $H_2$ and C, and aggregated spherical carbon and bulky carbon fibers were observed [21]. It was reported that rate of catalytic decomposition of methane and kinds of formed carbon species depended on catalysts and reaction temperature [22]. Therefore, it is suggested that not only the activity of cermet catalyst but also the morphology of the deposited carbon affects the rate of the carbon deposition at this experimental conditions.

$$CH_4 \rightarrow C + 2H_2 \qquad (3)$$

The carbon deposition rate on YSZ was 0.045 C g/ cermet g min. While Rh addition promoted coke formation, Ru, Pd, and Pt additions produced a smaller amount of coke. It was reported that precious metal-modified Ni catalyst showed high activity and produced a small amount of coke owing to the spill over effect of precious metal [23]. In this experiment, it was suggested that these precious metals had the function of hydrogen spill over, and hydrogen formed by decomposition was spilled over from Ru, Pd and Pt to the carbon species; therefore, C–C bond formation was suppressed.

### 3.2. Steam reforming of $CH_4$ on various cermets

The effect of precious metal addition to the Ni-YSZ cermet on steam reforming of $CH_4$ is also summarized in Table 1. When steam/carbon ratio is high, it is generally accepted that steam reforming of methane initiates via methane decomposition that is the rate-determining step. Reaction steps have been considered as follows:

$$CH_4 \rightarrow C + 2H_2 \qquad (3)$$

$$C + H_2O \rightarrow CO + H_2 \qquad (4)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2)$$

When the reaction rate is proportional to partial pressure of $CH_4$, it is indicated that reaction (3) is the rate-determining step. However, reaction (3) is not proportional to the above-mentioned carbon deposition rate. The carbon species, which was precursor of coke and formed in the steam reforming experiment, was rapidly removed by reactions (2) and (4); therefore, the morphology of the carbon species does not affect the rate of decomposition.

The addition of all the precious metals improved the steam reforming of methane, indicating that precious metal functioned as the steam reforming catalyst. Precious metals promoted the $CH_4$ decomposition reaction and $H_2$ production effectively. Therefore, Ru and Pt additions were effective for promotion of the reforming as well as for suppression of the coke depositions.

Table 1
Comparison of decomposition and steam reforming of $CH_4$ conversion on various cermets

| Cermet (before reduction) | Weight ratio | Carbon deposition rate[a] | $CH_4$ conversion (%)[b] | | |
|---|---|---|---|---|---|
| | | (C g/cermet g min) | 600 °C | 700 °C | 800 °C |
| Ni:YSZ | 1.00:0.32 | 0.045 | 54.8 | 90.7 | 99.3 |
| Ni:YSZ:Ru | 1.00:0.32:0.01 | 0.030 | 65.1 | 93.6 | 99.3 |
| Ni:YSZ:Rh | 1.00:0.32:0.01 | 0.062 | 57.3 | 84.5 | 98.2 |
| Ni:YSZ:Pd | 1.00:0.32:0.01 | 0.037 | 57.1 | 90.3 | 98.6 |
| Ni:YSZ:Pt | 1.00:0.32:0.01 | 0.027 | 62.1 | 91.3 | 99.1 |

[a] Gas composition: 67% $CH_4$, 33% $N_2$; total flow rate: 45 ml/min at STP; temperature: 1000 °C.
[b] Gas composition: 40% $N_2$, 20% $CH_4$, 40% $H_2O$; total flow rate: 71.2 ml/min at STP.

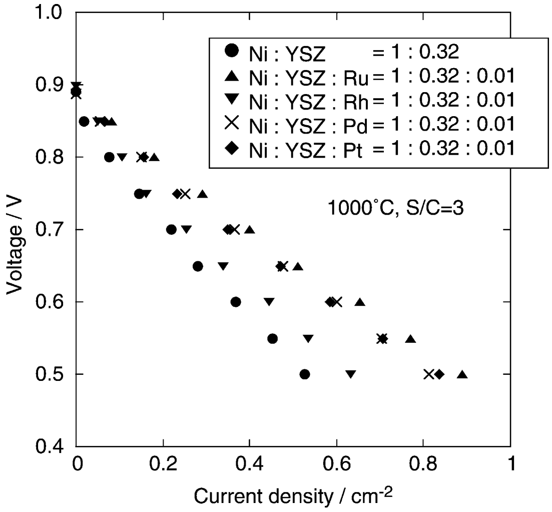

Fig. 1. Current–voltage characteristics in SOFC operation using precious metal-modified Ni-YSZ cermets at 1000 °C. Anode gas: 40% $N_2$, 15% $CH_4$, 45% $H_2O$; flow rate, 150 ml/min at STP; cathode gas: $O_2$; flow rate, 150 ml/min at STP.

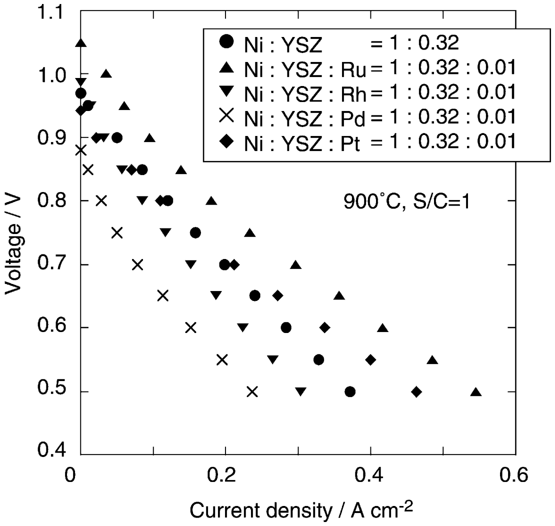

Fig. 2. Current–voltage characteristics in SOFC operation using precious metal-modified Ni-YSZ cermets at 900 °C. Anode gas: 70% $N_2$, 15% $CH_4$, 15% $H_2O$; flow rate, 150 ml/min at STP; cathode gas: $O_2$; flow rate, 150 ml/min at STP.

### *3.3. Electrochemical property of modified Ni-YSZ cermets*

Next, the effect of precious metal addition was investigated. Results are shown in Fig. 1. The open circuit voltage for the cells with precious metal-modified Ni-YSZ cermets was 0.90 V, which also almost agreed with the theoretical value of 0.95 V. *I–V* curves show that Ru, Pd and Pt additions promoted the electrochemical activity as the anode catalysts, indicating that these precious metals effectively functioned as the anode catalysts.

To emphasize the effect of coke deposition, the current–voltage characteristics of SOFC were examined at 900 °C with $S/C = 1$. The open circuit voltages for the cells with precious metal-modified Ni-YSZ cermets were smaller than theoretical value of 1.2 V. Since this condition was on the boundary of carbon deposition [21], deposited the coke suppressed the electrochemical activity owing to the inhabitation of gas diffusion. As shown in Fig. 2, the electrochemical activity of Ni-YSZ cermets modified with Ru and Pt was much higher than unmodified Ni-YSZ cermets.

Impedance spectra for the anode/electrode interface of fuels using Ni-YSZ cermets modified with Ru and Pt are shown in Fig. 3. For Ni-YSZ, this plot had one large semicircle with its resistance of ca. 1.5 Ω and one small semicircle with its resistance of ca. 0.7 Ω. The characteristic frequencies defined as $\omega = (RC)^{-1}$ at the summit of the semicircles were ca. 1000 and 20 Hz, respectively. Since low frequency semicircle and high frequency semicircles were ascribed to electrochemical reaction and gas diffusion, respectively [24], the large semicircle could be related to reaction process, while the small semicircle could be related to gas diffusion process. By Ru and Pt addition, the small semicircle disappeared, while the large semicircles did not change. This result indicates that Ru and Pt addition did not affect the impedance caused by reaction, and greatly reduced the impedance caused by gas diffusion. As shown in Table 1, since steam reforming of methane on Ni-YSZ modified with Ru and Pt was rapid, the carbonaceous species, which is precursor of coke, is effectively converted by reaction (4). Therefore, the hydrogen supply was rapid owing to deficiency of carbonaceous species or coke. To promote the electrochemical activity, it is important to convert the carbonaceous species effectively. These data mean that the modified anode was considerably stable without suffering from coke formation.

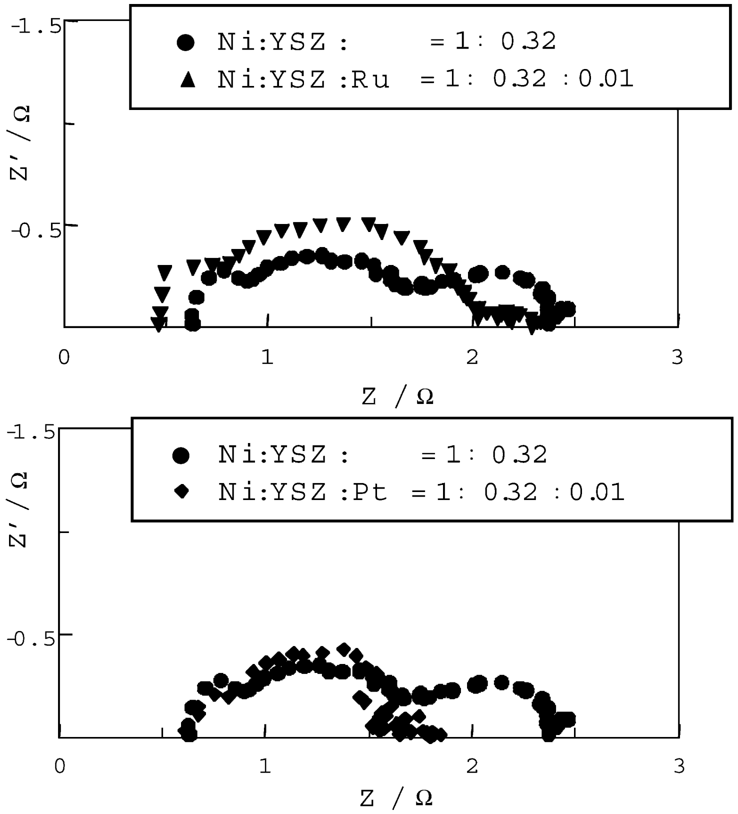

Fig. 3. Impedance spectra for anode/electrolyte interface of SOFC using Ni-YSZ cermets modified with Ru and Pt at 1000 °C. Steam/carbon = 3 and bias = open circuit voltage.

## 4. Conclusions

The additive to the cermet significantly affected the kinetic parameters of steam reforming of $CH_4$ on Ni-YSZ cermet. Ru and Pt additions promoted the electrochemical activity as anode, indicating that these precious metals effectively functioned as the anode catalysts. The impedances caused by gas diffusion were greatly reduced by addition of Ru and Pt, and this contributed to the high performance and stability of the anode catalyst of SOFC.

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