

Study on steam reforming of CH₄ and C₂ hydrocarbons and carbon deposition on Ni-YSZ cermets

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Abstract

Equilibrium partial pressure of oxygen and the boundary of carbon deposition region were calculated in the C–H–O phase diagram at temperatures ranging from 400 to 1000 °C. The open circuit voltage for the solid oxide fuel cell (SOFC) was directly connected to the calculated partial pressure of oxygen at higher temperatures. These calculations suggested that the development of the anode catalyst without carbon deposition was one of the most promising ways to achieve high efficiency in SOFC because the amount of added water could be reduced. The characteristics of steam reforming of methane and carbon deposition on Ni-Y₂O₃-stabilized zirconia (Ni-YSZ) cermets anodes were examined. The effect of MgO, CaO, SrO and CeO₂ addition to Ni-YSZ cermets on their catalytic activity and carbon deposition was investigated. Although, the CaO addition slightly deteriorated the electrochemical activity as anode, the CaO addition was effective in suppressing carbon deposition and promoted steam reforming of CH₄.

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Keywords: Methane; Steam reforming; Ni-YSZ cermets; Carbon deposition; CaO

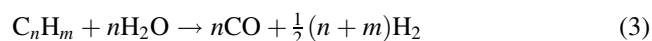
1. Introduction

Power generation by solid oxide fuel cells (SOFCs) is one of the most attracting energy conversion systems because of high efficiency, low pollution and multi-fuel compatibility. The high operating temperature gives rise to excellent fuel flexibility, which allows to reform hydrocarbon fuels on the anode internally in a SOFC module. Such simplified internal reforming operation of SOFC system results in low costs owing to the elimination of pre-reformer. Natural gas is regarded as a relatively cheap and popularly available fuel, which is suitable for SOFC. The main component of natural gas is methane, and the Ni-Y₂O₃-stabilized zirconia (Ni-YSZ) anode material catalyzes the following reforming of methane: steam reforming of methane :

(1)

water gas shift reaction : CO + H₂O → CO₂ + H₂ (2)

Natural gas usually contains ca. 10% of higher hydrocarbons, which also react with steam:



In steam reforming of methane, a large amount of steam in excess of the stoichiometric requirement of reaction (1) was usually supplied, and this addition promotes the shift reaction (2) to forward direction. The formed CO₂ suppressed disproportionation (4):



However, internal reforming of hydrocarbon often accompanies carbon deposition. The active sites of the anode are covered with deposited carbon, resulting in the deactivation, loss of cell performance and lower SOFC reliability [1,2].

The majority of studies on Ni-YSZ-based cermet anode have focused on kinetics of internal reforming of hydrocarbons [3–5], the effect of CeO₂ addition to the Ni-YSZ cermet [6], the influence of microstructure [7–9] and

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electrochemical performance as an electrode [10,11]. Few reports dealt with carbon deposition on the anode and catalysis for reforming of fuel.

The Ni-YSZ cermet has been popularly used as the anode in most of the research and development of SOFCs. 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 have been reported as effective in suppressing carbon deposition. For example, alkaline earth oxides were added to reduce carbon deposition [18–20]. The forms of supported nickel catalysts are different from Ni-YSZ cermet, and these catalysts have own pore structures and nickel particle sizes. The sizes of Ni grains in the cermet were much larger than those of the supported catalysts.

In the present investigation, the catalytic properties of Ni-YSZ cermets for steam reforming of methane and carbon deposition were investigated. Alkaline earth oxides (MgO, CaO, SrO) and CeO₂ were added to Ni-YSZ cermets to avoid carbon deposition.

2. Calculation

2.1. Partial pressure of oxygen and carbon deposition region by equilibrium calculation

The theoretical voltage of SOFC for an electrolyte with its ionic transference number of unity can be obtained by the Nernst equation (5):

$$E = \left(\frac{RT}{4F} \right) \ln \left[\frac{p(\text{O}_2, \text{cathode})}{p(\text{O}_2, \text{anode})} \right] \quad (5)$$

Partial pressure of O₂ at the anode depends on the equilibrium composition of reaction gas, while partial pressure of O₂ in cathode is usually constant. In this calculation, equilibrium compositions were determined by the following reactions ((6)–(8), or reactions (6)–(9) when carbon is deposited):



When reactions (7) and (8) attained the equilibrium, the shift reaction (2) must attain the equilibrium. The equilibrium partial pressure of oxygen in gas mixtures for the C–H–O phase diagram was calculated at temperatures ranging from 400 to 1000 °C. The boundary of carbon deposition region was also calculated. To expand the fuel flexibility, it is important to determine the equilibrium composition of anode gas and the boundary of carbon deposition.

3. Experimental

3.1. Shift reaction and steam reforming of methane on the conventional Ni-YSZ cermet

Shift reaction (2) and steam reforming of methane (1) were carried out at atmospheric pressure using a conventional flow system, where catalyst made by TOTO Ltd. was loaded. A commercial YSZ tube painted with the Ni-YSZ cermet was used for the reaction. The area of the active catalytic surface for the Ni-YSZ cermet was 25.8 cm². Steam was generated in a temperature-controlled humidifier by bubbling the gas mixture. Reaction gas mixture composed of 22.2% H₂O, 11.1% CO, 33.3% H₂ and 33.4% N₂ was fed at the total rate of 374 standard temperature and pressure (STP) ml/min. This contact time between reaction gas and Ni-YSZ corresponds to 0.25 s at 1000 °C. Prior to the reaction, the catalyst was reduced in a 50% H₂/N₂ stream from room temperature to 1000 °C at a constant heating rate of 200 °C/h. Then, the reactants were introduced into the reactor. Reaction products were analyzed by an on-line gas microchromatograph (Chrompack, Micro-GC CP2002).

For steam reforming of methane, reaction gas mixture composed of 42.9% H₂O, 14.3% CH₄, and 42.8% N₂ was fed at the total rate of 291 STP ml/min. This corresponds to the conditions of the above-mentioned steam reforming of methane and the ordinal operating condition of SOFC applied in power generation test of current density of 300 mA/cm² and fuel utilization of 60%. This contact time between reaction gas and Ni-YSZ corresponds to 0.32 s at 1000 °C. The behaviors of steam reforming of ethane and ethylene were compared with that of methane. Reaction gas mixture composed of 46.2% H₂O, 7.7% C₂H₆ (or C₂H₄) and 46.1% N₂ was fed at the total rate of 270 STP ml/min. This contact time between reaction gas and Ni-YSZ corresponds to 0.34 s at 1000 °C. In all cases, the S/C ratio was set at 3.

3.2. Preparation of modified Ni-YSZ cermets

Eight mole percent YSZ (Tosoh Co., TZ-8YS), NiO, MgO, CaO, CeO₂ (Wako Pure Chemical Industries Ltd.) and SrO (Nacalai Tesque Inc.) were used with further treatment. The Ni-YSZ cermets were prepared as follows: NiO, YSZ and alkaline earth or CeO₂ were mixed by weight ratio of 4:(1 – x):x with x = 0, 0.01, 0.05 and 0.10. After mixed samples were milled for 24 h, the samples were calcined at 1400 °C for 5 h in air. The sintered samples were then pulverized into powder or granular shape.

3.3. Methane decomposition

A YSZ disk (8 mm φ, 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 Ltd., average molecular weight = 300) and the cermet powder prepared in Section 3.2. It was 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% H₂/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, H₂/Ar flow was changed to the flow of 67% methane and 33% N₂. The carbon deposition rate for first 1 min was defined as follows:

$$\text{carbon deposition rate} = \frac{\text{weight increase by deposited carbon}}{\text{cermet weight} \times 1 \text{ min}}$$

3.4. Steam reforming of methane on modified Ni-YSZ cermets

The YSZ (Nikkato Co.) tube was used as the support. Outer surface of the tube was painted with the slurry of the mixture of polyethylene glycol and the cermet prepared in Section 3.2. The coated tube was calcined at 1400 °C for 5 h in air, and the area of the resulting cermet film was 16.3 cm². Reaction system and reduction treatment were the same as those in Section 3.1. To emphasize the effect of additive on the steam reforming of methane, the concentration of H₂O was lower than that in Section 3.1. A gas mixture composed of 20% CH₄, 40% H₂O and 40% N₂ was fed at the total rate of 71.2 STP ml/min for steam reforming reaction of methane. Catalytic activity was measured on decreasing reaction temperature from 1000 to 600 °C.

3.5. Electrochemical property of Ni-YSZ and CaO–Ni-YSZ cermets

An perovskite-type La_{0.6}Sr_{0.4}MnO₃ mixed oxide was prepared. Calculated amounts of (CH₃COO)₃La·nH₂O, (CH₃COO)₂Sr·(1/2)H₂O, and (CH₃COO)₂Mn·4H₂O (Wako Pure Chemical Industries Ltd.) 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 (20 mm φ, 0.5 mm thick) was used as the support. One side of the disk was painted with the slurry of the mixture of polyethylene glycol and the cermet prepared in Section 3.3. It was calcined at 1400 °C for 5 h in air. The slurry of the mixture of polyethylene glycol and the La_{0.6}Sr_{0.4}MnO₃ was applied on the other side of the disk. It was calcined at 1150 °C for 5 h in air.

A gaseous mixture of 15% CH₄, 45% H₂O and 40% N₂ was supplied as anode gas to the Ni-YSZ and CaO-modified Ni-YSZ cermets at 150 STP ml/min. Gaseous oxygen was fed to the La_{0.6}Sr_{0.4}MnO₃ cathode, and current–voltage characteristics were measured at 1000 °C on a Hokuto Denko HA-301 gavlanoostat.

3.6. Characterization

The samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD profiles were recorded on a Shimadzu XD-D1 diffractometer with a carbon monochromator by using Cu Kα radiation. SEM observation was carried out on Hitachi S-2500CX.

4. Results and discussion

4.1. Partial pressure of oxygen and carbon deposition region by equilibrium calculation

The calculated equilibrium partial pressure of oxygen was expressed as a contour map in the C–H–O phase diagram at temperatures ranging from 400 to 1000 °C, as shown in Fig. 1. The open circuit voltage is directly connected to theoretical voltage of SOFC calculated by Eq. (5). As the fraction of oxygen in the C–H–O phase diagram increased, the cell voltage significantly decreased. The partial pressure of oxygen in the reducing atmosphere was generally lowered as the temperature was reduced. The drop of the partial pressure was drastic when the composition crossed the line of H₂O–CO₂ at every temperature, which was the stoichiometric composition of combustion. The broken lines indicating the boundary of carbon deposition region are also plotted in Fig. 1. The S/C ratio of unity is just located at the boundary at 1000 °C, and this composition on anode led to the highest theoretical cell voltage in the carbon free region as expected from Fig. 1. Operation in the carbon free region does not lead deposition from the thermodynamic expectation, whereas carbon is sometimes observable due to dissociation of C–H bond and rapid growth of carbon–carbon chain. It was suggested that the development of the anode catalyst without carbon deposition was one of the most promising ways to achieve high efficiency in SOFC because the steam addition may be reduced without carbon deposition.

The catalytic activity for steam reforming is expected to affect the power generation characteristics in internal reforming operation. As for internal reforming of methane, the steam reforming reaction (1) and water gas shift reaction (2) proceed during the brief contact with the cermet thick film. It should be meaningful to clarify the rough estimate of the rates of these catalytic reactions and the conversions at a practical contact time for the catalytic reaction for the cermet catalyst.

4.2. Shift reaction and steam reforming of methane on conventional Ni-YSZ cermet

Catalytic activity of the Ni-YSZ cermets for shift reaction is shown in Fig. 2. The equilibrium CO₂ yield and CO conversion in Fig. 2 were estimated, assuming that four gas species, CO, CO₂, H₂, and H₂O excluding CH₄ were in the

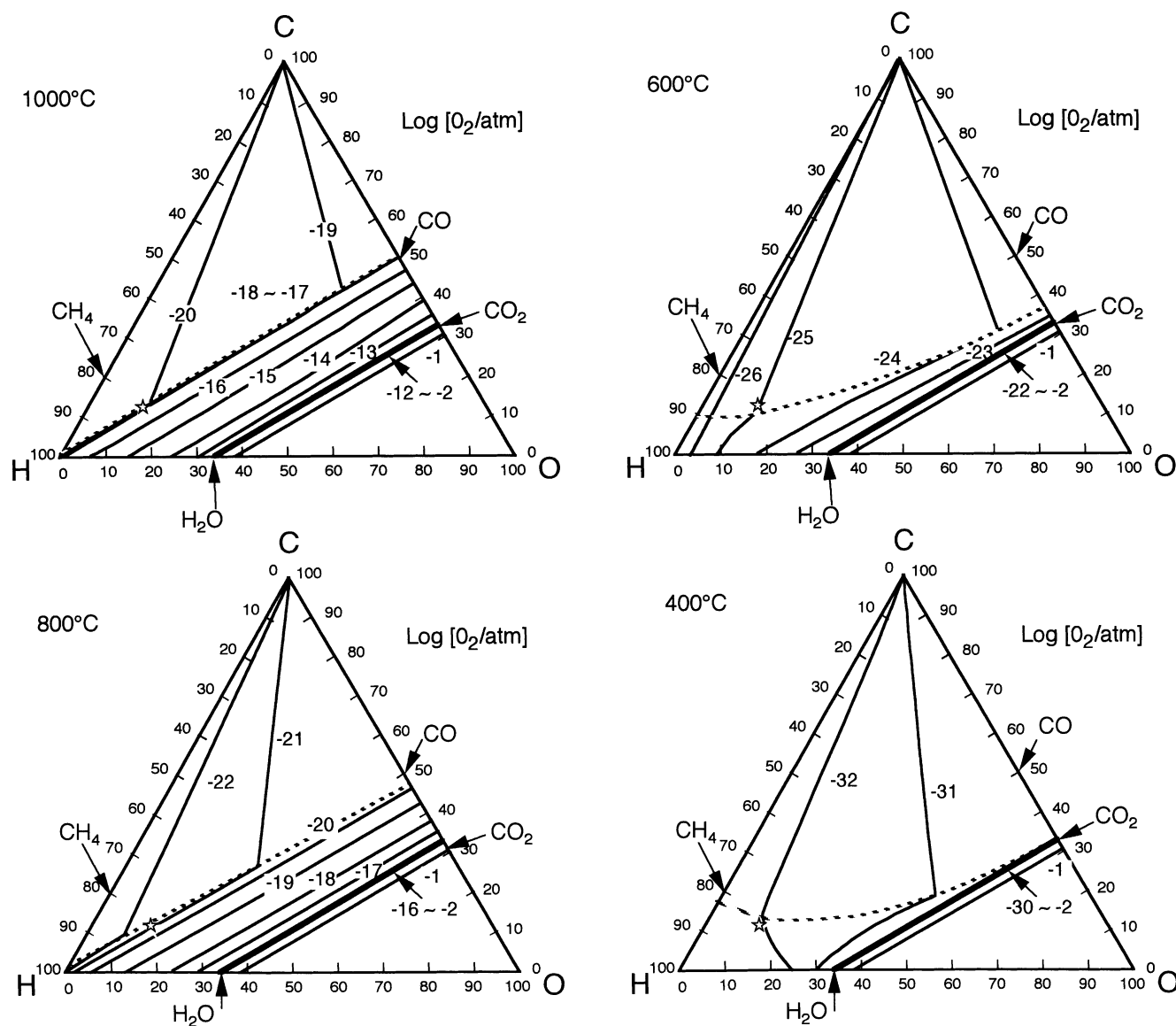


Fig. 1. The equilibrium partial pressure of oxygen and the boundary of carbon deposition region in gas mixtures for the C–H–O diagram at temperatures ranging from 400 to 1000 °C. Broken lines show the boundary of carbon deposition region; therefore, carbon deposition is expected in carbon-rich composition beyond the lines.

thermodynamic equilibrium. CO conversion approached the equilibrium at 600 °C and reached the equilibrium over 850 °C, although it is generally accepted that the shift reaction reaches the equilibrium on transition metal catalyst at relatively low temperatures around 250–300 °C. In the present experiment, the reaction approached the equilibrium from low temperatures (550–600 °C), whereas complete agreement was difficult due to very short contact time of 0.25 s. This indicates that open circuit voltage below 600 °C may deviate from theoretical voltage calculated from partial pressure of O₂ in Fig. 1 because of the deviation from equilibrium gas composition.

Steam reforming of methane was investigated as shown in Fig. 3. The equilibrium CH₄ conversion reached 100% at 750 °C or higher temperatures, while the observed one

stayed far below the equilibrium below 850 °C. The comparison with Fig. 2 indicates that the rate of steam reforming of methane was much slower than that of the shift reaction. The observed conversion was 100% at 900 °C; thus, almost complete conversion was attained under the operation conditions of SOFC at 1000 °C with contact time of 0.25 s. This indicates that open circuit voltage over 900 °C is expected to be theoretical voltage calculated from partial pressure of O₂ in Fig. 1. The equilibrium CO₂ yield in Fig. 3 was estimated, assuming that four gas species, CO, CO₂, H₂, and H₂O excluding CH₄ were in the thermodynamic equilibrium. The measured CO₂ yield agreed with the expected one in the whole temperature range examined. The shift reaction in Fig. 3 reached the equilibrium more easily than that in Fig. 2, indicating that CO formed by the steam reforming was

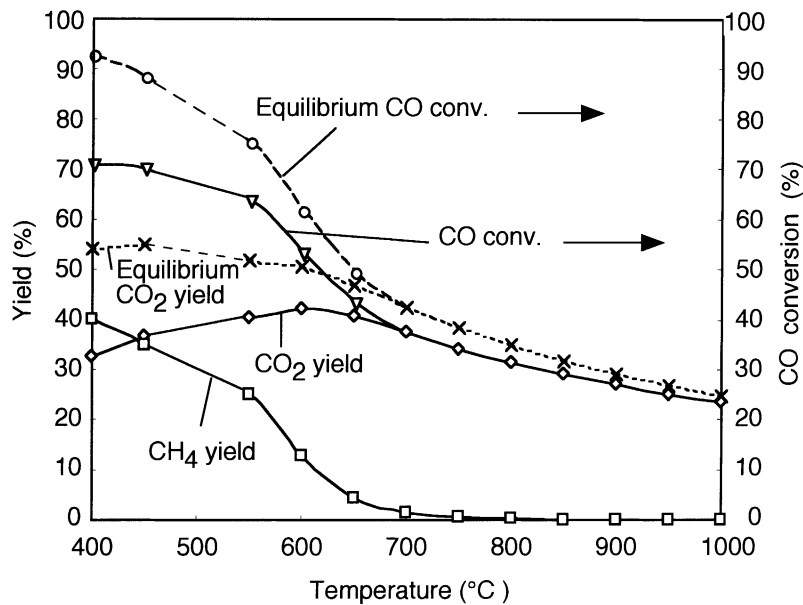


Fig. 2. Influence of reaction temperature on shift reaction. Gas composition: 22.2% H₂O, 11.1% CO, 33.3% H₂, 33.4% N₂; total rate of 374 STP ml/min.

located near the active sites and rapidly reacted with H₂O to form CO₂.

Steam reforming of C₂H₄ and C₂H₆ was carried out as in the case of CH₄. Since both C₂H₄ and C₂H₆ were almost completely converted over 800 °C, the CO₂ yield for steam reforming of C₂H₄ and C₂H₆ is summarized in Table 1. The equilibrium CO₂ yield was again calculated, assuming that four gas species, CO, CO₂, H₂, and H₂O were in the thermodynamic equilibrium. The CO₂ yield slightly deviated from the equilibrium even at 800 °C for the steam reforming of C₂H₆ and C₂H₄, though that for CH₄ reached the equilibrium

over 600 °C. It is generally accepted that steam reforming initiates via decompositions of hydrocarbons ((10) and (11)) that is the rate-determining step; this will be discussed later:



Therefore, carbon was deposited on catalysts after steam reforming even in the carbon free regions shown in Fig. 1. It was suggested that deposited carbon covered the active site, resulting in the deactivation for steam reforming.

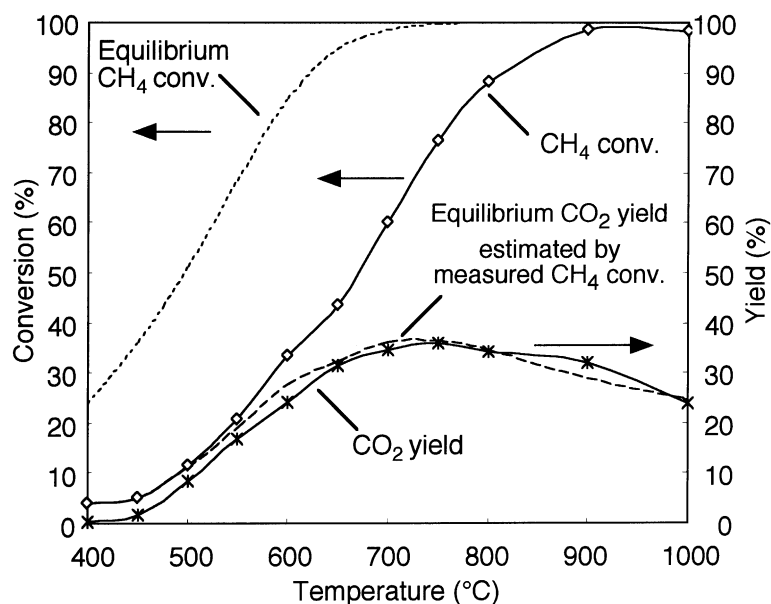


Fig. 3. Influence of reaction temperature on steam reforming of methane. Gas composition: 42.9% H₂O, 14.3% CH₄, 42.8% N₂; total rate of 291 STP ml/min.

Table 1
The CO₂ yield on steam reforming of C₂H₄ and C₂H₆

Fuel	Temperature (°C)	CO ₂ yield ^a (C-at.%)	Equilibrium CO ₂ yield (C-at.%)
C ₂ H ₄	800	36.8	41.4
	900	33.6	35.3
	1000	29.1	30.6
C ₂ H ₆	800	33.3	37.7
	900	28.2	31.8
	1000	24.4	27.2

Gas composition: 46.2% H₂O, 7.7% C₂H₆ (or C₂H₄), 46.1% N₂; total rate of 270 STP ml/min.

^a Conversion of C₂H₄ and C₂H₆ = 100%.

4.3. Effect of alkaline earth addition on carbon deposition

In the conventional steam reforming catalysts, some additives to the alumina support have been known to be effective in avoiding carbon deposition. An effect of alkaline earth addition to the Ni-YSZ cermet on rate of the carbon deposition is summarized in Table 2. The addition of CaO or SrO to the Ni-YSZ cermet obviously suppressed the carbon deposition, while the MgO addition to the Ni-YSZ cermet rather promoted the carbon deposition. For CeO₂-modified Ni-YSZ cermet, the rate of carbon deposition was related to the CeO₂ amount, and this will be discussed later. Although NiO in Ni-YSZ cermet is reduced to metallic Ni in the working state of the SOFC operation, the addition of CaO or SrO with their strong basicity modified metallic Ni to slightly cationic state; therefore, carbon deposition was suppressed. Such an additive effect of alkaline earth oxide for carbon deposition has been known for conventional supported catalysts for steam reforming, whereas the present investigation demonstrated the same effect for the cermet catalyst.

4.4. Effect of alkaline earth addition on steam reforming of CH₄

It is generally accepted that steam reforming initiates via methane decomposition that is the rate-determining step. Reaction steps have been considered as follows:



The effect of alkaline earth addition to the Ni-YSZ cermet on steam reforming of CH₄ is also summarized in Table 2. Correlation between carbon deposition rate and the CH₄ conversion for the steam reforming of CH₄ was not observed clearly. Therefore, in this experimental condition, deterioration of steam reforming reaction appears to be caused by either alkaline earth addition or deposited carbon and to determine the CH₄ conversion. When MgO is added to the Ni-YSZ cermet, the catalytic activity increased in the case of $x = 0.05$ or 0.10 . The CaO addition to the Ni-YSZ cermet promoted the reforming activity in every additive level investigated. The SrO addition to the Ni-YSZ cermet extremely deteriorated catalytic activity at $x = 0.10$. For CeO₂-modified Ni-YSZ cermet, the catalytic activity depended on the CeO₂ amount. Since Ni particles on CeO₂-ZrO₂ solid solutions were stable [6,21–23], the CeO₂-modified Ni-YSZ cermet with low CeO₂ contents exhibited a high performance for steam reforming. On the other hand, since CeO₂ components which are not contained in CeO₂-ZrO₂ solid solutions deactivate the Ni catalysts [21], the CeO₂-modified Ni-YSZ cermet with high CeO₂ contents exhibited a low performance for steam reforming and produced a large amount of carbon. Among the catalysts tested, the CaO-modified Ni-YSZ cermet demonstrated

Table 2
Comparison of decomposition and steam reforming of CH₄ conversion on various cermets

Cermet (before reduction)	Weight ratio	Carbon deposition rate ^a (C g/(cermet g min))	CH ₄ conversion (%) ^b		
			600 °C	700 °C	800 °C
NiO:YSZ	4.00:1.00	0.045	54.8	90.7	99.3
NiO:YSZ:MgO	4.00:0.99:0.01	0.056	33.4	67.8	93.8
	4.00:0.95:0.05	0.046	65.8	91.6	99.3
	4.00:0.90:0.10	0.049	63.4	92.9	99.3
NiO:YSZ:CaO	4.00:0.99:0.01	0.024	62.1	91.9	99.2
	4.00:0.95:0.05	0.027	61.7	91.9	99.2
	4.00:0.90:0.10	0.024	65.1	93.7	99.4
NiO:YSZ:SrO	4.00:0.99:0.01	0.032	64.5	93.2	99.4
	4.00:0.95:0.05	0.031	64.7	92.9	99.3
	4.00:0.90:0.10	0.031	0.1	0.3	2.7
NiO:YSZ:CeO ₂	4.00:0.99:0.01	0.028	50.5	87.1	98.6
	4.00:0.95:0.05	0.042	31.3	62.1	86.4
	4.00:0.90:0.10	0.059	17.6	42.2	70.6

^a Gas composition: 67% CH₄, 33% N₂; total flow rate: 45 STP ml/min; temperature: 1000 °C.

^b Gas composition: 40% N₂, 20% CH₄, 40% H₂O; total flow rate: 71.2 STP ml/min.

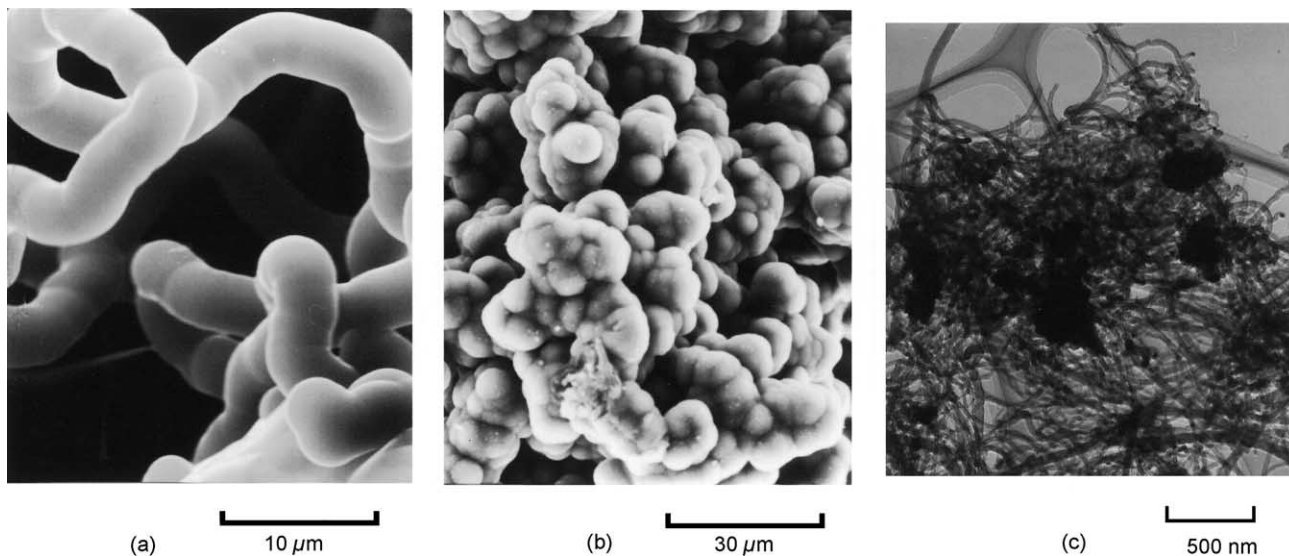


Fig. 4. SEM images of deposited carbon on Ni-YSZ cermet and Ni catalyst supported on ZrO_2 : (a) Ni-YSZ cermet; (b) Ni-YSZ cermet; (c) Ni catalyst supported ZrO_2 .

low carbon deposition rate and high CH_4 conversion for the steam reforming of CH_4 .

4.5. SEM observation of deposited carbon

In Table 2, carbon is deposited on the Ni-YSZ cermet in the basket of the balance in thermogravimetric analyzer during CH_4 decomposition at $1000^\circ C$. SEM image of carbon deposited on the Ni-YSZ cermet is shown in Fig. 4. It was well known for conventional supported Ni catalysts that carbon deposited in nano-tube like or fibrous microstructure with the decomposition of CH_4 as shown in Fig. 4(c) [21]. On the Ni-YSZ cermet catalyst aggregated spherical carbon was often observed in Fig. 4(b). As shown in Fig. 4(a), bulky carbon fibers were observed, though the diameter of the fibers was far different from that observed for supported Ni catalysts. It has been reported for supported Ni catalysts to catalyze carbon fiber formation. The diameter of carbon is, therefore, almost equal to that of Ni particle on the support oxide. Nano-sized fiber could be grown from supported Ni fine particles as shown in Fig. 4(c). On the other hand, since the Ni-YSZ cermet was prepared from the powder mixture of NiO and YSZ and calcined at $1400^\circ C$, the Ni particles were too large to produce carbon nano-tube.

4.6. Electrochemical property of Ni-YSZ and CaO-modified Ni-YSZ cermets

Since the CaO-modified Ni-YSZ cermet shows lower carbon deposition rate and higher activity for steam reforming of CH_4 than the conventional Ni-YSZ cermet, CaO-modified Ni-YSZ cermet is promising as anode of SOFC for direct internal reforming. The current–voltage characteristics of SOFC were examined using Ni-YSZ

and CaO-modified Ni-YSZ cermets, as shown in Fig. 5. The ideal open circuit voltage is expected to be 0.95 V based on the data in Fig. 1. The open circuit voltage for the cells with Ni-YSZ and CaO-modified Ni-YSZ cermets was 0.92 V, which almost agreed with the expected value. Both unmodified and modified cermets functioned as the reforming catalysts. When the voltages are compared at current density of 300 mA/cm^2 , the voltage of CaO-modified Ni-YSZ cermets was slightly lower than that of Ni-YSZ cermets. Although the CaO addition is effective in suppressing carbon deposition and promoting the reforming, the electrochemical activity as anode is slightly deteriorated. The alkaline earth oxides can be easily dissolved in the cubic zirconia lattice, the observed deterioration in the power generation characteristics may result from local deviation

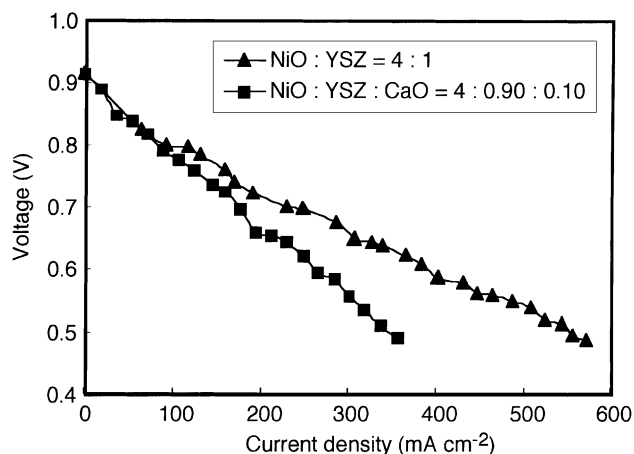


Fig. 5. Current–voltage characteristics in SOFC operation using Ni-YSZ and CaO-modified Ni-YSZ cermets at $1000^\circ C$. Anode gas: 40% N_2 , 15% CH_4 , 45% H_2O ; flow rate: 150 STP ml/min. Cathode gas: O_2 ; flow rate: 150 STP ml/min.

of the alkaline earth concentration of the electrolyte at the electrocatalytic sites.

5. Conclusion

It is of primary importance for the investigation of internal reforming of SOFC to evaluate the thermodynamic equilibrium concerning on carbon deposition and oxygen potential in multi-component gas in reformat. The second approach should be elucidation of kinetic effects, such as reforming activity, the rate of carbon deposition, and electrochemical overpotential. The additive to the cermet significantly affected the kinetic parameters of steam reforming of CH₄ on Ni-YSZ cermet. CaO-modified Ni-YSZ cermet was effective in suppressing carbon deposition without deteriorating the reforming activity though the addition of CaO slightly deteriorated the cell performance for design of active catalysts in many catalytic reactions. The catalyst design using the well-controlled metal–oxide interaction is promising approach to improve Ni-based cermet anode for internal reforming of SOFC.

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