—Technical Paper—

Power Generation Characteristics of SOFC with Internal CO₂ Reforming of Methane

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Direct internal CO₂ reforming of methane was carried out on the anode of a planar solid oxide fuel cell (SOFC), which was composed of Ni-yttria-stabilized zirconia (YSZ)/YSZ/La_{0.6}Sr_{0.4}MnO₃. I-V characteristics of SOFC were found to be basically similar to those obtained in internal steam reforming of methane. At CO₂/CH₄ = 2.6 or higher, a stable voltage output was obtained without coke formation. The equilibrium open circuit voltage (OCV) for steam reforming of methane was expected to be slightly higher than that for CO₂ reforming of methane at the same ratio of CO₂/CH₄ and H₂O/CH₄, whereas higher OCV was observed for CO₂ reforming than for steam reforming of methane. The reason should be ascribed to the non-equilibrium states of the reaction gas mixture due to deficient amount of the Ni catalyst. CO₂ reforming of methane is another suitable way to generate electrical power from methane fueled SOFC.

Key Words : Solid Oxide Fuel Cell, Methane, Steam Reforming, CO₂ Reforming

1 Introduction

Internal steam reforming of methane can be employed in a power generation system of solid oxide fuel cells (SOFCs) for the purpose to produce hydrogen on an Ni-YSZ anode instead of supplying hydrogen as a fuel of SOFC.¹⁻³⁾ Steam reforming reaction is a heavy endothermic reaction. It can remove a part of the heat produced from the electrochemical reaction.^{4,5)}

However, it may also cause a large temperature gradient in a cell stack at the same time. Fortunately, it is possible to average the temperature of the cell stack by adopting an appropriate cell structure and gas supply system. But, another disadvantage, which seems somewhat difficult to overcome, is that excessive steam tends to cause a degradation of the anode.⁶⁾ Substitution of CO₂ for steam should be interesting to improve the efficiency of power generation. CO₂ reforming of methane has been extensively studied in recent years to produce a synthesis gas with a lower H₂ / CO molar ratio or for other purposes.⁷⁻¹⁰⁾

The reaction (1)-(4) helps to recognize that the CO₂ reforming of CH₄ is a preferable reaction in the point of endothermic reaction and the formation of synthesis gas at 1000 °C. Carbon deposition leads to deactivation of the catalyst when CO₂ and CH₄ are fed at 1 / 1 or less in molar ratio over Ni or other metal-supported catalysts. Excessive CO₂ prevents carbon deposition but lowers the H₂ / CO ratio to less than unity through reverse water-gas shift reaction. Although such many investigations have been performed from the petrochemical aspect, a study of utilizing CO₂ reforming of methane for internal reforming of SOFC has scarcely reported satisfactorily so far. CO₂ reforming of methane is also endothermic and should be suitable for maximizing the efficiency of high temperature SOFC. In this work, we investigated the basic behavior of I-V characteristics for CO₂ reforming of CH₄. I-V characteristics were observed at low fuel utilization region in order to reduce hazardous effect of concentration overvoltage. The result of internal CO₂ reforming was also compared with that of steam reforming of CH₄ under the same molar ratio of CO₂ / CH₄ and H₂O / CH₄.

2 Experimental

2.1 Cell fabrication

A planar cell of Ni-YSZ / YSZ / $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ was used to evaluate I-V characteristics of SOFC with internal CO_2 reforming reaction. Commercially available yttria-stabilized zirconia (YSZ) powder (Tosoh Corp.) with 8 mol % Y_2O_3 stabilized ZrO_2 was used for preparation of YSZ disks. YSZ electrolyte disk of 18 mm in diameter and 0.5 mm in thickness was obtained by firing a YSZ green body prepared by a slip casting process at 1400 °C for 5 h. The anode powder was a mixture of NiO and YSZ (NiO : YSZ=8 : 2 wt/wt) fired at 1400 °C for 5 h. The cathode powder was prepared from metallic acetates corresponding to the formula composition of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$. After the anode powder with turpentine oil was coated on one surface of the YSZ disk and fired at 1400 °C for 5 h, cathode powder was coated on the opposite surface of the YSZ disk followed by a firing at 1100 °C for 5 h. The anode and cathode have the same area of 0.196 cm² (5 mm in diameter). Details of the cell construction has been shown elsewhere.¹¹⁾

2.2 I-V measurements

I-V characteristics were measured at 1000 °C. Pure oxygen was used as an oxidant and supplied at a flow rate of 150 ml min⁻¹. A fuel gas mixture of $\text{CO}_2 + \text{CH}_4 + \text{N}_2$ (balance) or $\text{H}_2\text{O} + \text{CH}_4 + \text{N}_2$ (balance) was also supplied at 150 ml min⁻¹ in every experiment. Before introducing the fuel gas into the cell, the NiO-YSZ anode was reduced into Ni-YSZ with a H_2 - N_2 mixture after bubbling in water at room temperature. The gas mixture at the cell outlet was analyzed by on-line gas chromatography. A partial pressure of oxygen was estimated from the OCV of the cell and conversions of CO_2 in the reforming reaction and the following reverse water-gas shift reaction (RWGS) were calculated respectively.

3 Results and Discussion

CO_2 reforming of methane produces a synthesis gas with H_2 and CO at a molar ratio of 1 : 1 when CO_2 and CH_4 were fed with an equal concentration to a conventional catalytic reactor. This indicates that only CO_2 reforming reaction ($\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2$) takes place when carbon deposition is negligible. A mechanism of this reaction has been reasonably proposed by Bradford and Vannice.¹²⁾ However, carbon deposition generally occurred when the gas mixture was fed continuously at about $\text{CO}_2 / \text{CH}_4 = 1$ or less. Carbon deposition was avoided when CH_4 was fed with CO_2 at $\text{CO}_2 / \text{CH}_4 = 2.6$ or higher in the present study and a stable voltage output was obtained. Table 1 summarizes the H_2 / CO ratios

detected in the outlet of the cell under the open circuit condition. The measured H_2 / CO ratio was less than unity in every case and decreased with increasing CO_2 concentration. This suggests that excessive CO_2 further reacted with H_2 which was formed by the reforming reaction, via reverse water-gas shift (RWGS) reaction (4). The RWGS reaction was promoted with increasing CO_2 concentration. Figure 1 shows I-V characteristics of SOFC supplied with different CO_2 concentrations. Efficient power generation can also be realized in the case of CO_2 reforming of methane as was observed in the case of internal steam reforming. The open circuit voltage (OCV) decreased with increasing concentration of CO_2 . The increase in CO_2 concentration led to a decrease in H_2 production and an increase in H_2O formation and resulted in high equilibrium $P(\text{O}_2)$. However, the gas mixture at the outlet was not in equilibrium for CO_2 reforming reaction nor for reverse water-gas shift reaction.^{13,14)}

I-V characteristics for different CH_4 concentrations are shown in Fig. 2. An increase in CH_4 concentration led to a higher OCV. This corresponds to the

Fig. 1 The dependence of I-V characteristic on CO_2 concentration. CH_4 concentration=6.7 %

Fig. 2 The dependence of I-V characteristic on CH_4 concentration. CO_2 concentration=35.5 %

Table 1 Gas chromatographic analysis results and open circuit voltages (OCV).

Feed gas	CH ₄ (%)	6.7	6.7	6.7	6.7	10.4	13.7
	CO ₂ (%)	19.7	35.5	53.4	35.5	35.5	35.5
	CO ₂ / CH ₄	2.94	5.30	7.97	5.30	3.41	2.59
Effluent gas	CH ₄ (%)	2.4	3.7	4.7	3.7	6.0	7.9
	CO ₂ (%)	8.9	26.4	51.2	26.4	26.1	23.4
	H ₂ O (%)	2.2	3.2	2.9	3.2	3.7	3.7
	H ₂ (%)	1.8	1.5	1.3	1.5	3.5	5.4
	CO (%)	4.6	7.1	9.2	7.1	11.0	12.8
	H ₂ / CO ratio	0.39	0.22	0.14	0.22	0.32	0.42
	Conversion of CH ₄ (%)	39.9	36.7	35.9	36.7	37.5	36.5
Conversion of CO ₂ (%)		25.4	15.8	11.4	15.8	22.0	26.0
Estimated OCV from H ₂ / H ₂ O (V)		0.932	0.886	0.856	0.886	0.915	0.940
measured OCV (V)		0.905	0.857	0.828	0.857	0.891	0.917
Estimated OCV from CO / CO ₂ (V)		0.855	0.819	0.797	0.819	0.844	0.858

Table 2 OCV(V) and gas composition at the outlet(%) for CO₂ reforming and the steam reforming.

System	Observed ^{a)}	Equilibrium ^{b)}	Estimated OCV from ^{c)}		Composition at the outlet				
	OCV	OCV	H ₂ / H ₂ O	CO / CO ₂	H ₂	H ₂ O	CO	CO ₂	CH ₄
CH ₄ -CO ₂	0.905	0.929	0.937	0.823	3.8	2.7	9.2	31.9	8.0
CH ₄ -H ₂ O	0.864	0.946	0.837	0.888	7.9	35.3	1.1	1.1	9.5

a) Observed OCV for SOFC supplied with CH₄-CO₂ or CH₄-H₂O, b) Equilibrium OCV expected from the equilibrium gas composition,¹⁷⁾ c) OCV estimated from measured H₂ / H₂O or CO / CO₂ ratio in the outlet gas. Inlet gas composition : 12.0 % CH₄, 40.0 % CO₂ or H₂O, N₂ balance.

increase of H₂ production with abundant supply of CH₄ as indicated in Table 1. Meanwhile, H₂O formation was also promoted by the increased H₂ production, but the ratio of H₂ / CO kept increasing with an increase in CH₄ concentration. As presented in Table 1, the conversions of methane under all conditions reached at around 37 %, which were far below the level of the equilibrium.

The equilibrium partial pressure of oxygen can be estimated from either H₂ / H₂O or CO / CO₂ ratio by assuming a combustion equilibrium of H₂ or CO.^{15,16)} Then, an OCV value is estimated from the equilibrium $P(\text{O}_2)$. The H₂ / H₂O and CO / CO₂ ratios at the outlet gave different OCV values respectively calculated from the Nernst equation as listed in Table 1, though they should exhibit a unique OCV in the equilibrium state. The calculated OCV values from the oxygen potential of H₂ / H₂O ratio in the effluent gas turned out to be greater than the measured OCV values. However, the calculated OCVs based on CO / CO₂ couple were found lower than the measured OCVs. This means that the partial pressure of oxygen at the triple-phase boundary (TPB) is an intermediate between the two values estimated from the H₂ / H₂O and CO / CO₂ ratios in the outlet gas. This fact is easily understood, since the reverse water-gas shift reaction (1) occurred subsequently to the CO₂ reforming reaction. As the catalytic RWGS

reaction proceeded as the gas mixture flew along the pore of the anode before arriving at TPB, the H₂ / H₂O ratio at TPB should be smaller than that in the effluent gas as a result of the longer contacting path with the Ni surface. The H₂ / H₂O ratio detected at the outlet should be an average of those produced on the whole Ni surface of the anode.

The open circuit voltage of CO₂ reforming was compared with that of steam reforming of methane at the same molar ratio of CO₂ / CH₄ with H₂O/CH₄ as listed in Table 2 with equilibrium OCVs and estimated OCVs. The equilibrium values were calculated from the equilibrium gas compositions in their respective systems and the Nernst equation.¹⁷⁾ The estimated values of OCV from the H₂ / H₂O and CO / CO₂ ratios are obtained based on the measured gas compositions at the outlet under the experimental conditions. Similar to the case of CO₂ reforming, the observed OCV value for steam reforming is an intermediate between those estimated from H₂ / H₂O and CO / CO₂. In this case, however, the H₂ / H₂O ratio gave lower estimated OCV because of the abundant supply of H₂O.

If the thermodynamic equilibrium was established, the steam reforming would generate a slightly higher OCV than the CO₂ reforming in this experimental condition. However, as shown in Table 2, the observed OCV in CO₂ reforming was higher than that in

steam reforming of methane. The lower observed OCV compared to the equilibrium OCV explains that the CH_4 reforming reaction did not reach to the equilibrium state in both $\text{CH}_4\text{-H}_2\text{O}$ and $\text{CH}_4\text{-CO}_2$ systems. The unequilibrated gas composition in the effluent gas owes to deficient amount of the Ni catalyst for reforming and / or high rate of fuel supply. Although it is difficult to compare OCVs between both systems simply due to the non-equilibrium conditions, the larger deviation of OCV from the equilibrium one for steam reforming than for CO_2 reforming was observed in spite of the opposite result for equilibrium OCVs. It implies that water deteriorates the overall reaction on the Ni surface. Therefore, it indicates that CO_2 reforming of CH_4 is one of preferable fuels for internal reforming SOFC. The reaction on the Ni surface should be very rapid whereas the reaction surface was not sufficiently large in the present experiment. Thus the produced gas from the Ni surface is diluted with the reactant gas. For power generation, the concentrations of the reactants and products (H_2 , H_2O , CO and CO_2) on the Ni surface are very important since they determine the partial pressure of oxygen on the reaction site for the electrochemical reaction. However, the concentrations of components on the Ni surface were greatly influenced by the extent of equilibration in WGS or RWGS.

4 Conclusion

Internal CO_2 reforming of methane was investigated for SOFC application. Power generation could be easily achieved as in the case of internal steam reforming of methane. The gaseous mixture was not equilibrated but the reverse water-gas shift reaction proceeded as the reaction gas approaches to the triple phase boundary. Comparison of CO_2 reforming with steam reforming showed a higher OCV for CO_2 reforming than that for steam reforming of methane. Internal CO_2 reforming of methane is another suitable way to generate electrical power by using methane

fueled SOFC.

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