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고체산화물 연료전지 내에서 합성가스와 전기의 Cogeneration

류종우, 강동민, 박종민, 김용식, 남석우, 이병권, 이상득, 문동주*
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Cogeneration of Syngas and Electricity in SOFC System

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1. Introduction

Carbon dioxide is a greenhouse gas and contributes to global warming [1-2]. The reduction and sequestration of carbon dioxide has been a hot issue. The CO_2 catalytic reforming by CH_4 is an attractive conversion technology because of the possibility of enhancing natural gas utilization with the sequestration of CO_2. However this reaction has two serious problem because of the high energy consuming process and the catalyst deactivation caused by carbon formation [2-3]. To improve these problems, much effort has been focused on the development of catalyst which shows high activity and resistance against coke deposition for long-term operation. One of these efforts is an electrocatalytic reforming in a solid oxide fuel cell (SOFC) system.

In our previous works [1, 4-5], it was reported that the electrocatalytic reforming of CO_2 by CH_4 in a solid oxide fuel cell system has some advantages over the catalytic reforming. Because the syngas generated by internal reforming can be used as fuels for power generation in SOFC. In this work, the cogeneration of a syngas and an electricity by the electrocatalytic reforming of CO_2 by CH_4 in SOFC system was suggested, and the effects of electrochemically pumped oxygen ion on the reaction rates of CO_2 and CH_4 were investigated.

2. Experiments

2-1. Preparation of a Single Cell

NiO-MgO catalyst was prepared by a precipitation method. BET surface area and pore size distributions of of the NiO-MgO catalyst was analysed by N_2 physisorption [Quantachrome Co. Autosorb-1C] and the structure of catalysts before and after the reaction was investigated by XRD [Shimazdu Co., XRD-6000].

The single cell was prepared by a tape casting method. The binder solution for slurry was prepared by adding 0.87g of methyl cellulose (MC), 1.14g of carbonyl methyl cellulose (CMC) and 1.74g of polyethylene oxide (Polyox) as binder and isopropyl alcohol (IPA) of 3 ml as a dispersing agent in a deionized water of 100 ml. After the catalyst was added to the binder solution, the slurry was coated by using a blade on one side of a half cell (TZ3Y//KS1). Half cell was supported from InDec Co. of Netherlands, and consists of the perovskite type cathode of $(La,Sr)MnO_3$ and the Y_2O_3 stabilized ZrO_2(YSZ) electrolyte. The coated disk was dried at 50℃ for 24 h and sintered at 125

0℃ for 4 h under air. The thickness and area of the catalyst electrode layer were ca. 20 ㎛ and 2.25cm^2 (1.5 cm × 1.5 cm), respectively. The micro structure properties of the catalyst electrode before and after the electrocatalytic reforming were characterized by SEM [Hitachi Co., S-4200].

2-2. Electrocatalytic membrane reactor system

The schematic diagram of an electrocatalytic membrane reactor (ECMR) system is illustrated in Fig. 1. Flow rates of reactants were controlled by mass flow controllers [Bronkhorst HI-TEC Co.]. A mixture of 12.5 vol. % CO_2 and 12.5 vol. % CH_4 was passed through the anode chamber with a flow rate of 20 ml/min, while air (20 ml/min) was passed through the cathode side. The outlet gas from the anode side was analyzed by an on-line GC [Hewlett Packard Co., HP5890 series II] equipped with a carbosphere column (3.18×10^{-3} m O.D. and 2.5 m length) and a thermal conductivity detector (TCD). Pt wire (0.5×10^{-3} m diameter) was used to connect both electrodes to an electrical circuit for controlling the oxygen flux across the YSZ electrolyte. The electrochemical cell was sealed onto the alumina tube (O.D. = 0.025 m, I.D. = 0.019 m) using pyrex glass (O.D. = 0.025 m, I.D. = 0.021 m, h = 0.003 m). The single cell reactor was placed in an electrical furnace equipped with a PID controller [Han Young Co. P-100]. The temperature of the single cell was measured by a thermocouple positioned near the electrochemical cell. Electrochemical properties were measured by a Solartron 1287 Electrochemical Interface (Potentiostat-Galvanostat) with Solatron 1260 Impedance /Gain-phase analyzer (Frequency Response Analyser (FRA)). The current and voltage of electrochemical cell were measured for the power generation performance of the electrochemical cell. The current and voltage were controlled by a galvanostatic method. Current and voltage were measured by Potentiostat-Galvanostat at a steady state. The carbon dioxide reforming by methane over NiO-MgO catalyst electrodes in an electrochemical cell (NiO-MgO | YSZ | $(La,Sr)MnO_3$) under open- and closed- circuit conditions was carried out at 800℃ and atmosphere.

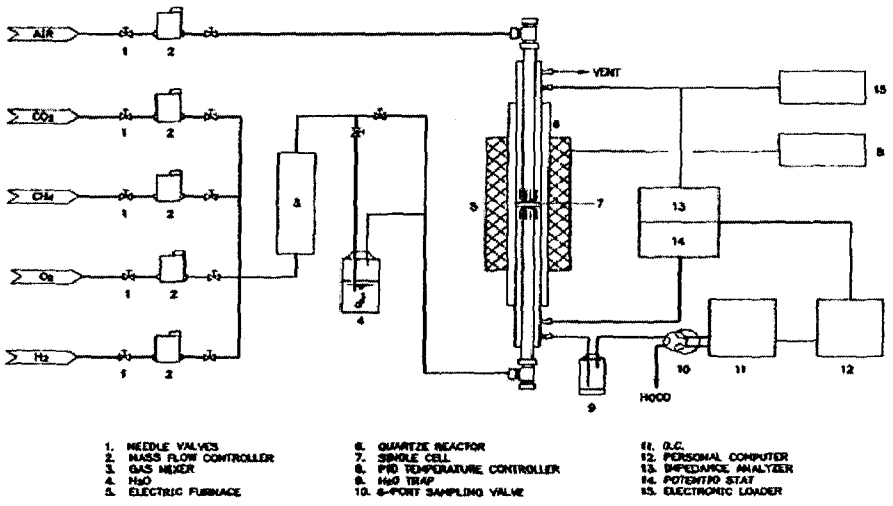

Figure 1. Electrocatalytic Membrane Reactor System for internal reforming of CO_2 by CH_4.

3. Results and discussion

Figure 2 shows the reaction rates of CH_4 and CO_2 and the current density over the electrocatalytic cell (NiO-MgO | YSZ | $(La,Sr)MnO_3$) with a time on stream under the open- and the closed-circuit conditions. The apparent surface area of coated anode catalyst used to define the reaction rates in the electocatalytic reaction system. The electrocatalytic reforming reaction in SOFC system was carried out at atmospheric pressure and temperature of 800℃ and atmosphere. It was found that the reaction rates of CH_4 and CO_2 under the open-circuit condition were lower than those of CH_4 and CO_2 under the closed-circuit condition. It was also found that the reaction rates of CH_4 and CO_2, and the current density under the closed-circuit condition were stable after undergoing the electrocatalytic reaction for 3 h, whereas those of CH_4 and CO_2 under the open circuit condition slowly decreased by the deposition of coke. These results showed that the catalyst electrode under the closed circuit was stable during the electrocatalytic reforming of CO_2 by CH_4, because oxygen ion flux under the closed-circuit condition is fast enough to remove coke deposition.

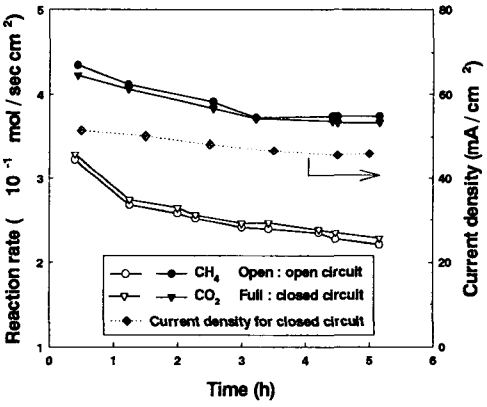

Figure 2. The reaction rates of CH_4 and CO_2 and the current density over the electrocatalytic cell (NiO-MgO | YSZ | $(La,Sr)MnO_3$) with a time on stream under the open- and closed-circuit conditions at 800℃.

Table 1 shows the product distributions of for the electrocatalytic reaction of CO_2 and CH_4, and the amount of coke formed at 800℃ for 5 h in the electrocatalytic cell (NiO-MgO | YSZ | $(La,Sr)MnO_3$) under the open- and the closed-circuit conditions. The selectivities of CO_2 and CO under the closed circuit condition were 28.87 % and 13.12 %, respectively, whereas those of CO_2 and CO under the open circuit were 14.8 % and 18.59 %. The amount of coke formed under the open-circuit condition was ca. 120 mg C/g_{cat} for 5 h. But the amount of coke under the closed-circuit condition drastically decreased compared to that under the open-circuit. The results are interpreted that the carbon deposited on the surface of anode catalyst under the closed circuit condition was mainly desorbed to carbon dioxide by the reaction ($Cs + 2O^{2-} \rightarrow CO_2 + 4\ e$) of oxygen ion transferred from the cathode with the surface carbon.

Table 1. Product distributions for the electrocatalytic reaction of CO_2 and CH_4, and the amount of coke formed at 800℃

Reaction mode	Product Distribution (mol%)				Coke formtion
	CO	H_2	CH_4	CO_2	mg C / $g_{catalyst}$
Open-circuit	18.59	51.07	15.51	14.83	120
Closed-circuit	13.12	28.69	29.32	28.87	-

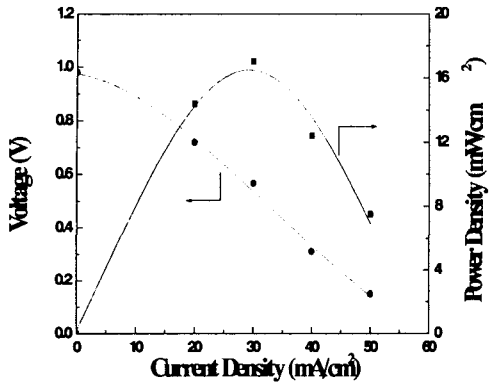

Figure 3. The performance of current voltage and power density with current density in the electrocatalytic cell (NiO-MgO | YSZ | (La, Sr) MnO_3) at 800℃.

It was found that surface carbon under the open-circuit condition was accumulated on the surface of anode and it filled up pore. It was also found that the amount of carbon formed under the closed-circuit condition drastically decreased compared to that under the open-circuit. It was identified that the oxygen ions were pumped to the catalyst electrode bypassing an anodic current through the electrochemical cell.

Figure 3 shows the performance of current voltage and power density with current density in the electrocatalytic cell (NiO-MgO | YSZ | (La,Sr)MnO_3) when CH_4 and CO_2 were used as a reactant. It showed that the open-circuit voltage (OCV) obtained for the single cell tested at 800℃ and atmosphere was 0.96 V. This value is lower than the theoretical (V = 1.24 V). It had a maximum power density at 30 mA, and considering electrode area, power of 37 mW was produced in the single cell.

4. Conclusions

It was found that the reaction rates of CH_4 and CO_2, and the current density under the closed-circuit condition were stable after undergoing the electrocatalytic reaction for 3 h, whereas those of CH_4 and CO_2 under the open circuit slowly decreased. The electric power was generated by electrons released in the reactions of CO with oxygen ion, H_2 with oxygen ion, and surface carbon with the oxygen ion. It was considered that the electrocatalytic internal reforming of CO_2 by CH_4 is an attractive option for improving the energy utilization of the fuel. It was concluded that the stability of catalyst electrode was dependent on the reaction of oxygen ion transferred from the cathode with the surface carbon formed in the internal CO_2 reforming by CH_4 in SOFC system.

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