

고체산화물 연료전지의 anode극 내부에서 메탄에 의한 이산화탄소의
전극촉매 반응에 의해 합성가스와 전기의 동시 생성

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**Cogeneration of a Syngas and an Electricity by the Electrocatalytic
Reforming of Carbon Dioxide by Methane in SOFC System**

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Introduction

Carbon dioxide (CO₂) is a greenhouse gas and contributes to global warming. The reduction and sequestration of carbon dioxide has been a hot issue. The CO₂ catalytic reforming by CH₄ is an attractive conversion technology because of the possibility of enhancing natural gas utilization with the sequestration of CO₂. However this reaction has two serious problems. The reaction is an intensively endothermic reaction, which consumes much energy and the other is carbon formation on surface of catalyst used in the reforming. 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 [1-3, 5], authors suggested that SOFC is a promising technology for the efficient production of a syngas and an electricity from CO₂ and CH₄.

In this work, the electrocatalytic internal reforming of CO₂ by CH₄ over Ni-CeO₂, Ni-MgO and perovskite type catalyst electrodes was investigated to coproduce a syngas and an electricity under the open- and closed-circuit conditions in the SOFC system.

Experiments

NiO-MgO catalyst was prepared by a precipitation method. BET surface area and pore size distributions of the NiO-MgO catalyst was measured by N₂ physisorption [Quantachrome Co. Autosorb-1C] and the structure of catalysts before and after the reaction was investigated by XRD [Shimadzu 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 a 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)MnO₃ and the Y₂O₃ stabilized ZrO₂ (YSZ) electrolyte. The coated disk was dried at 50 °C for 24 h and sintered at 1250 °C for 4 h under air. The thickness and the area of catalyst electrode layer were ca. 20 μm and 2.25 cm², respectively. The micro structure properties of the catalyst electrodes before and after the electrocatalytic reforming were characterized by SEM [Hitachi Co., S-4200].

The schematic diagram of the electrocatalytic membrane reactor is shown in Fig. 1. It consists of five sections: feed supply, electrical furnace, electrochemical cell, electrocatalytic reactor and GC analysis sections. Flow rates of reactants were controlled by mass flow controllers [Bronkhorst HI-TEC Co.]. A mixture of 12.5 vol. % CO₂ and 12.5 vol. % CH₄ 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 x 10⁻³ m O.D. and 0.25 m length) and a thermal conductivity detector (TCD). Pt wire (0.5 x 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.

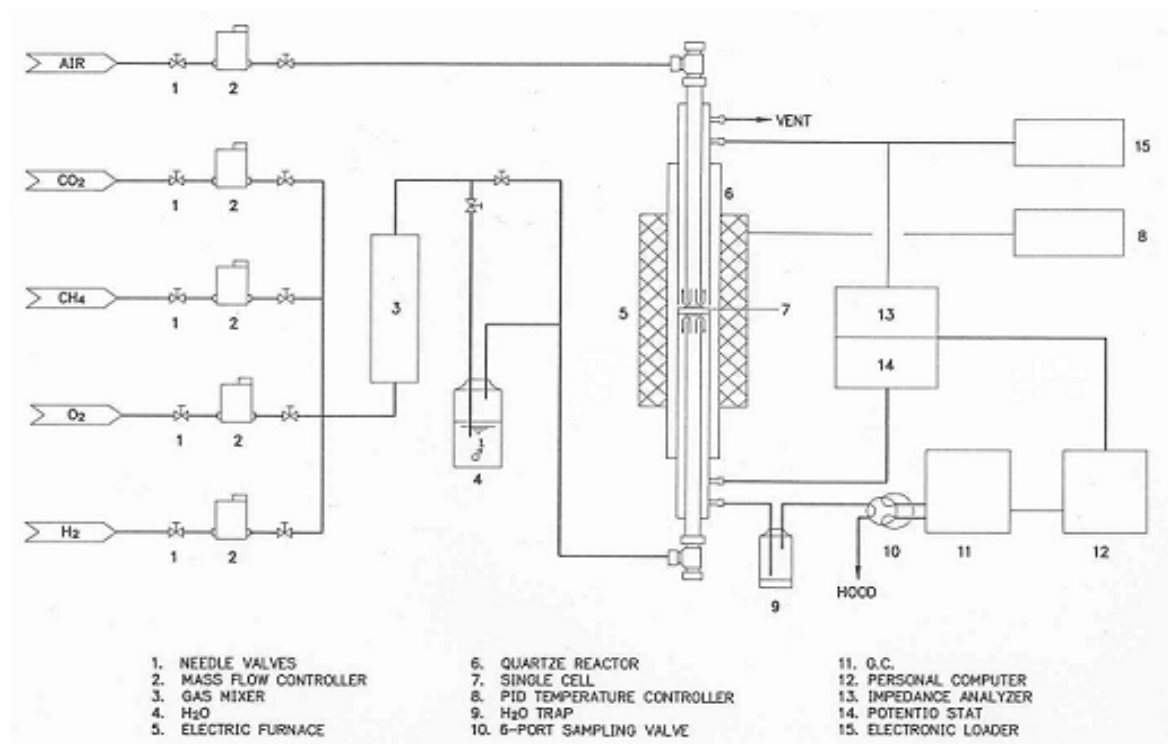


Figure 1. The schematic diagram of the electro membrane system.

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 (CO_2 , CH_4 , NiO-MgO | YSZ | (La,Sr)MnO₃, air) under open- and closed- circuit conditions was carried out at 800 °C and atmosphere.

Results and discussion

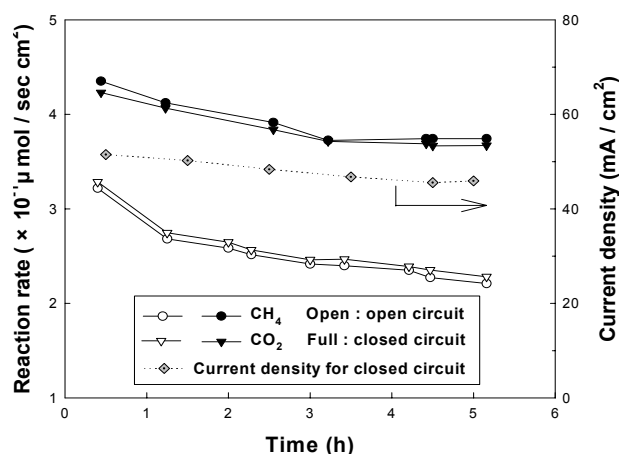


Figure 2. The reaction rates of CH₄ and CO₂ and the current density over the electrocatalytic cell (NiO-MgO | YSZ | (La,Sr)-MnO₃) with a time on stream under the open- and closed-circuit conditions at 800 °C.

that the reaction rates of CH₄ and CO₂, and the current density under the closed-circuit condition were stable after undergoing the electrocatalytic reaction for 3 h, whereas those of CH₄ and CO₂ 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 CO₂ by CH₄ because oxygen ion flux under the closed-circuit condition is fast enough to remove coke formed during the reaction.

Table 1 shows the product distributions for the electrocatalytic reaction of CO₂ and CH₄, and the amount of coke formed at 800 °C for 5 h in the electrocatalytic cell (NiO-MgO | YSZ | (La,Sr)-MnO₃) under the open- and the closed-circuit conditions. The selectivities of CO₂ and CO under the closed circuit condition were 28.87 % and 13.12 %, respectively, whereas those of CO₂ and CO under the open circuit were 14.8 % and 18.59 %. The amount of coke formed under the open-circuit

Figure 2 shows the reaction rates of CH₄ and CO₂ and the current density over the electrocatalytic cell (NiO-MgO | YSZ | (La,Sr)-MnO₃) 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 electrocatalytic reaction system. The electrocatalytic reforming reaction in SOFC system was carried out at atmospheric pressure and temperature of 800 °C and atmosphere. It was found that the reaction rates of CH₄ and CO₂ under the open-circuit condition were lower than those of CH₄ and CO₂ under the closed-circuit condition. It was also found

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 were 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 ($C_s + 2O^{2-} \rightarrow CO_2 + 4e^-$) of oxygen ion transferred from the cathode with the surface carbon. 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 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 by passing an anodic current through the electrochemical cell.

Table 1. Product distributions for the electrocatalytic reaction of CO₂ and CH₄ and the amount of coke formed at 800 °C for 5 h in the electrochemical cell (NiO-MgO | YSZ | (La,Sr)MnO₃).

Reaction mode	Product Distribution (mol%)				mg C / g catalyst
	CO	H ₂	CH ₄	CO ₂	
Open-circuit	18.59	51.07	15.51	14.83	120
Closed-circuit	13.12	28.69	29.32	28.87	-

The performance of current voltage and power density with current density in the electrocatalytic cell (NiO-MgO | YSZ | (La,Sr)-MnO₃) were investigated when CH₄ and CO₂ were used as the reactants. It showed that the open-circuit voltage for the single cell obtained at 800 °C and atmosphere was 0.96 V. This value is lower than the theoretical (V=1.24V). It had a maximum power density at 30 mA, and considering electrode area, the power of 37 mW was produced in the single cell. It was concluded that the electrocatalytic internal reforming of CO₂ by CH₄ is an attractive option for improving the energy utilization of the fuel.

Acknowledgement

This paper was performed for the Carbon Dioxide Reduction & Sequestration Center, one of 21st Century Frontier R&D Programs funded by the Ministry of Science and Technology of Korea.

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