

고체산화물 연료전지 시스템에서 메탄에 의한 이산화탄소의 내부개질반응을 위한 전해질 지지형 단전지 개발

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Development of Electrolyte Supported Cell for Internal Reforming of CO₂ by CH₄ in SOFC System

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Introduction

Considering environmental perspective, the reduction and sequestration of CO₂ have been received much attention due to its greenhouse gas and global warming effect. So, the CO₂ reforming by CH₄ has been considered as an attractive technology. Above all, this reaction has an advantage such as the production of synthesis gas and the reduction of greenhouse gas, simultaneously. It is of special interest from an industrial perspective since it produces synthesis gas with a low H₂ / CO ratio, which can be preferentially used for Fischer-Tropsch synthesis [1]. Furthermore, both CH₄ and CO₂ are the cheapest reactants and most abundant carbon-containing materials. However, the CO₂ reforming by CH₄ has significant drawbacks, a highly energy consuming and coke forming process. In order to overcome the problems, author suggested the electrocatalytic internal reforming of CO₂ by CH₄ as a new reforming system which coproduce a syngas and electricity in a solid oxide fuel cell (SOFC) system [2]. In this system, the catalytic anode material is one of the most important factors to determine the entire performance in SOFC system.

In this work, we have studied the CO₂ reforming by CH₄ over Ni-based catalysts to investigate the possibility of development as a high performance anode catalyst for application in an electrocatalytic reforming in the SOFC system. The prepared catalysts were characterized by N₂ physisorption, CO chemisorption, X-ray diffraction (XRD), SEM and temperature programmed reduction (TPR).

Experimental

Anode catalysts (NiO-YSZ-MgO, NiO-YSZ-CeO₂, NiO-Ce_xSm_{1-x}O_{1.9}) were prepared by a precipitation method and physical mixing of NiO (99.99%, Sigma-Aldrich Co.), YSZ(TZ-8Y,

TOSOH Co.), $\text{Sm}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich Co.), $\text{SrNO}_3 \cdot 6\text{H}_2\text{O}$ (99.9965%, Alfa Aesar Co.) and CeO_2 (99.9%, Sigma-Aldrich Co.). Structure of prepared catalyst was investigated by XRD (target = Cu, voltage = 40.0 kV, current = 30.0 mA and scan speed = 5.0 deg/min)

The CO_2 reforming by CH_4 was carried out in a conventional fixed bed reactor system. Flow rates of reactants were controlled by mass flow controllers (Bronkhorst HI-TEC Co.). The reactor with an inner diameter of 7 mm was heated in an electric furnace. The reaction temperature was controlled by a PID temperature controller and was monitored by a separated thermocouple placed in the catalyst bed. The product gases were analyzed by an on-line GC (Hewlett Packard Co., HP-6890 Series II) equipped with a thermal conductivity detector (TCD) and a carbosphere column (0.0032 m O.D. and 2.5 m length, 80/100 meshes). Catalysts before and after the reaction were characterized by N_2 physisorption (Quantachrome Co., Autosorb-1C), CO chemisorption (Micromeritics, Autochem II), XRD (Shimadzu Co., XRD-6000) and TPR (Micromeritics, Autochem II).

Results and discussion

In this work, MgO and CeO_2 were selected as a modification agent of NiO anodic catalyst for the cogeneration of syngas and electricity in the SOFC system to reduce the formation of carbon deposited on the anode side [3]. The characteristics of prepared catalysts are summarized in Table 1. BET surface area and total pore volume of NiO-YSZ-MgO catalyst were $8.9 \text{ m}^2/\text{g}$ and 0.003 cc/g , while those of the NiO-YSZ- CeO_2 catalyst were $10.2 \text{ m}^2/\text{g}$ and 0.004 cc/g , respectively.

Table 1. The structural properties of catalysts prepared in this work

Catalyst	BET surface area (m^2/g)		Total pore volume (cc/g)	
	Before	After	Before	After
Ni-YSZ-MgO	8.9	13.4	0.003	0.007
Ni-YSZ- CeO_2	10.2	15.7	0.004	0.007

To evaluate the performance of Ni-based anode catalyst, catalytic CO_2 reforming by CH_4 was carried out in a fixed bed reactor system. The effect of time on the conversions of CO_2 and CH_4 and the selectivities over NiO-YSZ-MgO and NiO-YSZ- CeO_2 catalyst was shown in Fig. 1. and 2.

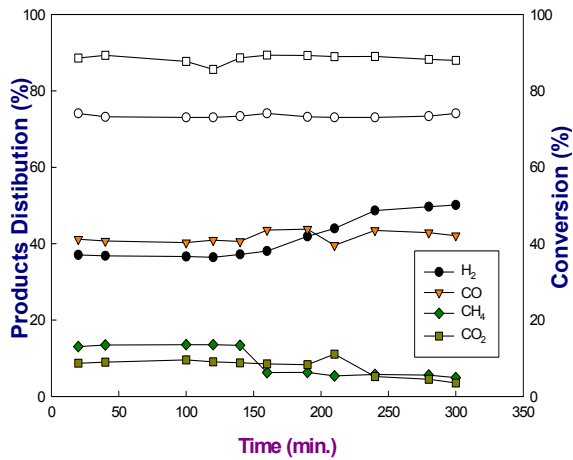


Figure 1. The effect of time on the conversions of CO₂ and CH₄ and the selectivities over NiO-YSZ-MgO catalyst at 800°C.

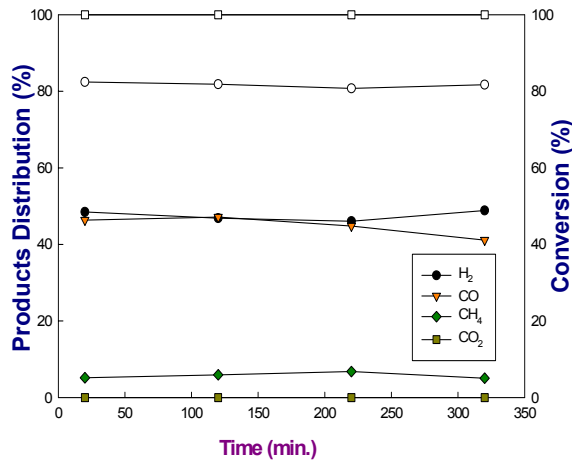


Figure 2. The effect of time on the conversions of CO₂ and CH₄ and the selectivities over NiO-YSZ-CeO₂ catalyst at 800°C.

It was found that the conversions of CO₂ and CH₄ over NiO-YSZ-CeO₂ catalyst were higher than those over NiO-YSZ-MgO at 800°C, optimum temperature for internal reforming in SOFC system [4]. Moreover, the concentrations of H₂ and CO over NiO-YSZ-CeO₂ catalyst was slightly better than those over NiO-YSZ-MgO. The X-ray diffraction (XRD) patterns of NiO-YSZ-MgO and NiO-YSZ-CeO₂ catalysts before and after the reaction were represented in Fig. 3. and 4. It was found that the amount of carbon deposited on the NiO-YSZ-CeO₂ was less than that on NiO-YSZ-MgO catalyst [5].

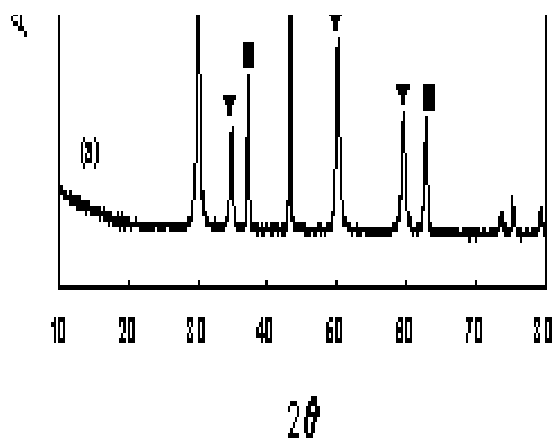


Figure 3. XRD patterns of NiO-YSZ-MgO catalyst (a) before and (b) after catalytic reforming (■ : NiO, □ : NiC, ▼ : YSZ)

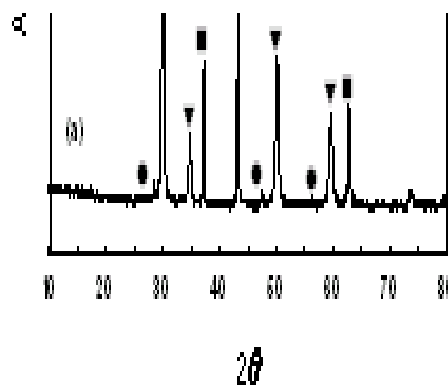


Figure 4. XRD patterns of NiO-YSZ-CeO₂ catalyst (a) before and (b) after catalytic reforming (■ : NiO, □ : NiC, ▼ : YSZ, ● : CeO₂)

The results on the stability of catalyst and the characterization will be discussed. It was concluded that NiO-YSZ-CeO₂ is good candidate material as an anode catalyst for internal reforming in the SOFC system.

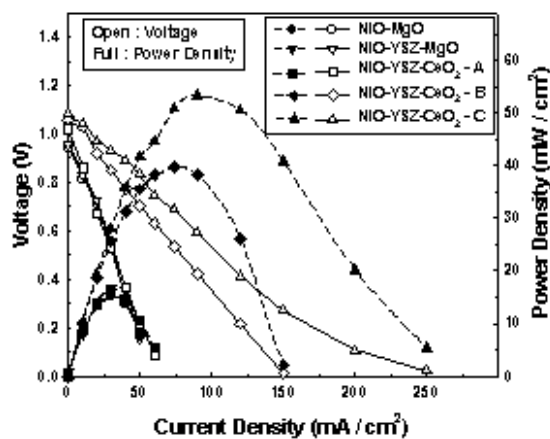


Figure 5. The performance of voltage and power density with current density in the electrochemical cells (Ni based anodes | YSZ | (La,Sr)MnO₃) at 800°C

The internal reforming of CO₂ by CH₄ in SOFC system was performed with electrochemical cell prepared by Ni based anode materials.

Figure 5. shows the performance of voltage and power density with current density in the electrocatalytic cells (Ni based anodes | YSZ | (La,Sr)MnO₃) at 800°C when CH₄ and CO₂ were used as reactants. The open-circuit voltage (OCV) over the Ni-YSZ-MgO catalyst electrode was 0.96 V. It had a maximum power density at 30 mA. The open-circuit voltage over the Ni-YSZ-CeO₂ catalyst electrode was 1.02 V. It had a maximum power density at 100 mA.

Conclusions

The Ni-YSZ-CeO₂ catalyst anode displayed higher performance than Ni-YSZ-MgO in the Ni based anodes | YSZ | (La,Sr)MnO₃ system. The reaction rates of CH₄ and CO₂, and the current density were stable after undergoing the electrocatalytic reaction for 5 h. The results suggest that the electrocatalytic internal reforming of CO₂ with CH₄ in SOFC system is an attractive process to co-produce electricity and a syngas with the reduction of CO₂.

Acknowledgement

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