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Electrocatalytic reforming of carbon dioxide by methane in SOFC system

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Abstract

The reaction of carbon dioxide catalytic reforming with methane is an attractive route because these greenhouse gases can be converted into variable feedstocks. However this reaction is a highly energy consuming and coke forming process. These problems were improved by the electrocatalytic reforming of CO_2 with CH_4 in a solid oxide fuel cell (SOFC) membrane reactor system, which generates high electrical power and synthesis gases. The single cell consists of catalyst electrode (NiO–MgO), counter electrode ((La,Sr)MnO_3) and Y_2O_3 stabilized ZrO_2 (YSZ) electrolyte. The reaction rates of CO_2 and CH_4, and the electrochemical properties were investigated by an on-line GC and impedance-analyzer under open- and closed-circuit conditions, respectively. It was found that reaction rates of CO_2 and CH_4 under the closed-circuit condition were more stable than those of the open-circuit. The results were interpreted that the stability of catalyst anode was maintained by 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.

Keywords: SOFC; CH_4; CO_2; NiO–MgO; Y_2O_3 stabilized ZrO_2 (YSZ) electrolyte; Internal reforming

1. Introduction

For many years, researchers have agreed that the climate change was generally caused by carbon dioxide (CO_2) from burning of fossil fuels such as coal, oil, and gas. Because CO_2 is a main source of global warming, the technology for the reduction and sequestration of CO_2 in the environmental perspective has been a hot issue. Especially, the CO_2 reforming by methane, yielding synthesis gas, has received renewed interests today because of the possibility of enhancing natural gas utilization and converting carbon resources inherently contained in CO_2 and CH_4 into valuable products [1].

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad (\Delta H^\circ_{298} = 247\,\mathrm{kJ/mol}) \tag{1}$$

The synthesis gas generated has a low H_2/CO ratio which can be used for the Fischer–Tropsch synthesis of higher hydrocarbons and for the oxy-synthesis or synthesis of oxygenates [2]. Furthermore, both CH_4 and CO_2 are the cheapest reactants and abundant carbon-containing materials. Therefore, studies on the development of catalysts with high activity and resistance against coking have been reported during past decades. It was reported that the noble metal catalysts (Rh, Ru, Ir, Pd and Pt) have been showing the promising catalytic performance and the high resistance against coking for this reaction [3–5]. But, there is no

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possibility for commercialization of the process because of the high cost of noble metal catalysts. Nickel supported on oxides such as Al_2O_3, MgO, TiO_2, ZrO_2, SiO_2, CeO_2 and La_2O_3 have been extensively investigated [6–8]. The effect of metal-supported interactions and acid–base properties of supports on the activity and stability of the catalysts have been identified [9,10]. However, the CO_2 reforming by CH_4 has two serious problems. This reaction is an intensively endothermic reaction, which consumes much energy and the other is carbon formation on the surface of catalysts.

Recently, Park et al. [11] reported studies on the direct oxidation of CH_4 in a solid oxide fuel cell (SOFC). They demonstrate that the direct electrocatalytic oxidation of dry methane is possible, with the reasonable performance. Ishihara et al. [12] presented studies on the partial oxidation of methane over a fuel cell reactor for simultaneous generation of synthesis gas and electric power. SOFCs are still in development as power generation technologies. They are potentially efficient and low-emissions power generation technologies with a wide range of applications.

In our previous works [1,13–15], 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. 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.

In this work, the cogeneration of a syngas and 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 catalyst

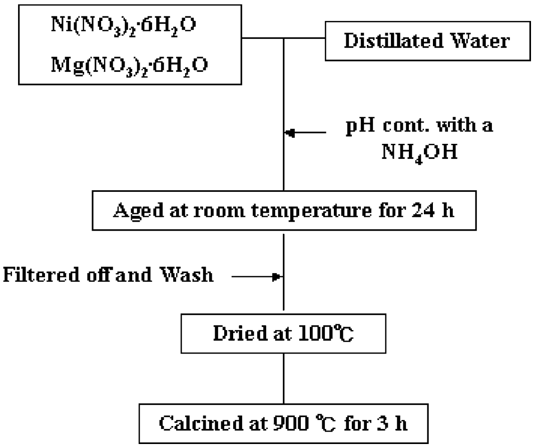


Fig. 1. Preparation procedure of NiO–MgO catalyst for catalytic reforming of carbon dioxide by methane.

NiO and NiO–MgO catalysts were prepared by a precipitation method using raw materials such as $Ni(NO_3)_2{\cdot}6H_2O$ and $Mg(NO_3)_2{\cdot}6H_2O$. NiO–MgO catalyst consists of 90 mol% NiO and 10 mol% MgO. Aqueous solutions with adequate molar ratios were prepared at room temperature and then continuously stirred magnetically until pH was maintained at the value of 9 with a 55% NH_4OH. The precipitate was aged at room temperature for 24 h in the mother liquor, and then separated by filtering. The solid cake was washed with distilled water until nitrate and sodium ions were removed. The solid material was dried at 100 °C for 24 h in air and calcined at 900 °C for 6 h. The procedure for preparation of Ni-based oxide catalyst is summarized in Fig. 1.

The characteristics of prepared catalysts were analyzed by N_2 physisorption and XRD. BET surface area and total pore volume of the catalyst before and after the reaction were determined from N_2 adsorption isotherm measured at liquid nitrogen temperature with a sorption analyzer [Quantachrome Co., Autosorb-1C]. Structure of the catalyst before and after the reaction was analyzed by an XRD analyzer [Shimazdu Co., XRD-6000] equipped with a Cu Kα source, at 40 kV, current of 30 mA and scanning speed of $5^{\circ}C\ min^{-1}$.

2.2. Preparation of a single cell

The single cell was prepared by a tape casting method. The binder solution for slurry was prepared by adding 0.87 g of methyl cellulose (MC), 1.14 g of carbonyl methyl cellulose (CMC) and 1.74 g of polyethylene oxide (Polyox) as binder and isopropyl alcohol (IPA) of 3 ml as a dispersing agent in deionized water of 100 ml. After catalyst was added to 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 °C for 24 h and sintered at 1250 °C for 4 h under air. The thickness and area of the catalyst electrode layer were ca. 20 μm and 2.25 cm^2 (1.5 cm × 1.5 cm), respectively. The microstructure properties of the catalyst electrode before and after the electrocatalytic reforming were characterized by SEM [Hitachi Co., S-4200].

2.3. Electrocatalytic membrane reactor (ECMR) system

The schematic diagram of an electrocatalytic membrane reactor (ECMR) system is illustrated in Fig. 2. 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 OD 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 (OD = 0.025 m, ID = 0.019 m) using pyrex glass (OD = 0.025 m, ID = 0.021 m, h = 0.003 m). The single cell reactor was placed in an electrical furnace equipped with a PID controller [Han Young

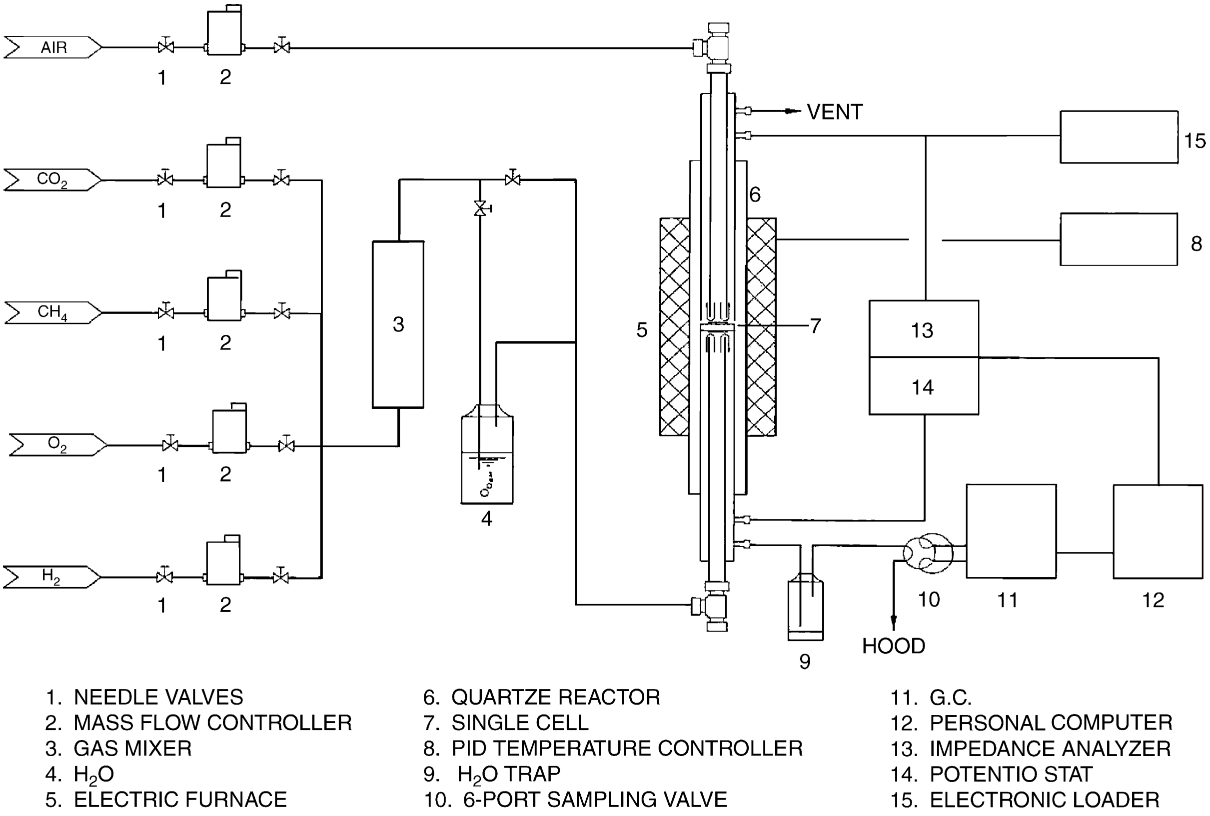


Fig. 2. Electrocatalytic membrane reactor system for internal reforming of CO_2 by CH_4.

Co., P-100]. The temperature of the single cell was measured by a thermocouple positioned near the electrochemical cell. The electrocatalytic reactor was operated at 800 °C for 6 h under the open- and close-circuit conditions.

2.4. Electrochemical properties

Electrochemical properties were measured by a Solatron 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 counter electrode side was left open to flowing of air at an atmospheric pressure. The current and voltage were controlled by a galvanostatic method. Current and voltage were measured by Potentiostat–Galvanostat at a steady state. Characteristics of impedance were tested with the frequency response. The carbon dioxide reforming by methane over NiO–MgO catalyst electrode in an electrochemical cell (CO_2, CH_4, NiO–MgO|YSZ|(La,Sr)MnO_3, air) under open- and closed-circuit conditions was carried out at 800 °C and an atmosphere.

3. Results and discussion

3.1. Characteristics of catalyst

It was known that alkali or alkaline earth substrates are often added for controlling carbon formation [16], and Ni-based anodes are generally used for the SOFC system. In this work, MgO was selected as a modification agent for NiO catalyst anode for the cogeneration of syngas and electricity in the SOFC system.

The characteristics of prepared catalysts are summarized in Table 1. It was found that the BET surface area and total pore volume of NiO catalyst were 1.34 m^2/g and 6.14×10^{-4} cm^3/g, while those of the NiO–MgO catalyst were 4.08 m^2/g and 7.64×10^{-4} cm^3/g, respectively.

Fig. 3 represents the X-ray diffraction (XRD) patterns of NiO and NiO–MgO catalysts before and after the catalytic reforming of CO_2 by CH_4. We could not observe any major differences in the XRD patterns between NiO and NiO–MgO catalysts before and after the reaction. Because of their very similar structure, NiO and MgO are completely miscible over the entire mole fraction range and form an ideal solution [16]. These results can be explained by the *d*-value of the (2 2 0), (3 1 1) and (2 2 2) faces for the NiO and MgO. The *d*-value of the (2 2 0), (3 1 1) and (2 2 2) for NiO are 1.476, 1.259 and 1.206 Å, respectively, while those for MgO are 1.489, 1.270 and 1.216 Å, respectively. It was identified that $NiMgO_2$ phase was produced in NiO (90 mol%)–MgO (10 mol%) catalyst. However, it was found that NiC phase did not produce after catalytic CO_2 reforming over NiO and NiO–MgO catalysts, respectively.

Table 1
The BET surface area and total pore volume of NiO and NiO–MgO catalysts before and after the catalytic reaction

Catalyst	BET surface area (m^2/g)	Total pore volume (cm^3/g)
NiO		
Before reaction	1.34	6.13×10^{-4}
After reaction	0.32	1.17×10^{-4}
NiO–MgO		
Before reaction	4.08	7.64×10^{-4}
After reaction	6.28	1.07×10^{-3}

3.2. Catalytic reaction

In order to investigate the catalytic activity of prepared catalysts, CO_2 reforming by CH_4 was carried out in the fixed reactor system. The product was analyzed by an on-line GC equipped with the same column used in the ECMR system. The reaction rates (γ_i) of CO_2 and CH_4, and the formation rate of CO were determined as

$$\gamma_{CH_4} = F_{in}[CH_4]_{in} - F_{out}[CH_4]_{out}$$

$$\gamma_{CO_2} = F_{in}[CO_2]_{in} - F_{out}[CO_2]_{out}$$

$$\gamma_{CO} = F_{out}[CO]_{out}$$

where the reaction rate per BET surface area of the catalyst is expressed in μmol/cm^2 s, [CH_4], [CO_2] and [CO] are concentrations of CO_2, CH_4 and CO, respectively, and F is the total flow rate of the gas mixture (μmol/s). The production rate of H_2O and the

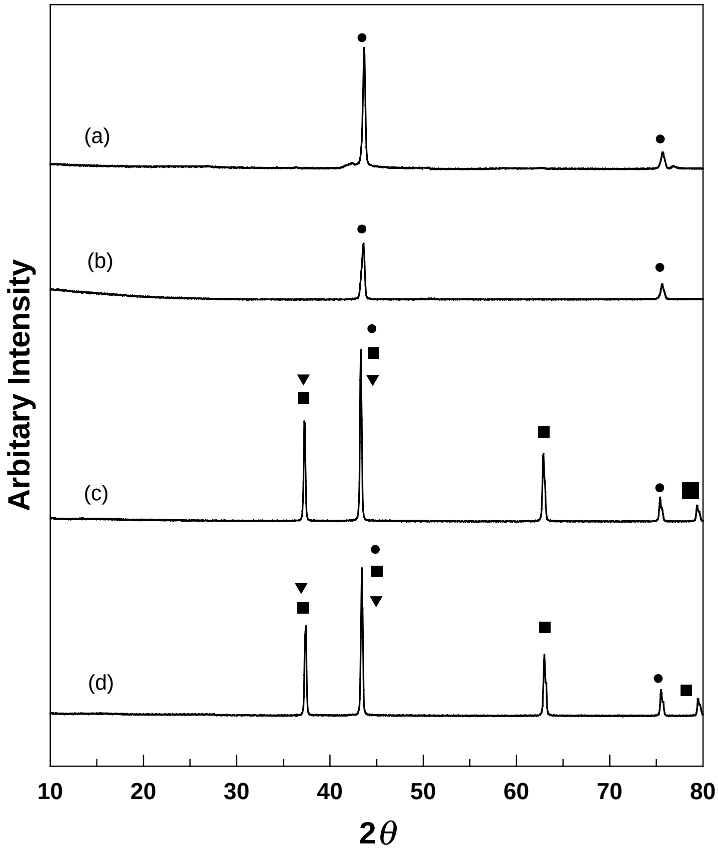


Fig. 3. XRD patterns of NiO and NiO–MgO catalysts before and after the catalytic reforming of CO_2 by CH_4: (●) NiO, (▼) MgO, (■) $NiMgO_2$. (a) NiO before reaction, (b) NiO after reaction, (c) NiO–MgO before reaction, (d) NiO–MgO after reaction.

formation rate of deposited carbon were calculated from a mass balance of the hydrogen and carbon.

Fig. 4 shows the reaction rates of CO_2 and CH_4 over NiO and NiO–MgO catalysts with a time on stream. The catalytic reforming reaction of a mixture of CO_2 (12 vol.%) and CH_4 (12 vol.%) was carried out at the reaction conditions of 800 °C, atmosphere and total flow rate of 20 cm^3/min. It was found that NiO–MgO catalyst presented higher reaction rate than NiO catalyst under the tested conditions. The reaction rates of CO_2 and CH_4 over NiO–MgO catalyst were obtained 4.3×10^{-1} and 4.7×10^{-1} $\mu mol/cm^2$ s, respectively. The formation rates of CO and H_2 over the NiO–MgO catalyst slowly decreased with a time on stream, whereas the formation rate of coke slowly increased. The reaction rates of CO_2 and CH_4 over the NiO catalyst decreased more drastically than those of CO_2 and CH_4 over the NiO–MgO catalyst. The BET surface area and total pore volume of the prepared catalysts before and after reaction are summarized in Table 1. BET surface area and total pore volume of the NiO catalyst after the reaction decreased 76 and 80%, respectively. However, those of the NiO–MgO catalyst after the reaction increased 5 and 40%, respectively. It was identified that BET surface area of the NiO catalyst decreased by sintering of Ni, but those of the NiO–MgO catalyst increased by the formation of carbon.

It was concluded that the Mg doped NiO catalyst is a more promising candidate than the NiO catalyst for the cogeneration of syngas and electricity by the internal reforming of CO_2 and CH_4 in the SOFC system.

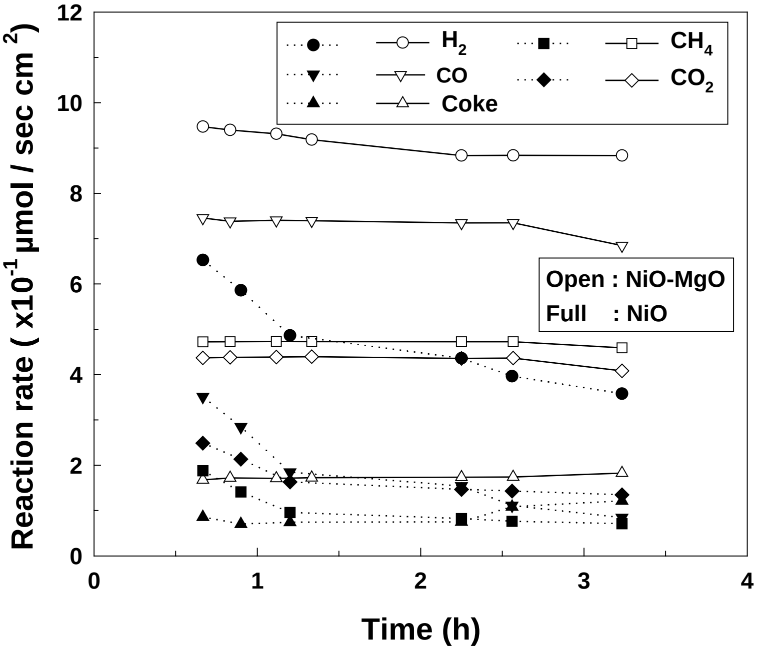


Fig. 4. The reaction rates of CO, CH_4, CO_2 and coke over NiO–MgO and NiO catalysts with a time on stream. Reaction temperature = 800 °C, total flow rate = 20 ml/min: CH_4 (12.5 vol.%), CO_2 (12.5 vol.%).

3.3. Electrocatalytic reaction

Fig. 5 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 closed-circuit conditions. The apparent surface area of coated anode catalyst, instead of BET surface area of NiO–MgO catalyst, was 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. 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. 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 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. Table 2 shows the product distributions of the electrocatalytic reaction of CO_2 and CH_4, and the amount of coke

Table 2
Product distributions for the electrocatalytic reaction of CO_2 and CH_4 and the amount of coke formed at 800 °C for 5 h in the electrochemical cell (NiO–MgO|YSZ|(La,Sr)MnO_3) system[a]

Reaction mode	Product distribution (mol%)				Coke formation (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	–

[a] Total flow rate of fuel = 20 ml/min: CH_4 (12.5 vol.%), CO_2 (12.5 vol.%), flow rate of air = 20 ml/min.

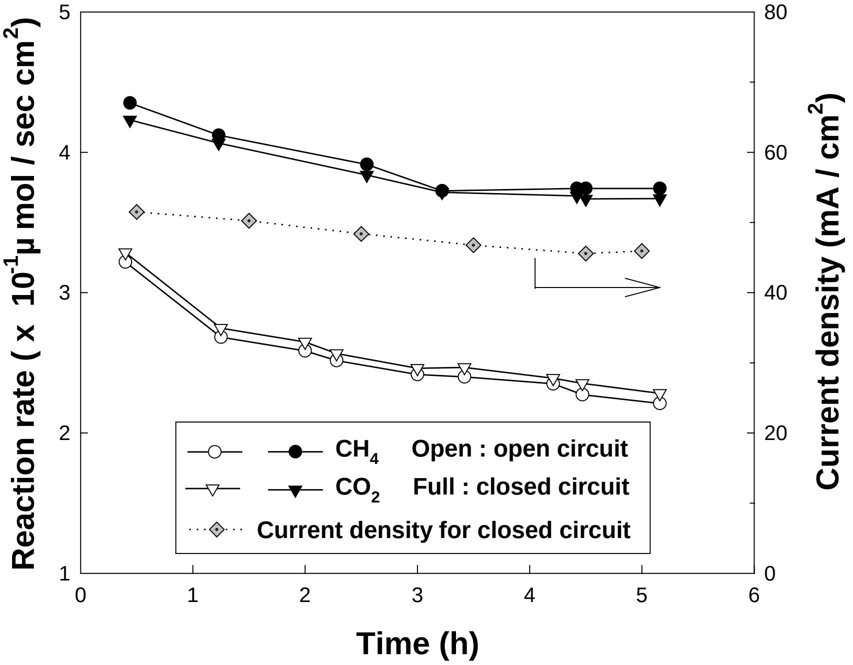


Fig. 5. The reaction rates of CH_4 and CO_2 and the current density over the electrocatalytic cell (NiO–MgO|YSZ|(La,Sr)MnO_3) with a time on stream under the open- and closed-circuit conditions at 800 °C. Total flow rate of fuel = 20 ml/min: CH_4 (12.5 vol.%), CO_2 (12.5 vol.%), flow rate of air = 20 ml/min.

formed at 800 °C for 5 h in the electrocatalytic cell (NiO–MgO|YSZ|(La,Sr)MnO_3) under the open- and 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/$g_{catalyst}$ for 5 h. But the amount of coke under the closed-circuit condition drastically decreased compared to that under the open-circuit. The results interpreted that the carbon deposited on the surface of anode catalyst under the open-circuit condition was mainly desorbed to carbon dioxide by the reaction (Eq. (15)) of oxygen ion transferred from the cathode with the surface carbon.

3.4. Electrocatalytic reaction mechanisms

Concerning the mechanism of CO_2 reforming of methane over catalysts based on Ni, Ru, Rh, Pd and Pt, etc. in general, the following steps (Eqs. (2)–(8)) are supposed to be involved in the reaction mechanism [16–18]; CO_2 reforming reaction can be produced by CH_4 decompositions (Eqs. (2)–(6)), CO_2 disproportionation (Eq. (7)) and partial oxidation of surface carbon (Eq. (8)). Also, surface carbon can be produced by methane decomposition (Eq. (9)) and CO disproportionation (Eq. (10))

$$CH_4 \rightarrow CH_3\,(ads) + H\,(ads) \quad (2)$$

$$CH_3\,(ads) \rightarrow CH_2\,(ads) + H\,(ads) \quad (3)$$

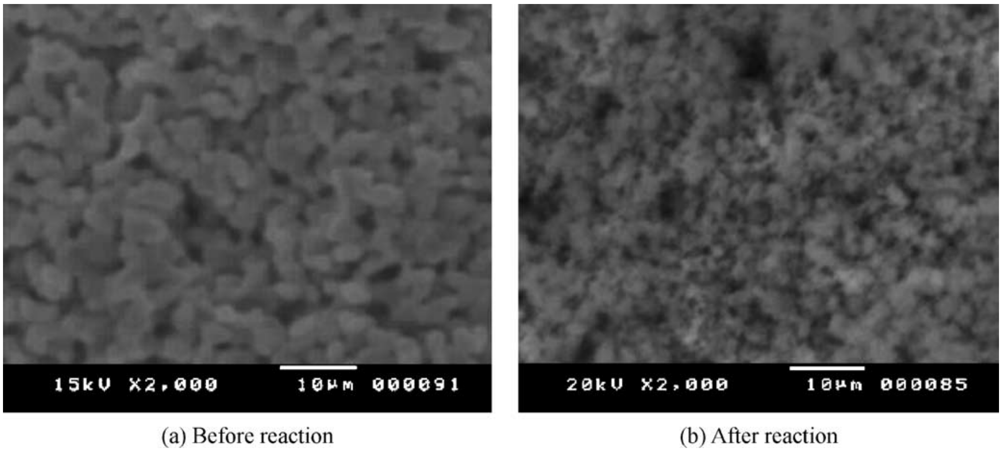
$$CH_2\,(ads) \rightarrow CH\,(ads) + H\,(ads) \quad (4)$$

$$CH\,(ads) \rightarrow C\,(ads) + H\,(ads) \quad (5)$$

$$CH_4 \rightarrow C\,(ads) + 2H_2 \quad (6)$$

$$CO_2 \rightarrow CO\,(ads) + O\,(ads) \quad (7)$$

$$C\,(ads) + O\,(ads) \rightarrow CO \quad (8)$$



(a) Before reaction (b) After reaction

Fig. 6. SEM image for the surface electrode catalyst before and after the reaction in the electrocatalytic cell (NiO–MgO|YSZ|(La,Sr)MnO_3) under the closed-circuit.

$$CH_4 \rightarrow C\,(ads) + 2H_2 \quad (\Delta H^{\circ}_{298} = 74.9\,kJ/mol) \tag{9}$$

$$2CO \rightarrow C\,(ads) + CO_2 \quad (\Delta H^{\circ}_{298} = -172.4\,kJ/mol) \tag{10}$$

Fig. 6 shows the SEM images for the surface of the catalyst anode before and after the reaction under the closed-circuit condition in the electrocatalytic cell (NiO–MgO|YSZ|(La,Sr)MnO_3) system. It was found that surface carbon under the open-circuit condition was accumulated on the surface of anode and it filled up pore. The reforming of CO_2 by CH_4 was performed in the electrochemical cell under closed-circuit condition to investigate the effect of anodic current on the reforming. 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.

In the electrochemical cell, oxygen ions (O^{2-}) are formed on the counter electrode according to the following reaction:

$$0.5O_2 + 2e^- \rightarrow O^{2-} \tag{11}$$

These oxygen ions are transferred to the catalyst electrode through the YSZ electrolyte. The possible electrocatalytic reactions with the oxygen ions transferred to the catalyst electrode can be occur by the following reactions (Eqs. (12)–(15)):

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \tag{12}$$

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \tag{13}$$

$$Cs + O^{2-} \rightarrow CO + 2e^- \tag{14}$$

$$Cs + 2O^{2-} \rightarrow CO_2 + 4e^- \tag{15}$$

It was interpreted that carbon deposition was prevented by the reaction (Eqs. (14) and (15)) of surface carbon with the oxygen ion transferred from cathode electrode in SOFC system.

3.5. *Electrochemical properties*

The electrochemical properties were obtained at a steady state value within a few minutes after first introduced the reactants to the catalyst electrode side of the electrochemical cell. All currents and voltages were measured at the steady state. Fig. 7 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 °C 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

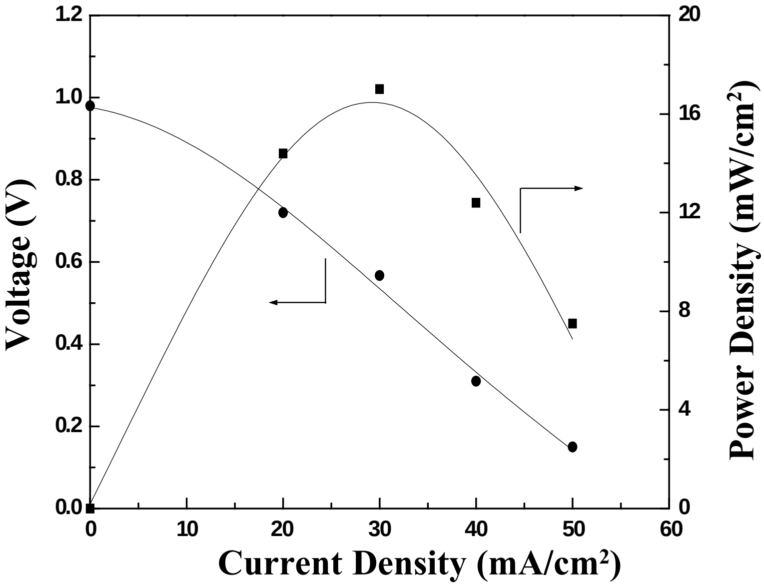


Fig. 7. The performance of current voltage and power density with current density in the electrochemical cell (NiO–MgO|YSZ|(La,Sr)MnO_3) at 800 °C when CH_4 (12.5 vol.%) and CO_2 (12.5 vol.%) was used as a reactant. Flow rates of a reactant and air are 20 ml/min, respectively.

in the single cell. The electricity can be produced by the electrochemical reactions such as the oxidation of CO and H_2 (Eqs. (12) and (13)), the oxidation of surface carbon (Eqs. (14) and (15)) and the oxidation of CH_4 (Eqs. (16) and (17))

$$CH_4 + O^{2-} \rightarrow CO + 2H_2 + 2e^- \quad (16)$$

$$CH_4 + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^- \quad (17)$$

Even though Park et al. [11] reported the proof of the direct oxidation of CH_4 from chemical analysis of the products leaving the cell, and suggested the electricity was produced by the total oxidation of CH_4 (Eq. (17)), it was considered that the electricity was mainly produced by the electrochemical reactions (Eqs. (12)–(15)) because the reaction rates of CO_2 and CH_4 leaving the anode in Fig. 5 showed a similar trend and the rate of the CO_2 reforming by CH_4 is faster than that for the total oxidation of CH_4 in this system. It was found that carbon deposition was prevented by the reaction (Eqs. (14) and (15)) of surface carbon with the oxygen ion transferred from cathode electrode in SOFC system.

For H_2 as a reactant, the OCV obtained for the single cell tested at 800 °C and atmosphere was 1.04 V. The electricity was produced by the electrochemical reaction (Eq. (13)). It was identified that Ni-based catalyst was suitable as an electrode of SOFC in terms of voltage-power performances.

4. Conclusions

Catalytic reforming and electrocatalytic reforming of CO_2 by CH_4 were investigated over Ni-based catalysts and the electrocatalytic cell (NiO–MgO|YSZ|(La,Sr)MnO_3), respectively. It was concluded that the cogeneration of syngas and electricity by the electrocatalytic reforming of CO_2 by CH_4 is an attractive process for the cogeneration of syngas and electricity. The NiO–MgO catalyst presented higher reaction rates than NiO catalyst under the tested conditions. 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 ions. 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. Catalyst deactivation by coking was suppressed by the oxygen ions which were being supplied electrochemically to the catalyst electrode through the solid electrolyte.

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