Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 6713–6721

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Electrochemical reforming of CH_4-CO_2 mixed gas using porous Gd-doped ceria electrolyte with Cu electrode

Yuta Suga, Rie Yoshinaga, Naoki Matsunaga, Yoshihiro Hirata*, Soichiro Sameshima

Department of Chemistry, Biotechnology, and Chemical Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

Received 17 April 2012; received in revised form 18 May 2012; accepted 20 May 2012
Available online 26 May 2012

Abstract

This paper reports on the composition and flow rate of outlet gas and current density during the reforming of CH_4 with CO_2 using three different electrochemical cells: cell A, with Ni−GDC (Gd-doped ceria: $Ce_{0.8}Gd_{0.2}O_{1.9}$) cathode/porous GDC electrolyte/ Cu−GDC anode, cell B, with Cu−GDC cathode/ porous GDC electrolyte/Cu−GDC anode and cell C, with Ru−GDC cathode/ porous GDC electrolyte/ Cu−GDC anode. In the cathode, CO_2 reacts with supplied electrons to form CO fuel and O^{2-} ions ($CO_2+2e^-\rightarrow CO+O^{2-}$). Too low affinity of Cu cathode to CO_2 in cell B reduced the reactivity of the CO_2 with electrons. The CO fuel, O^{2-} ions and CH_4 gas were transported to the anode through the porous GDC mixed conductor of O^{2-} ions and electrons. In the anode, CH_4 reacts with O^{2-} ions to produce CO and H_2 fuels ($CH_4+O^{2-}\rightarrow 2\,H_2+CO+2e^-$). The reforming efficiency at 700−800 °C was lowest in cell B and highest in cell A. The Cu anode in cells A and C worked well to oxidize CH_4 with O^{2-} ions ($2Cu+O^{2-}\rightarrow Cu_2O+2e^-$, $Cu_2O+CH_4\rightarrow 2Cu+CO+2H_2$). However, a blockage of the outlet gas occurred in all the cells at 700−800 °C. The gas flow is inhibited due to a reduction in pore size in the cermet cathode, as well as sintering and grain growth of Cu metal in the anode during the reforming.

Keywords: A. Sintering; C. Chemical properties; E. Electrodes

1. Introduction

Biomass energy attracts attention as an environmentally friendly energy because it is a renewable source of energy. Biogas produced from waste food or drainage contains 60 vol% CH_4 and 40 vol% CO_2. Reforming of CH_4 with CO_2 produces H_2 and CO fuels

$$CH_4+CO_2\rightarrow 2H_2+2CO, \quad (1)$$

which can be supplied to a solid oxide fuel cell to get electric power [1–5]. In our previous papers [6,7], reforming of CH_4 with CO_2 on Al_2O_3-supported 30 vol% Ni catalyst was investigated at 400−900 °C. The supplied CH_4 reacted well with CO_2 in a temperature range of 700−900 °C, but the pyrolysis of CH_4

$$CH_4\rightarrow C+2H_2 \quad (2)$$

proceeded as a parallel reaction at 400–600 °C. The carbon powder formed by the decomposition of CH_4 caused a blockage in the gas flow during the reforming of CH_4. On the other hand, our group clarified that electrochemical reforming of CH_4 with CO_2 is an effective process to produce H_2-CO fuel with suppression of carbon deposition [8]. Mixed gas of 50% CH_4−50% CO_2 was supplied to a cell with a porous Ni−Gd-doped ceria (GDC, $Ce_{0.8}Gd_{0.2}O_{1.9}$) cathode, a porous GDC electrolyte and a porous Ru−GDC anode system operated at 1.25−6.25 V/cm of electric field strength at 400−800 °C. CO_2 is reduced to CO in the cathode

$$CO_2+2e^-\rightarrow CO+O^{2-}. \quad (3)$$

The formed CO gas and O^{2-} ions are transported to the anode through a porous GDC electrolyte. CH_4 reacts with the transported O^{2-} ions to form H_2 and CO fuels

$$CH_4+O^{2-}\rightarrow 2H_2+CO+2e^-. \quad (4)$$

*Corresponding author. Tel.: +81 99 285 8325; fax: +81 99 257 4742.
E-mail address: hirata@apc.kagoshima-u.ac.jp (Y. Hirata).

0272-8842/$36.00 © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.05.061

The yield of H_2-CO fuel was close to 100% at 800 °C. As a result, it was possible to continuously produce the H_2-CO fuel for more than 10 h. The flow of a small amount of electrons through the electrochemical cell enhanced the reactivity between CH_4 and CO_2 in a wide temperature range. The metal catalysts in the electrodes provide a significant influence on the reforming of CH_4. Use of Ni in the anode accelerated the decomposition of CH_4 rather than aiding the reforming of CH_4 and caused blockages of supplied gas [9]. On the other hand, Ni in the cathode worked well in reducing CO_2 to CO and O^{2-} ions. The use of Ru in both electrodes suppressed the carbon deposition, and facilitated the reforming of CH_4 with CO_2.

In this paper, the performance of electrochemical cells with Cu electrodes is studied and compared to the reforming results of Ni or Ru electrodes as mentioned above. Igneous rock contains, on average, 70, 80 and 0.001 ppm of Cu, Ni and Ru, respectively, and Cu is abundant on earth. A porous GDC layer composed of $Ce_{0.8}Gd_{0.2}O_{1.9}$ was used as an electrolyte. Three different cells were tested in this paper: (A) Ni–GDC cathode/porous GDC electrolyte/Cu–GDC anode, (B) Cu–GDC cathode/porous GDC electrolyte/Cu–GDC anode, and (C) Ru–GDC cathode/porous GDC electrolyte/ Cu–GDC anode. Furthermore, the reforming of CH_4 with CO_2 when using a Cu–GDC catalyst with no external current was also examined to understand the role of the electric field in CH_4 reforming.

2. Experimental procedure

2.1. Preparation of electrochemical cells and Cu-GDC catalyst

Table 1 shows the components of the electrochemical cells used. The electrodes of each cell contained 30 vol% metal and 70 vol% GDC. The detailed preparation methods for GDC, Ni–GDC and Ru–GDC powders and the fabrication method of the layered electrochemical cell were reported in our previous papers [8–10]. The GDC powder composed of $Ce_{0.8}Gd_{0.2}O_{1.9}$ was prepared by heating the oxalate solid solution precursor $(Ce_{0.8}Gd_{0.2})_2(C_2O_4)_3$ at 600 °C for 2 h in air. The GDC powder was milled with 3 mm diameter alumina balls for 24 h. The milled GDC powder was immersed into 1.4 M $Ni(NO_3)_2$ solution, 1.4 M $Cu(NO_3)_2$ solution, or 0.2 M $RuCl_3$ solution to make cermet electrodes. The mixed suspensions were stirred for 6 h and then freeze-dried. The freeze-dried powders were then heated at 600–800 °C for 1 h in air.

The 10 mm-diameter and 1 mm-thick porous GDC powder disk was sandwiched between a cathode powder layer (4 mm thick) and an anode powder layer (4 mm thick) and pressed uniaxially at 100 MPa, followed by isostatic pressing at 150 MPa, and then heated at 900 °C for 2 h in air. Similarly, the 10 mm-diameter and 9 mm-thick CuO–GDC powder catalyst was pressed uniaxially at 100 MPa, followed by isostatic pressing at 150 MPa, and then heated at 800 °C for 2 h in air. The phases of the heated electrochemical cells and CuO–GDC catalyst were identified by X-ray diffraction (RINT 2200PCH/KG, Rigaku Co., Japan). The bulk and apparent densities of the sintered porous electrodes were measured by the Archimedes method in distilled water. The true densities of the NiO–GDC, CuO–GDC and RuO_2–GDC compacts were calculated to be 7.128, 6.844 and 7.108 g/cm^3, respectively, for the cermet composition (30 vol% metal), using the true densities of 7.246 g/cm^3 for GDC [10], 6.96 g/cm^3 for NiO [11], 6.315 g/cm^3 for CuO [12] and 6.97 g/cm^3 for RuO_2 [13].

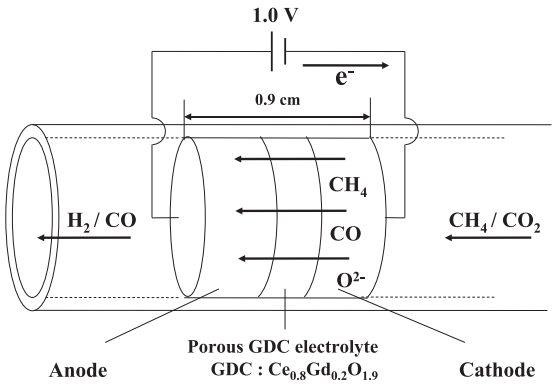
2.2. Electrochemical reforming of CH_4 with CO_2

Fig. 1 shows the diagram of the electrochemical reaction apparatus for reforming of CH_4 with CO_2. Pt meshes with Pt wires were attached to both the electrodes using Pt paste. The electrochemical cell was set to an alumina holder and sealed by heating a glass O-ring at 870 °C for 15 min. After cooling to 800 °C, 3 vol% H_2O-containing H_2 gas was fed into the cathode at 50 ml/min for 24 h to reduce the oxides to metals ($NiO+H_2 \rightarrow Ni+H_2O$, $CuO+H_2 \rightarrow Cu+H_2O$, $RuO_2+2H_2 \rightarrow Ru+2H_2O$). Then, 1 V of external voltage was applied with a potentiostat (HA-501G, Hokuto Denko Co., Japan). The 50% CH_4–50% CO_2 mixed gas was fed into the cathode at 50 ml/min. The composition of the outlet gas was analyzed by gas chromatography (GT 3800, Yanaco Co., Japan) with active carbon (60/80 mesh) and using a thermal conductivity detector at 100 °C. A 0.2 ml sample of the outlet gas of was injected into an Ar carrier gas at 100 °C. The bulk and apparent densities of the electrodes after the reduction with 3 vol% H_2O-containing H_2 gas at 700–800 °C were measured by the Archimedes method in kerosene. The true densities were calculated to be 7.743 g/cm^3 for Ni–GDC cermet, 7.760 g/cm^3 for Cu–GDC cermet and 8.795 g/cm^3 for Ru–GDC cermet. The thermal expansion of

Table 1
Components of electrochemical cells.

Cell	Cathode (volume ratio) (thickness, open porosity)	Electrolyte[a] (thickness)	Anode (volume ratio) (thickness, open porosity)
A	30Ni-70GDC(4 mm, 38.2%)	GDC(1 mm)	30Cu-70GDC(4 mm, 32.1%)
B	30Cu-70GDC(4 mm, 32.1%)	GDC(1 mm)	30Cu-70GDC(4 mm, 32.1%)
C	30Ru-70GDC(4 mm, 40.4%)	GDC(1 mm)	30Cu-70GDC(4 mm, 32.1%)

[a]GDC: Gd-doped ceria, $Ce_{0.8}Gd_{0.2}O_{1.9}$.



$M + O^{2-} \rightarrow MO + 2e^-$ (7) $M + CO_2 \rightarrow MO + CO$ (5)

$MO + CH_4 \rightarrow M + CO + 2H_2$ (8) $MO + 2e^- \rightarrow M + O^{2-}$ (6)

$CH_4 + O^{2-} \rightarrow 2H_2 + CO + 2e^-$ (Oxidation) (4) $CO_2 + 2e^- \rightarrow CO + O^{2-}$ (Reduction) (3)

Total reaction : $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$ (1)

Fig. 1. Diagram of electrochemical reaction apparatus with metal catalysts.

the cermet electrodes was measured with a thermomechanical analyzer (TMA 8310, Rigaku Co., Japan) in an Ar atmosphere at 800 °C for 10 h.

3. Results and discussion

3.1. Properties of electrochemical cells and Cu−GDC catalyst

X-ray diffraction patterns of the electrodes heated at 600−800 °C (Table 1) indicated the coexistence of two phases of NiO−GDC, RuO_2−GDC and CuO−GDC, suggesting a phase compatibility at low temperatures. The cathodes and anodes of cells A−C after sintering at 900 °C had 32.1−40.4% open porosity. The flow of 3 vol% H_2O-containing H_2 gas through the electrochemical cells and Cu−GDC catalyst was measured at 800 °C and was smooth (40−48 ml/min).

3.2. Electrochemical reforming of CH_4 with CO_2

3.2.1. Cell A (Ni−GDC cathode/porous GDC electrolyte/ Cu−GDC anode)

Fig. 2(a) shows the fractions of CH_4, CO_2, H_2 and CO gases passing through cell A, operated at 1.1 V/cm. The 50 vol% CH_4−50vol% CO_2 mixed gas changed to H_2 and CO fuels with increasing temperature. The outlet gas for 2.5 h at 800 °C contained 1% CH_4, 2% CO_2, 52% H_2 and 45% CO. The gas composition was comparable to that of reformed gas from a cell using a Ni−GDC cathode/ porous GDC electrolyte/ Ru−GDC anode in a previous experiment [8]. Fig. 2(b) shows the time dependence of the flow rate of outlet gas and the current density. The flow rate of the outlet gas at 400−700 °C increased slightly with increasing temperature. This result is explained by the increased volume of the outlet gas (Eq. (1)). However, after

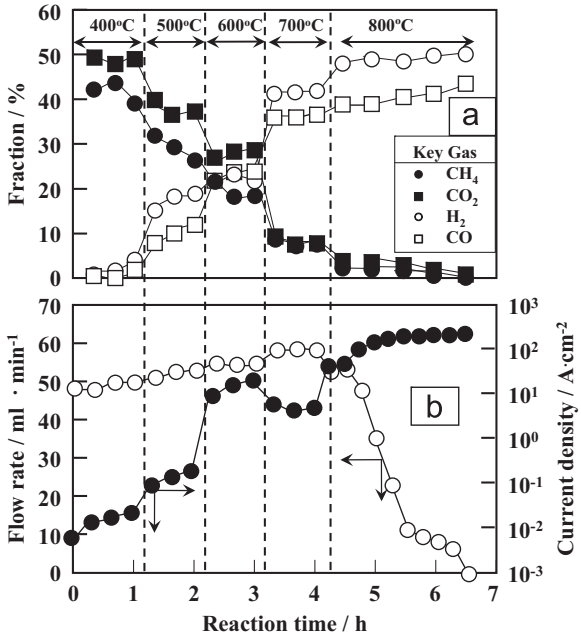


Fig. 2. (a) Fractions of CH_4, CO_2, H_2 and CO gases through electrochemical cell A and (b) flow rate of outlet gas and current density at 1.1 V/cm. See Table 1 for cell A.

the reforming experiment at 800 °C, carbon deposition was observed in the Ni catalyst cathode. The deposited carbon powder inhibited the gas flow as seen in Fig. 2(b). Fig. 3(a) shows the X-ray diffraction pattern of the cathode used in cell A. In addition to the GDC and Ni, graphite was detected. This indicates that the gradual decrease of flow rate at 800 °C in Fig. 2(b) is due to carbon deposition caused by the pyrolysis of CH_4 in the cathode. Furthermore, sintering and grain growth of Cu in the anode is also responsible for the blockage of the gas flow at 800 °C, which is discussed in Section 3.2.5. Fig. 3(b) shows the

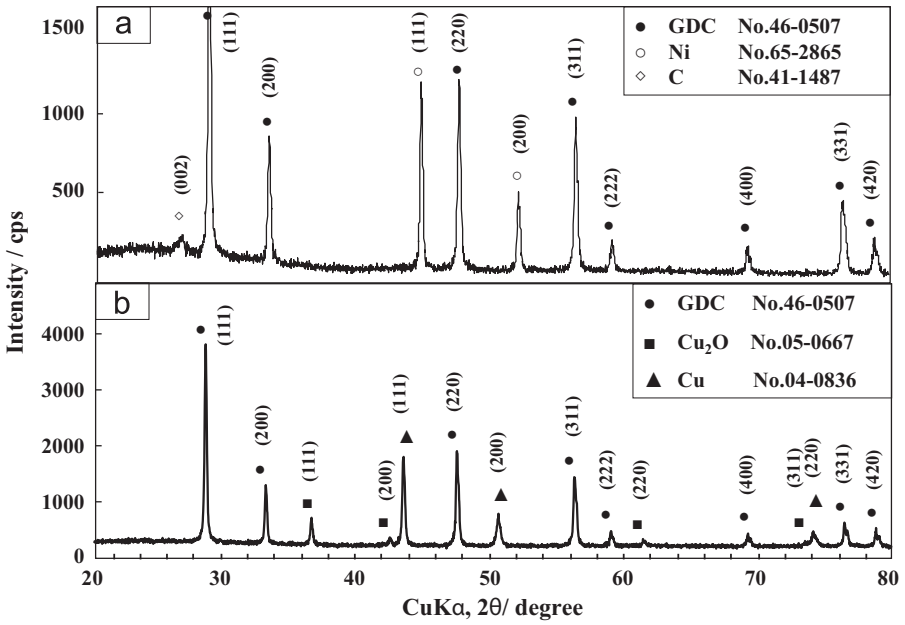


Fig. 3. X-ray diffraction patterns of cathode (a) and anode (b) of cell A after reforming at 800 °C.

X-ray diffraction pattern of the anode of cell A when tested at 800 °C. GDC coexisted with Cu and Cu_2O was also detected. However, no carbon-related phase was formed in the anode. The above result indicates that (1) Ni in the cathode accelerates the thermal decomposition of CH_4 (Eq. (2)) in addition to the reduction of CO_2 (Eq. (3)) at 800 °C and (2) Cu in the anode promotes the oxidation of CH_4 and suppresses the pyrolysis of CH_4 (Eq. (4)). The formation of both Cu and Cu_2O in the anode suggests the following catalytic reactions in the anode.

$$2Cu + O^{2-} \rightarrow Cu_2O + 2e^- \quad (9)$$

$$Cu_2O + CH_4 \rightarrow 2Cu + 2H_2 + CO \quad (10)$$

Carbon deposition in the Ni−GDC cathode increases the possibility of decreasing the Ni catalyst activity and the conversion efficiency of CH_4-CO_2 mixed gas. However, a high conversion efficiency (above 90%) of inlet gas was measured continuously for 13 h at 800 °C in a cell with a Ni−GDC cathode/porous GDC/Ru−GDC anode system [9]. After electrochemical reforming at 800 °C, 5.0−7.2 mass% of carbon was deposited in the Ni−GDC cathode. This result indicates that there is little influence from deposited carbon on the Ni catalyst activity. In our previous paper [14], it is shown that (1) a part of the deposited carbon is removed as CO gas due to a reaction with O^{2-} ions formed from CO_2 in the cathode

$$CO_2 + 2e^- \rightarrow CO + O^{2-}, \quad (3')$$

$$C + O^{2-} \rightarrow CO + 2e^-, \quad (11)$$

and that (2) the CO gas and electrons produced (Eq. (11)) are transported to the anode through the porous mixed conductor GDC electrolyte of oxide ions and electrons. The above mechanism limits the amount of carbon deposited in the cathode and leads to the long durability of the electrochemical cell when a suitable cermet catalyst is used in the anode.

On the other hand, the current density in Fig. 2(b) increased logarithmically at a higher temperature. The relation among current density (J), conductivity (σ) and electric field strength (E) is shown in Eq. (12).

$$J = \sigma E \quad (12)$$

With $E = 1.1$ V/cm, the J value calculated for dense GDC ($\sigma = 0.125$ S/cm at 800 °C in air [15]) is 1.38×10^{-1}, for Ni ($\sigma = 2.20 \times 10^4$ S/cm at 900 °C [16]) is 2.42×10^4, for Cu ($\sigma = 1.23 \times 10^5$ S/cm at 1000 °C [16]) is 1.35×10^5, and for graphite ($\sigma = 1.56 \times 10^3$ S/cm at 800 °C [17]) is 1.72×10^3 A/cm^2. This indicates that the current density of cell A is affected by the high resistance of the GDC electrolyte. The ratio of measured current density to the calculated current density for dense GDC electrolyte was 16.9 at 500 °C, 598.8 at 600 °C, 65.2 at 700 °C and 914.3 at 800 °C [15]. The decreased flow rate at 800 °C due to the pyrolysis of CH_4 in the cathode and the large current density ratios for GDC electrolyte at 500−800 °C indicated above suggest that (1) the pyrolysis of CH_4 proceeds together with the reforming of CH_4 in the lower temperature range of 400−600 °C, (2) the carbon particles formed in the cathode may be conveyed toward the GDC electrolyte by the supplied CH_4-CO_2 mixed gas, (3) the carbon powders deposited in the cathode and porous GDC electrolyte form electronic conduction paths along the contact of Ni−C−Cu, which may have a lower electrical resistance than porous GDC electrolyte. The change of current density in Fig. 2(b) expresses the gradual structure change of GDC electrolyte due to carbon deposition. The decrease of current density at 700 °C may reflect the removal of carbon by a reaction with O^{2-} ions formed in the

cathode ($C+O^{2-} \rightarrow CO+2e^{-}$ (11) [14]). The formed electrons are transported to the anode through the electronic conduction paths of Ni−C−Cu particles and GDC mixed conductor of O^{2-} ions and electrons. Therefore, three reactions occur in the cathode in parallel: (1) interaction between CO_2 and electrons to form CO fuel and O^{2-} ions, (2) pyrolysis of CH_4 to produce carbon particles, and (3) elimination of deposited carbon through a reaction with O^{2-} ions. The occurrence of each reaction is closely influenced by the reaction temperature. The results (Fig. 2) indicate that cell A should be operated below 700 °C to avoid the formation of electronic conduction paths and avoid the blockage of gas flow. Another possible phenomenon is the sintering of Ni or Cu particles in the electrodes, which inhibits the flow of outlet gas. Specifically, avoiding the sintering of Cu, which has a relatively low melting point of 1083 °C, is important in order to operate the cell for a long time. This possibility is discussed in Section 3.2.5.

3.2.2. Cell B (Cu-GDC cathode/GDC electrolyte/Cu-GDC anode)

Fig. 4(a) shows the fractions of CH_4, CO_2, H_2 and CO gases in the outlet gas passing through cell B at 800 °C while operated at 1.1 V/cm. The composition of the outlet gas was nearly independent of the reaction time and the 50 vol% CH_4−50vol% CO_2 mixed gas was converted to 36% CH_4, 29% CO_2, 14% H_2 and 21% CO at 800 °C. The reforming efficiency was lower for cell B with a Cu cathode than for cell A with a Ni cathode. After running the reforming experiment at 800 °C for 1.5 h, no carbon-related phase was formed in either of the electrodes with Cu catalyst. After the experiment at 800 °C, GDC and Cu were identified in the cathode and anode, respectively, by their X-ray diffraction patterns and no Cu_2O phase or no carbon-related phase was recognized.

Fig. 4(b) shows the time dependence of the flow rate of outlet gas and the current density during the reforming of CH_4-CO_2 mixed gas. The current density was 350−450 mA/cm^2 and significantly smaller than that measured in cell A at 800 °C, suggesting few electronic conduction paths were formed between the two electrodes. However, the flow rate dropped to 0 ml/min within 1.5 h of reaction time at 800 °C. The electrochemical reactions at both electrodes (Fig. 1) are related to each other because of the mass balance of atoms and electrons at both electrodes. As a result, the yield of H_2-CO fuel is controlled by the performance of the electrode with the lowest reactivity. Since both cells A and B contain Cu in their anodes, the difference of results in Figs. 2(a) and 4(a) comes from the reactivity of CO_2 at their cathodes. Low affinity of metal to O atoms inhibits the adsorption of CO_2 over the metal surface and decreases the reactivity of CO_2 and electrons (Eqs. (5) and (6)). The standard Gibbs free energy for the oxidation of Ni ($Ni+1/2O_2 \rightleftharpoons NiO$ (13), ΔG° (1073 K) = −138.3 kJ/mol Ni [18]) is lower than that for the oxidation of Cu ($2Cu+1/2O_2 \rightarrow Cu_2O$ (14), ΔG° (1073 K) = −88.2 kJ/mol Cu [18]), suggesting a high reactivity between Ni and CO_2.

3.2.3. Cell C (Ru−GDC cathode/porous GDC electrolyte/Cu−GDC anode)

Fig. 5(a) shows the fractions of CH_4, CO_2, H_2 and CO gases in the outlet gas passing through cell C while operated at 1.1 V/cm. This cell was more effective than cell B and the supplied 50% CH_4−50% CO_2 gas was

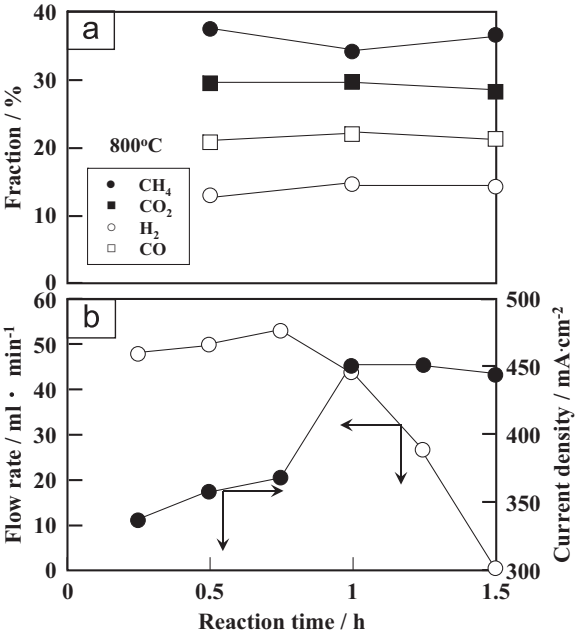


Fig. 4. (a) Fractions of CH_4, CO_2, H_2 and CO gases passing through electrochemical cell B and (b) flow rate of outlet gas and current density at 1.1 V/cm. See Table 1 for cell B.

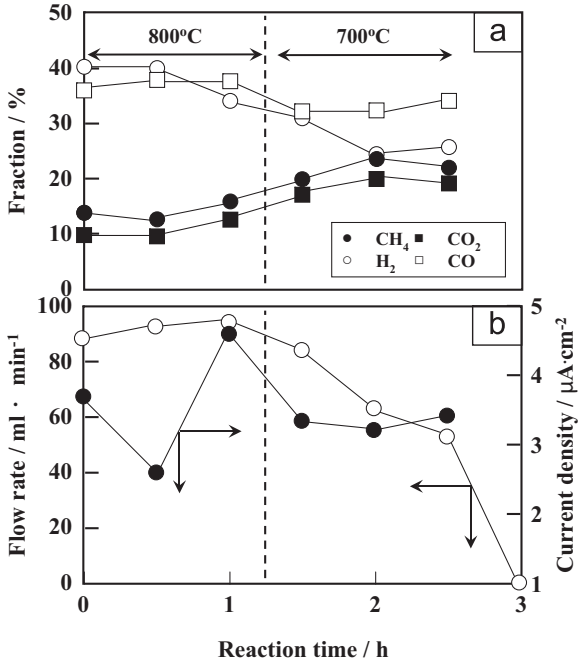


Fig. 5. (a) Fractions of CH_4, CO_2, H_2 and CO gases passing through electrochemical cell C and (b) flow rate of outlet gas and current density at 1.1 V/cm. See Table 1 for cell C.

changed to 14% CH_4, 11% CO_2, 38% H_2 and 37% CO at 800 °C. When the reaction temperature was decreased from 800 °C to 700 °C, the fractions of H_2 and CO fuels decreased to 27% and 33%, respectively. After the reaction at 700 °C, GDC and Ru were identified in the cathode by their X-ray diffraction patterns. In the anode, GDC, Cu, and Cu_2O coexisted. The phases of the anode were in accordance with the phases observed in the anode of cell A.

Fig. 5(b) shows the time dependence of the flow rate of outlet gas and the current density during the reforming of CH_4-CO_2 mixed gas. A smooth gas flow was measured for 1 h at 800 °C, but a blockage of outlet gas occurred at 700 °C. In addition, the current density at 700–800 °C was very low (Fig. 5(b)), suggesting few electronic conduction paths were formed between the two electrodes. A possible reason for the flow rate drop at 700 °C is the formation of Cu_2O in the anode due to a reaction between Cu and O^{2-} ions transported from the cathode. The oxidation of Cu is accompanied by an increase in volume because of the different densities of Cu (8.96 g/cm^3 [19]) and Cu_2O (6.04 g/cm^3 [20]), and suppression of the transportation of the inlet gas. The significantly low current density may be associated with the high electrical resistance of Cu_2O formed on Cu particles. The gas flow rate drop at 700 °C may be related to the lower reactivity between the transported Cu_2O and CH_4 (Eq. (10)), which stabilizes the formation of Cu_2O and reduces the oxidation rate of CH_4 with O^{2-} ions over a Cu catalyst (Eqs. (9) and (10)). Sintering of Cu in the anode may also be responsible for the blockage of gas flow.

3.2.4. Cu–GDC catalyst

Fig. 6(a) shows the fractions of CH_4, CO_2, H_2 and CO gases passing through the Cu–GDC catalyst and (b) the flow rate of outlet gas at 400–900 °C. No external current was supplied to the cermet catalyst. This catalyst worked to convert the 50vol% CH_4–50 vol% CO_2 gas to 20% CH_4, 10% CO_2, 35% H_2 and 35% CO at 900 °C. When compared to the results in Figs. 2 and 5, it was found that supplying a small amount of electrons with an external circuit greatly enhances the reactivity between CO_2 and CH_4. After the experiment at 900 °C, GDC and Cu were identified by their X-ray diffraction patterns and no Cu_2O phase and no carbon-related phase were recognized. A possible mechanism for the reforming of CH_4 with CO_2 over a Cu catalyst is (1) adsorption CO_2 molecules on the surfaces of a Cu catalyst to form

$$Cu_2O\ (2Cu + CO_2 \rightarrow Cu_2O + CO) \quad (15)$$

then (2) adsorption of CH_4 over Cu_2O and (3) interaction between Cu_2O and CH_4 molecules to form CO and H_2 fuels

$$Cu_2O + CH_4 \rightarrow 2Cu + 2H_2 + CO. \quad (10')$$

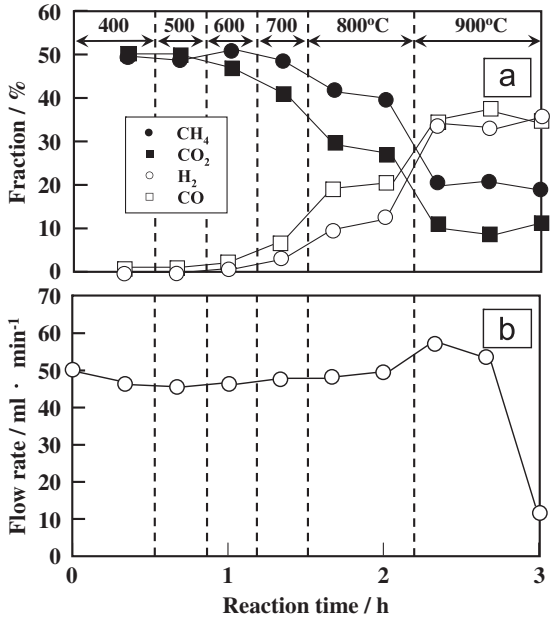


Fig. 6. (a) Fractions of CH_4, CO_2, H_2 and CO gases passing through Cu–GDC catalyst without external current and (b) flow rate of outlet gas.

The reduction of CO_2 at the cathode and oxidation of CH_4 at the anode (Fig. 1) proceeded over the Cu–GDC cermet catalyst. As discussed in Section 3.2.2, the weak interaction between CO_2 and Cu resulted in a low reforming efficiency in the temperature range of 400–800 °C. Fig. 6(b) shows the flow rate at 400–900 °C. A smooth flow of outlet gas was measured below 800 °C, but a blockage of gas flow occurred at 900 °C. This result may be closely related to sintering or grain growth of Cu particles in the cermet catalyst, and is discussed in the next section.

3.2.5. Shrinkage of electrodes during heating

As seen in Figs. 2, 4 and 5, a blockage of gas flow was observed at 700–800 °C. To analyze this phenomenon, the phase change and shrinkage of the electrodes during heating in a reduced atmosphere were examined. Figs. 7 and 8 show the X-ray diffraction patterns of (a) NiO–GDC, (b) CuO–GDC and (c) RuO_2–GDC cathodes after reduction with H_2O-containing H_2 gas at 700 °C (Fig. 7) and 800 °C (Fig. 8) for 24 h. NiO and RuO_2 were reduced to Ni and Ru at 700 °C, but CuO was stable at 700 °C. Increasing the heating temperature to 800 °C reduced CuO to Cu in the electrode. The phase change of oxide to metal in the electrode is accompanied by an increase of open porosity due to the elimination of O atoms and a decrease in size of the metal catalyst because of the difference in the density of oxide and metal (for instance, 6.96 g/cm^3 for NiO compared to 8.902 g/cm^3 for Ni [19]). The increased porosity is favorable to the flow of the reformed fuel gas. On the other hand, the decrease of the melting point from CuO (1236 °C [19]) or Cu_2O (1235 °C [19]) to Cu (1083 °C [19]) promotes sintering

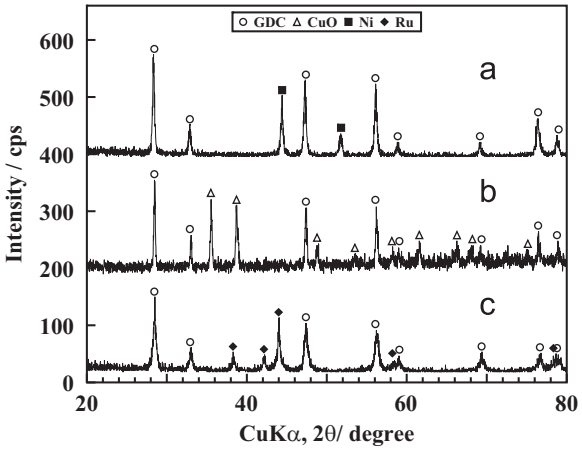


Fig. 7. X-ray diffraction patterns of cathodes composed of NiO–GDC (a), CuO–GDC (b) and RuO_2–GDC (c) after reduction with H_2O-containing H_2 gas at 700 °C for 24 h.

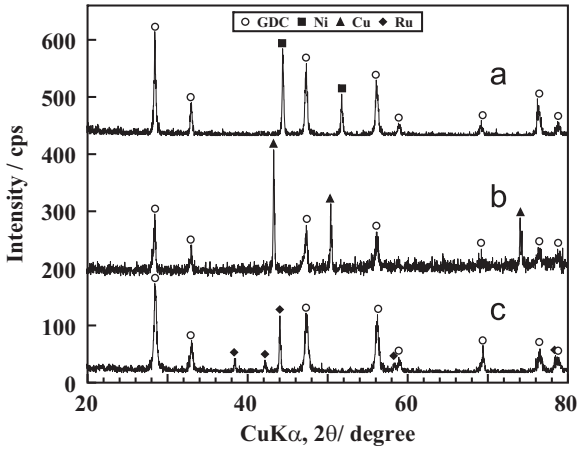


Fig. 8. X-ray diffraction patterns of cathodes of NiO-GDC (a), CuO-GDC (b) and RuO_2-GDC (c) after the reduction with H_2O-containing H_2 gas at 800 °C for 24 h.

during the reforming of CH_4-CO_2 mixed gas at 700–800 °C.

Fig. 9 shows the change in the size of (a) Ni–GDC, (b) CuO–GDC and (c) Ru–GDC compacts at 800 °C in Ar atmosphere, which were treated with H_2O-containing H_2 gas at 700 °C for 24 h before the measurement of the size. These compacts showed a low thermal expansion of 0.02–0.12% after 10 h, indicating that no densification of these compacts occurred at 800 °C. On the other hand, (a) Ni–GDC, (b) Cu–GDC and (c) Ru–GDC compacts treated at 800 °C in the H_2O/H_2 atmosphere exhibited shrinkage of 0.1–0.3% after 10 h in an Ar atmosphere at 800 °C. Although the measured shrinkage was small, it is noted that the lengths of the cathode compacts increased in Fig. 9, but decreased in Fig. 10. This indicates that cermet compacts treated at 800 °C in H_2O/H_2 atmosphere have a tendency to suppress the flow of reforming gas. Fig. 11 shows the microstructures of the cermet electrodes after the measurement of thermal shrinkage after 10 h at 800 °C.

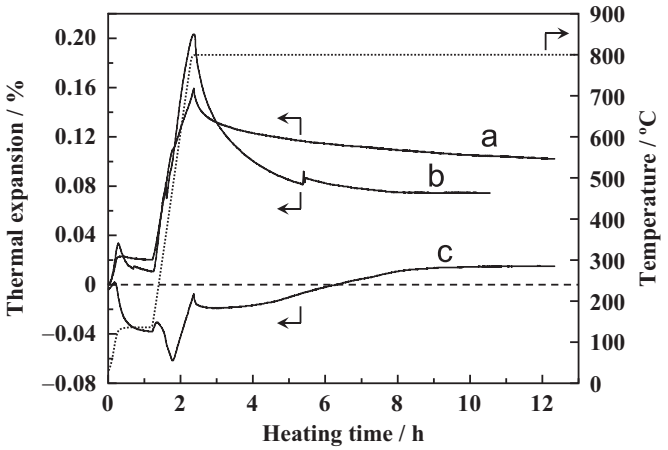


Fig. 9. Change in the size of Ni–GDC (a), CuO–GDC (b) and Ru–GDC (c) compacts at 800 °C in an Ar atmosphere, which were treated with H_2O-containing H_2 gas at 700 °C for 24 h before the measurement of the shrinkage.

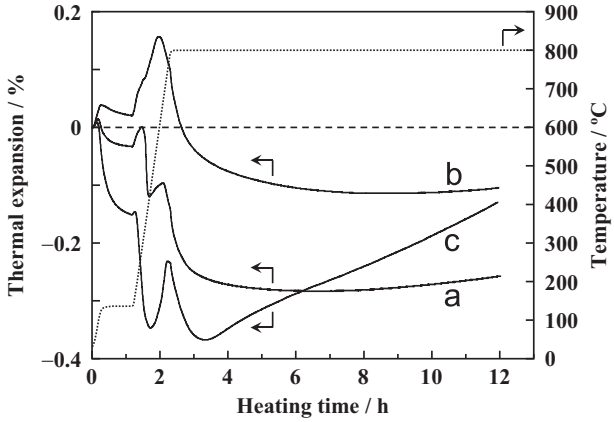


Fig. 10. Change in the size of Ni–GDC (a), Cu–GDC (b) and Ru–GDC (c) compacts at 800 °C in an Ar atmosphere, which were treated with H_2O-containing H_2 gas at 800 °C for 24 h before the measurement of the shrinkage.

No significant change was observed in the porous Ni–GDC (a, d) and Ru–GDC (c, f) compacts, which were treated at 700 °C and 800 °C in the H_2O/H_2 atmosphere. On the other hand, apparent densification and grain growth were observed in the Cu–GDC compact (e) treated at 800 °C in the H_2O/H_2 atmosphere. The Cu–GDC cermet was used as the anode in the cells A, B and C (Table 1). This grain growth and densification of Cu in the Cu–GDC cermet are greatly responsible for the blockage of gas flow measured, shown in Figs. 2(b), 4(b) and 5(b). On the other hand, the results in Figs. 9(b) and 11(b) suggest that the CuO–GDC compact is more thermally stable than the Cu–GDC cermet electrode. Therefore, the decrease in pore size in the cermet cathode due to shrinkage during heating at 800 °C (Fig. 10) and the grain growth and densification of Cu in the anode cermet inhibit the gas flow of reformed fuel.

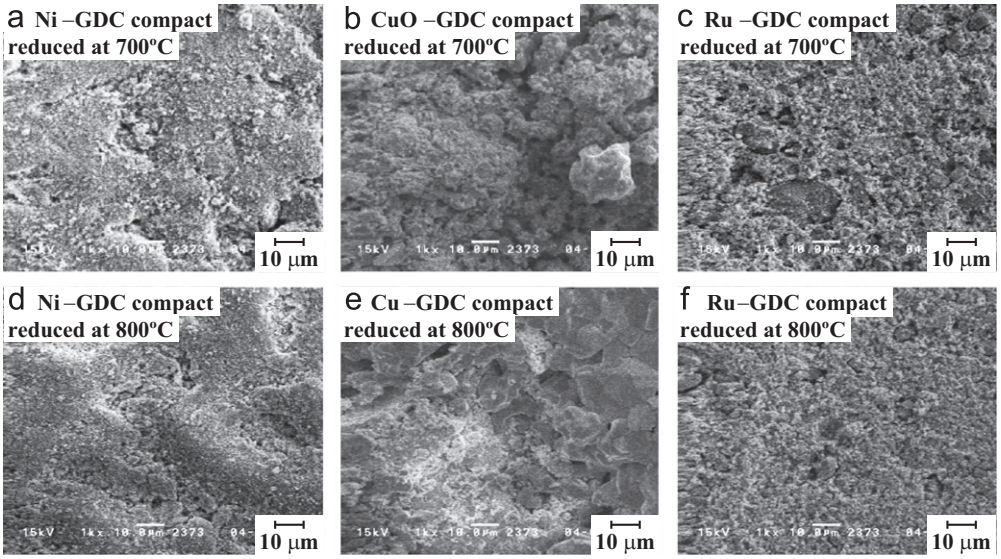


Fig. 11. Microstructure of cermet electrodes after thermal shrinkage measurement in an Ar atmosphere at 800 °C for 10 h. Cermet compacts (a), (b) and (c) were treated with H_2O-containing H_2 gas at 700 °C for 24 h before the thermal shrinkage measurement. Cermet compacts (d), (e) and (f) were treated with H_2O-containing H_2 gas at 800 °C for 24 h.

4. Conclusions

Electrochemical reforming of CH_4 with CO_2 with three types of Gd-doped ceria (GDC) porous cells with Cu in the anode was investigated. When the cathode contained a Ni catalyst (cell A), three parallel cathodic reactions occurred, depending on reaction temperature: reduction of CO_2 ($CO_2+2e^-\rightarrow CO+O^{2-}$), decomposition of CH_4 ($CH_4\rightarrow C+2H_2$) and removal of deposited carbon ($C+O^{2-}\rightarrow CO+2e^-$). Cu or Cu_2O formed in the anode worked well to oxidize CH_4 to form H_2 and CO fuels through a reaction with O^{2-} ions ($2Cu+O^{2-}\rightarrow Cu_2O+2e^-$, $Cu_2O+CH_4\rightarrow 2Cu+2H_2+CO$). The operation of cell A at 800 °C caused a blockage of gas flow because of carbon deposition in the cathode, a volume increase resulting from the phase change of Cu into Cu_2O in the anode, a decrease in pore size in the cermet cathode, and sintering and grain growth of Cu catalyst in the anode. The Cu−GDC cathode/porous GDC electrolyte/Cu−GDC anode cell (cell B) was poor at reforming of CH_4 with CO_2 because of the low affinity between the Cu cathode and CO_2. The Ru−GDC cathode/GDC electrolyte/Cu−GDC anode cell (cell C) showed a relatively high reforming ability, when compared to cell B. However, a blockage of gas flow was measured at 700 °C. This is mainly due to sintering and grain growth of Cu in the anode. The reliability of the gas flow at 700−800 °C was found to be an important issue in the cells with Cu electrodes. In addition, it was clarified that supplying a small amount of electrons with an external circuit enhances the reforming efficiency of CH_4 with CO_2 as compared to a Cu−GDC catalyst with no supply of electrons at a similar reaction temperature.

References

[1] F.Y. Wang, G.B. Jung, A. Su, S.H. Chan, X. Hao, Y.C. Chiang, Porous Ag-$Ce_{0.8}Sm_{0.2}O_{1.9}$ cermets as anode materials for intermediate temperature solid oxide fuel cells using CO fuel, J. Power Sources 185 (2008) 862–866.
[2] T.J. Huang, C.L. Chou, W.J. Chen, M.C. Huang, Coal syngas reactivity over Ni-added LSCF-GDC anode of solid oxide fuel cells, Electrochem. Commun. 11 (2009) 294–297.
[3] I.V. Yentekakis, Open- and closed-circuit study of an intermediate temperature SOFC directly fueled with simulated biogas mixtures, J. Power Sources 160 (2006) 422–425.
[4] G. Goula, V. Kiousis, L. Nalbandian, I.V. Yentekakis, Catalytic and electrocatalytic behavior of Ni-based cermet anodes under internal dry reforming of CH_4+CO_2 mixtures in SOFCs, Solid State Ionics 177 (2006) 2119–2123.
[5] I.V. Yentekakis, T. Papadam, G. Goula, Electricity production from wastewater treatment via a novel biogas-SOFC aided process, Solid State Ionics 179 (2008) 1521–1525.
[6] S. Sameshima, Y. Hirata, J. Sato, N. Matsunaga, Synthesis of hydrogen and carbon monoxide from methane and carbon dioxide over Ni-Al_2O_3 catalyst, J Ceram. Soc. Japan 116 (2008) 374–379.
[7] S. Sameshima, Y. Hirata, K. Hamasaki, H. Ohshige, N. Matsunaga, Synthesis of hydrogen-carbon monoxide fuel from methane-carbon dioxide mixed gases, J. Ceram. Soc. Japan 117 (2009) 630–634.
[8] Y. Hirata, Y. Terasawa, N. Matsunaga, S. Sameshima, Development of electrochemical cell with layered composite of the Gd-doped ceria/electronic conductor system for generation of H_2-CO fuel through oxidation-reduction of CH_4-CO_2 mixed gases, Ceram Inter. 35 (2009) 2023–2028.
[9] S. Matayoshi, Y. Hirata, S. Sameshima, N. Matsunaga, Y. Terasawa, Electrochemical reforming of CH_4-CO_2 gas using porous Gd-doped ceria electrolyte with Ni and Ru electrodes, J. Ceram. Soc. Japan 117 (2009) 1147–1152.
[10] K. Higashi, K. Sonoda, H. Ono, S. Sameshima, Y. Hirata, Synthesis and sintering of rare-earth-doped ceria powder by the oxalate coprecipitation method, J. Mater, Res. 14 (1999) 957–967.
[11] MSDS No. JW140536 of NiO given by Wako Pure Chemical Industries, Ltd., Japan.

[12] MSDS No. JW031479 of CuO given by Wako Pure Chemical Industries, Ltd., Japan.
[13] MSDS No. 238058 of RuO_2 given by Sigma-Aldrich Japan company, Japan.
[14] M. Ando, Y. Hirata, S. Sameshima, N. Matsunaga, Electrochemical reforming of CH_4-CO_2 mixed gas using porous yttria-stabilized zirconia cell, J. Ceram. Soc. Japan 119 (2011) 794–800.
[15] Y. Ibusuki, H. Kunigo, Y. Hirata, S. Sameshima, N. Matsunaga, Processing and performance of solid oxide fuel cell with Gd-doped ceria electrolyte, J. Eur. Ceram. Soc. 31 (2011) 2663–2669.
[16] Metal Data Book, Edited by The Japan Institute of Metals, Maruzen, Tokyo, 1987, pp. 12 – 13.
[17] M. Adachi, H. Shioyama, M. Narisawa, S. Ikeda, K. Tatsumi, I. Souma, H. Isozaki, K. Egawa, H. Kyutoku, T. Tanamura, The temperature dependence of electrical resistivity of polycrystalline graphite in the range of 900 K – 2800 K, Tanso 146 (1991) 33–36.
[18] Electrochemical Handbook, 5th Edition, Edited by The Electrochemical Society of Japan, Maruzen, Tokyo, 2000, p. 32, 38, 48, 54, 55.
[19] Chemical Handbook, Basic Part I, 3rd Edition, Edited by The Chemical Society of Japan, Maruzen, Tokyo, 1984, p. 26, 127.
[20] MSDS No. JW031320 of Cu_2O given by Wako Pure Chemical Industries, Ltd., Japan.