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Formation of hydrogen from the CO–H_2O system using porous Gd-doped ceria electrochemical cell with MnO cathode and Fe_3O_4 anode

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ABSTRACT

This paper reports the outlet gas composition and phase change of electrodes during the CO–H_2O reaction ($CO + H_2O \rightarrow H_2 + CO_2$) using an electrochemical cell with MnO–GDC (Gd-doped ceria: $Ce_{0.8}Gd_{0.2}O_{1.9}$) cathode/porous GDC electrolyte/Fe_3O_4–GDC anode system. In the cathode, oxidation of MnO by H_2O ($3MnO + H_2O \rightarrow Mn_3O_4 + H_2$) and electrochemical reduction of Mn_3O_4 occurred ($Mn_3O_4 + 2e^- \rightarrow 3MnO + O^{2-}$). In the anode, reduction of Fe_3O_4 by CO ($Fe_3O_4 + CO \rightarrow 3FeO + CO_2$) and electrochemical oxidation of FeO occurred ($3FeO + O^{2-} \rightarrow Fe_3O_4 + 2e^-$). H_2 and CO_2 gases were produced through the above catalytic reactions. The fraction of H_2 gas in the outlet gas increased at a high heating temperature and was 30–50% at 700 °C. As a parallel reaction of the CO–H_2O reaction, the supplied CO gas was decomposed to CO_2 and solid carbon over Fe_3O_4 in the anode at low temperatures (disproportion of CO, $2CO \rightarrow CO_2 + C$).

1. Introduction

The decrease in the concentration of CO_2 in atmosphere and the production of a H_2 fuel for fuel cells are two important strategies for the suppression of global warming. In this research group, (a) dry reforming of a biogas (typically 60% CH_4–40% CO_2 composition) to produce a H_2 fuel [1–4], (b) a water-gas shift reaction to produce a H_2 fuel [5] and (c) decomposition of CO gas into solid carbon and oxygen [6,7] have been intensively studied using a porous electrochemical cell. The above reactions are expressed by Eqs. (1)–(3).

$$\text{(reforming)}CH_4 + CO_2 \rightarrow 2H_2 + 2CO \quad (1)$$

$$\text{(shift reaction)}CO + H_2O \rightarrow H_2 + CO_2 \quad (2)$$

$$\text{(decomposition)}2CO \rightarrow 2C + O_2 \quad (3)$$

Reactions (1) and (2) proceed smoothly in a porous Gd-doped ceria electrolyte cell (GDC) with metal catalyst electrodes. The electrochemical decomposition of CO gas occurs through a porous or dense yttria-stabilized zirconia cell (YSZ) with Ni cathode and Ru anode. The combination of Eqs. (1)–(3) provides an ideal solution for the production of a H_2 fuel and the CO_2 decomposition at a same time, which is expressed by Eq. (4).

$$\text{Biogas}\,(3CH_4 + 2CO_2) + CO_2\text{(circulated)} + H_2O$$
$$\rightarrow 7H_2 + CO_2\,\text{(circulated)} + 5C + 5/2O_2 \quad (4)$$

Since the true biogas is enriched in CH_4 than Eq. (1), the CO_2 required in Eq. (4) is supplied from the shift reaction by Eq. (2). The CO_2 produced in Eq. (2) is circulated in Eq. (4). The excess CO gas produced in Eq. (1) is decomposed by Eq. (3). The reaction system in Eq. (4) can be also applied to a natural gas enriched with CH_4 (>90 vol%). Eq. (5) shows the combined chemical reaction for 100% CH_4 gas.

$$\text{Natural gas}\,(CH_4) + H_2O + CO_2\,\text{(circulated)}$$
$$\rightarrow 3H_2 + CO_2\,\text{(circulated)} + C + 1/2O_2 \quad (5)$$

Fig. 1 shows an electrochemical cell for the shift reaction of CO with H_2O. H_2O vapor in the cathode reacts with the supplied electrons to form H_2 and O^{2-} ions through the catalytic reactions of metals by Eqs. (7) and (8) in Fig. 1. The formed O^{2-} ions and CO gas

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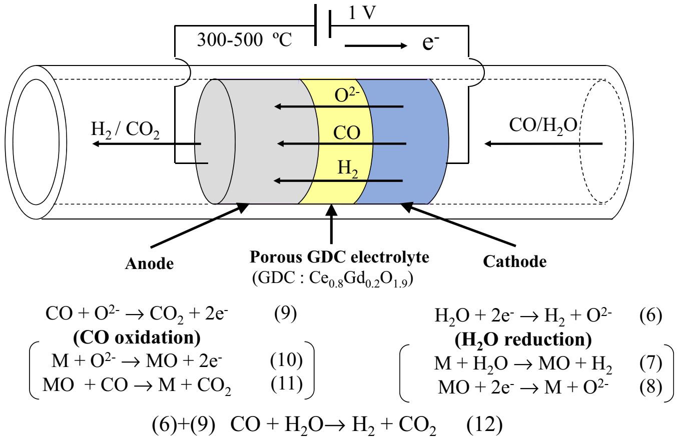

Fig. 1. Electrochemical cell for the reaction of CO with H_2O.

are transported to the anode through a porous GDC layer. In the anode, CO gas reacts with O^{2-} ions to produce CO_2 and electrons through catalytic reactions by Eqs. (10) and (11). The combination of Eqs. (6) and (9) yields the shift reaction by Eq. (12). The CO_2 gas separated from a H_2 fuel is mixed again with CH_4-rich biogas or natural gas (Eqs. (4) and (5)). Recently we have reported that a porous cell of Co–GDC (cathode)/porous GDC (electrolyte)/Fe–GDC (anode) system worked well to produce a H_2-enriched mixed gas of 15% CO–45% H_2–40% CO_2 at 400 °C [5]. Co metal and Fe ions in Fe_3O_4 accelerated the oxidation–reduction reactions in each electrode. Our next challenge is to examine the catalytic shift reaction with an abundant element except for Co metal (25 ppm in igneous rock). A candidate element is Mn (950 ppm in igneous rock) and its valence changes in the wide range of −3 to +7. In this paper, MnO was used in the cathode for the electrochemical shift reaction at 300–700 °C and the outlet gas composition was compared with the result measured in the cathode with Co metal.

2. Experimental procedure

2.1. Preparation of electrochemical cell

Table 1 shows the components of the electrochemical cell used. The electrode of the cell was designed to contain 30 vol% metal (Mn, Fe) and 70 vol% GDC. The detailed preparation method for the metal–GDC composite powder and the fabrication method of the layered electrochemical cell were reported in our previous papers [1–5]. 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 1000 °C for 1 h in air. The GDC powder was milled with 3-mm diameter alumina balls for 24 h. The milled GDC powder was immersed into a 0.4 M $MnSO_4$ solution to make MnO–GDC electrode. The suspension was stirred for 24 h and then freeze-dried. The freeze-dried powder was then heated at 1000 °C for 1 h in air. Fe_2O_3–GDC electrode was fabricated by mixing the milled GDC powder and Fe_2O_3 powder prepared by the pyrolysis of $Fe(NO_3)_3$ at 900 °C for 2 h in air. The 10-mm-diameter and 1-mm-thick porous GDC powder disk was sandwiched between a cathode powder layer (5 mm thick) and an anode powder layer (5 mm thick) and pressed uniaxially at 80 MPa, followed by isostatic pressing at 190 MPa, and then heated at 900 °C for 2 h in air. The phases of the heated electrochemical cells 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.

Table 1
Components of electrochemical cell used.

Cathode (thickness, open porosity)	Electrolyte (thickness, open porosity)	Anode (thickness, open porosity)
MnO–GDC (5 mm, 42%)	GDC (1 mm, 38%)	Fe_2O_3–GDC (5 mm, 36%)

2.2. Electrochemical shift reaction of CO with H_2O

Fig. 1 shows the diagram of the electrochemical reaction apparatus for shift reaction of CO with H_2O. 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 900 °C for 10 min. After cooling to 800 °C, a 47% H_2–3% H_2O–50% Ar mixed gas was fed into both the electrodes at 100 ml/min for 24 h to reduce the oxides ($Mn_3O_4 + H_2 \rightarrow 3MnO + H_2O$, $Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O$). Then, 1 V of external voltage was applied with a potentiostat (HA-501G, Hokuto Denko Co., Japan). The 10 vol% CO–90 vol% Ar gas was fed into the cathode at 60 ml/min and mixed with liquid H_2O supplied at 2.9 ml/h at the molar ratio of $CO/H_2O = 1/7.35$. The composition of the outlet gas was analyzed by gas chromatography (GC 7100T, J-Science Lab Co. Ltd., Japan) with active carbon (60/80 mesh) and a thermal conductivity detector at 100 °C. After the measurement of gas fraction at a constant temperature, the applied voltage was switched off and the supplied gases were substituted for an Ar gas. After the heating temperature reached the next reaction temperature, CO gas and H_2O vapor were supplied again and the applied voltage was switched on. Elementary distribution of C, O, Ce, Gd, and Fe of cross section of the porous GDC cell after the shift reaction was measured by electron probe microanalyzer (EPMA, JXA-8230, JEOL Ltd., Japan).

3. Results and discussion

3.1. Shift reaction

Fig. 2 shows the fraction of outlet gas through the porous GDC electrochemical cell with MnO–GDC cathode and Fe_3O_4–GDC anode at 300–700 °C where the inlet gas of $CO/H_2O = 1/7.35$ volume ratio was passed. This cell produced H_2 and CO_2 gases with the H_2/CO_2 volume ratio ≈1 at 600–400 °C. In the experiment at 700 °C, the H_2 content increased but was higher than the CO_2 content. This result is explained in the latter part. Fig. 3 shows the X-ray diffraction patterns of cathode (a) after the H_2 reduction and (b) after the shift reaction at 300 °C (Fig. 2). As produced Mn_3O_4 in the

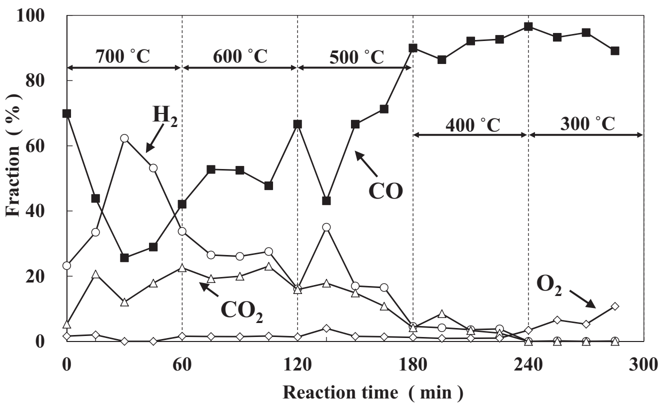

Fig. 2. Fraction of outlet gas through the porous GDC electrochemical cell at 300–700 °C where the inlet gas of $CO/H_2O = 1/7.35$ volume ratio was passed.