Reforming of biogas through oxide ion conductive porous cell: effects of pulsed current method and mixing of air with biogas

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The electrochemical cell consisting of a gadolinium-doped ceria porous electrolyte (GDC, Ce₀.₉₋₀.₁O₁.₉₅), Ni (20 and 30 vol %)–GDC bilayer cathode and Ru (20 and 30 vol %)–GDC bilayer anode was used for the dry-reforming of a real biogas with CO₂ or air using pulsed current (0.1, 1, 10, 100 Hz) under the applied voltage of 0.5 V. The composition of the supplied gas was adjusted to CH₄/CO₂ = 1/1 volume ratio in the dry-reforming with CO₂ at 800°C (CH₄ + CO₂ → 2H₂ + 2CO). The conversion ratios of the supplied CH₄ and CO₂ were 60.8–80.6 and 71.8–85.9%, respectively. The outlet gas contained 8.9–29.6 vol % H₂ gas. The increase in the frequency of the pulsed current decreased the formation rates of H₂ and CO gases. Carbon was deposited on the cathode by the disproportionation reaction of CO gas and the thermal decomposition of CH₄. When air was mixed with the biogas, stable reforming to produce H₂ and CO gases proceeded for 24 h at 700–800°C using pulsed current. The formation rates of H₂ and CO gases were independent of the frequency of the pulsed current. The oxygen gas of air reacted with the carbon deposited on the cathode and removed it as CO gas.

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1. Introduction

Hydrogen gas is a promising clean fuel with no carbon compounds, and has been produced mainly from naphtha through a steam-reforming process [CₙHₙ + mH₂O → (m + n/2) H₂ + m CO], followed by a water–gas shift reaction (mCO + mH₂O → mH₂ + mCO₂). Another attractive way to produce hydrogen from renewable resources have been also reported. A biogas, which is produced from organic matter through the anaerobic digestion, contains about 60% methane (CH₄) and 40% carbon dioxide (CO₂). The biogas can be converted to a hydrogen-rich H₂–CO syngas via the following catalytic reforming processes: dry-reforming (DR, CH₄ + CO₂ → 2H₂ + 2CO), steam-reforming (SR, CH₄ + H₂O → 3H₂ + CO), catalytic partial oxidation (PO, CH₄ + 0.5O₂ → 2H₂ + CO), and auto thermal reforming (ATR, combination of SR and PO, 2CH₄ + H₂O + 0.5 O₂ → 5H₂ + 2CO). A serious problem during the dry-reforming of a biogas is coke formation by dissociation of methane (CH₄ → C + 2H₂) and disproportionation reaction (2CO → C + CO₂). Carbon deposition causes the deactivation of catalyst used and blocks off a reactor. Recent studies on the dry-reforming of CH₄ with CO₂ focus on the development of new catalysts with high coking resistance and stable catalytic performance. Group VIII B metals, like Co, Pt, Ru, Rh etc., possess high catalytic activity in the dry-reforming of CH₄. Zagaynov et al. investigated the catalytic performance of Ni–Co– and Ni–Co– (Ni/Co = 1/1 mol) Gd₀.₁Ti₀.₁Zr₀.₁–Ce₀.₉ mesoporous materials in partial oxidation and dry-reforming of methane into syngas in the temperature range of 840–980°C. Co– and Ni–Co– containing systems were more active in partial oxidation of methane than Ni-containing sample, whereas Ni-containing system was more active in dry-reforming of methane.

Our previous studies applied the electrochemical cells with porous oxide ion conductors (e.g. Ni–GDC cathode/porous GDC electrolyte/Ru–GDC anode, GDC: Ce₀.₉–Gd₀.₁O₁.₉₃) in the reforming of a biogas at 400–800°C. Figure 1(a) shows the scheme of the porous electrochemical cell. In the direct current method, CO₂ gas of a sup-

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plied biogas reacts with electrons ($\text{CO}_2 + 2e^- \rightarrow \text{CO} + \text{O}^2-$) to form CO gas and $\text{O}^2-$ ions at the cathode. This $\text{CO}_2$–electrons interaction is divided into two reactions of Eqs. (1) and (2) in Fig. 1(b). On the other hand, CH$_4$ gas of a supplied biogas reacts with $\text{O}^2-$ ions at the anode ($\text{CH}_4 + \text{O}^2- \rightarrow 2\text{H}_2 + \text{CO} + 2e^-$) to form $\text{H}_2$ gas, CO gas and electrons. The anodic reaction is divided into two reactions of Eqs. (3) and (4) in Fig. 1(b). The total reaction in the cell is the dry-reforming reaction of CH$_4$ with CO$_2$: CH$_4$ + CO$_2$ → 2H$_2$ + 2CO. Ni in the cathode and Ru in the anode act as catalysts as presented in Fig. 1(b) and are refreshed by the supplied electrons and CH$_4$ gas, respectively. Yabe et al. also reported the dry-reforming reaction of CH$_4$ with CO$_2$: CH$_4$ + CO$_2$ → 2H$_2$ + 2CO. Ni in the cathode and Ru in the anode act as catalysts as presented in Fig. 1(b) and are refreshed by the supplied electrons and CH$_4$ gas, respectively. Qiny et al. demonstrated the direct electrochemical biogas reforming using iron loaded LSTO($\text{La}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$)–SDC–(Ce$_0.8\text{Sm}_{0.2}\text{O}_3$)–SDC anode/YSZ solid oxide electrolyser/LSM($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$)–SDC cathode at 800°C under an applied voltage of 0–1.6 V. The conversion rates of CO$_2$ and CH$_4$ increased with increasing applied voltage for 1.5 h. Labrecque et al. reported on the dry-reforming of methane with CO$_2$ in an electron-activated iron catalytic bed at 700–900°C. The electron flow (e.g., 100 A at 2.90 V) was supplied to heat the iron catalyst (50 g of steel wool) and provided a significant effect on the conversion of both methane and carbon dioxide. The effect of pressurization on dry-reforming of a biogas using kilohertz spark-discharge plasma was reported by Zin et al. The elevating the pressure from 0.1 to 0.2 MPa improved the CO$_2$ conversion rate and reduced the energy cost for conversion of CO$_2$. In this paper, the porous electrochemical cell using pulsed current in the frequency range from 0.1 to 100 Hz was applied for the dry-reforming of a real biogas to produce a $\text{H}_2$ fuel. A similar analytical method using an impedance spectrum of a wide alternative frequency range is applied to the cathodic or anodic reaction during the operation of a solid oxide fuel cell.

Fig. 1. (a) Scheme of the electrochemical cell, (b) outline of the pulsed current method and (c) standard Gibbs free energy change of the reactions in Fig. 1(b).
which may limit the numbers of oxide ions transported in Eqs. (2) and (3). Therefore, the application of external pulsed current affects the formation of H₂ and CO gases via oxide ions [Eqs. (2) and (3)]. On the other hand, the metal (M) of cathode or anode may work as a catalyst without electric current for the dry-reforming of a biogas expressed by Eqs. (6) and (7).

\[
\begin{align*}
M + CO_2 & \rightarrow MO + CO \quad (6) \\
MO + CH_4 & \rightarrow CO + 2H_2 + M \quad (7)
\end{align*}
\]

The ratio of the amounts of H₂ gas between the electrochemical formation [Eqs. (1)–(4)] and total reaction [thermodynamic reaction [Eqs. (6) and (7)] plus electrochemical reaction] is discussed in sections 3.1.2 and 3.1.3. In our previous research with a direct current method in the electrochemical dry-reforming of a biogas at 400–800°C, the formation rate of a H₂–CO fuel increased at a higher heating temperature. That is, the H₂ formation by the thermodynamic reaction was promoted by the increase in heating temperature. The pulsed current method is convenient to control the formation of a H₂–CO fuel by the electrochemical dry-reforming and thermodynamic dry-reforming through the on/off time ratio in Fig. 1(b).

In this paper, the on/off time ratio was set to be unity and the applied frequency was changed as a first step of the pulsed current dry-reforming of a biogas at 700–800°C. When the dry-reforming of a biogas proceeds successfully with a pulsed current, the electric power in the dry-reforming may be reduced as compared with a direct current method. Furthermore, oxygen gas of air was also mixed with a real biogas in this paper to produce a H₂ fuel and to eliminate carbon deposited during the reforming as CO gas. The supply of air was effective to keep the stable dry-reforming of CH₄ without carbon deposition. The purposes of this paper are (1) to examine the pulsed current method for the dry-reforming of a biogas and (2) to investigate the mixing effect of air with a biogas on the stable operation of the pulsed current reforming of a biogas.

2. Experimental procedure

2.1 Fabrication of electrochemical cell

An oxide ion conductive porous cell consisted of a gadolinium-doped ceria porous electrolyte (GDC, Ce₀.₉–Gd₀.₁O₁.₉₅), Ni–GDC cathode and Ru–GDC anode. The preparation methods of GDC powder, Ni–GDC powder and Ru–GDC powder were reported in our previous papers. In this study, bilayer electrodes were laminated to prevent the exfoliation between the electrolyte and the electrodes during co-sintering at 1200°C. The cathode and anode were composed of 20 vol% Ni–GDC/30 vol% Ni–GDC bilayer and 20 vol% Ru–GDC/30 vol% Ru–GDC bilayer, respectively. The GDC powder was prepared by a co-precipitation method of the mixed aqueous solution of 0.2 M-Ce(NO₃)₃, 0.2 M-Gd(NO₃)₃ and 0.4 M-oxalic acid. The formed oxalic solid solution was calcined at 600°C in air and was ball-milled with 3 mm diameter-alumina balls for 24 h. The milled GDC powder was mixed at 25 vol% solid with a non-aqueous solution of 33 vol% toluene–67 vol% isopropanol. Polyethylene glycol of 9 mass% and polyvinylbutyral of 5 mass% against the mass of GDC powder were added as a binder and as a plasticizer, respectively. The non-aqueous suspension was casted by a doctor blade apparatus with the front blade clearance of 170 μm to form an electrolyte film with about 80 μm thickness.

In the preparation of Ni–GDC cathode, the GDC powder was mixed with a 0.4 M-Ni(NO₃)₂ aqueous solution at the volume ratios of GDC/Ni = 70/30 and 80/20. The obtained suspensions were freeze-dried and then calcined at 600°C in air for 1 h to form the NiO–GDC mixed powders. On the other hand, in the preparation of Ru–GDC anode, the GDC powder and RuCl₃ solution were mixed at the volume ratios of GDC/Ru = 70/30 and 80/20 in air for 1 h to form the RuO₂–GDC mixed powders. The phases of the NiO–GDC powders and the RuO₂–GDC powders were identified by X-ray diffraction. The layers of GDC electrolyte (80 μm thick) and RuO₂–GDC (2 mm thick) cathode/GDC electrolyte (80 μm thick) were obtained by X-ray diffraction. The layers of GDC (2 mm thick) were laminated in a stainless mold of 10 mm diameter, and compressed uniaxially at 100 MPa for 1 min. The obtained five-layered compact was co-sintered at 1200°C for 2 h in air. The diameters of the sintered cathode and anode were about 7.8 and 9.10 mm, respectively. The thickness of the sintered cathode and anode was about 4 and 3 mm, respectively. Figure 2 shows the microstructures of the co-sintered cathode and anode. The relative density, open porosity and closed porosity were presented in Fig. 2. The relative density of Ni–GDC cathode was higher than that of Ru–GDC anode. The higher content of GDC in the electrode gave the higher sinterability. The sintering of the bilayer electrodes relieved the strain accompanied by the difference in shrinkage.

2.2 Electrochemical reforming of a real biogas

Each surface of the electrodes was attached to a Pt mesh connected to a Pt lead wire using Pt paste. The diameter and area of both the Pt current collectors were 5 mm and 0.196 cm², respectively. The electrochemical cell was set in an alumina holder using a glass powder at 1000°C in air. Then the alumina holder was sandwiched between upper and lower silica-alumina tubes. The spaces between the cell and the holder, and between the holder and the tubes were sealed with a glass powder and a glass ring, respectively, by heating at 870°C in air. NiO and RuO₂ in the electrodes were reduced to Ni and Ru metals, respectively, in a H₂–3 vol% H₂O atmosphere at 800°C for 12 h (H₂ + NiO → Ni + H₂O, 2H₂ + RuO₂ → Ru + 2H₂O). The oxygen partial pressure in the H₂–O₂–H₂O system is calculated from the equilibrium constant for the reaction of H₂O ⇌ H₂ + 0.5O₂ with 4.3 × 10⁻¹⁰ Pa at 800°C. Then the supplied H₂–H₂O gas was purged by an Ar gas for 2 h.
and the electrochemical reforming of a biogas was carried out at 800°C.\(^{11}\)

Table 1 shows the compositions of the biogases used, which were produced by CH\(_4\) fermentation of waste barley or sweet potato in Kagoshima, Japan (Sei-Satsu Clean Sunset Cooperative Association, Ichiki-Kushikino, Kagoshima 896-0046, Japan). The total concentrations of CH\(_4\) and CO\(_2\) were 93.3–97.5 vol\%.

\[^{21}\]N\(_2\) gas of 2.5–5.7\% was also included. The concentration of H\(_2\)S gas, which may react with the electrodes,\(^{21}\) was significantly low (1.1–2.1 ppm). Cyclosiloxane was hardly included in biogas No. 1. A high purity CO\(_2\) gas (purity >99.99\%) was mixed to the biogas to adjust the volume ratio of CH\(_4\)/CO\(_2\) = 1/1 for the stoichiometric chemical reaction (CH\(_4\) + CO\(_2\) → 2H\(_2\) + 2CO). The flow rates of biogas No. 1 and CO\(_2\) gas were 40 and 10 ml/min, respectively. In the dry-reforming of biogas No. 2 with air, the biogas of 40 ml/min was mixed with air of 10–50 ml/min to adjust the volume ratios of CH\(_4\)/CO\(_2\)/O\(_2\) = 3/2.034/(0.320–1.451). The direct and pulsed current (0.1, 1.0, 10, 100 Hz) was flowed to the cell at 0.5 V of applied voltage by a function generator (WF 1973, NF Kairosekkei Block Corp., Japan). The ratio of on/off time was unity, which saved 50\% of the reforming energy as compared with the case in the direct current reforming. The current flowing through the cell was measured by high speed data acquisition (SL-1000, Yokogawa Electric Co., Japan). The composition of the outlet gas after elimination of H\(_2\)O gas by ice-water trap was measured by a gas chromatograph equipped with a thermal conductivity detector (GC7100T, J-Science Lab Co. Ltd., Japan).

The temperatures of the injection, column and detector were 120, 70 and 100°C, respectively. The flow rate of the outlet gas was measured by a flow meter (Soapfilm Flow Meter, 3001-11002, GL Science Inc., Japan). The phases of the cell after the dry-reforming experiment were identified with an X-ray diffraction equipment (RINT2200 PCH/KG, Rigaku Co., Japan). The carbon deposition in the cell was analyzed with an electron-probe microanalyzer (EPMA, JXA-8230, JEOL Ltd., Japan).

3. Results and discussion

3.1 Electrochemical reforming of biogas with CO\(_2\) using pulsed current

3.1.1 Analysis of gas composition

Figure 3 shows (a) the flow rate of the outlet gas and (b) gas composition during the dry-reforming of a real biogas No. 1 with CO\(_2\) gas (CH\(_4\)/CO\(_2\) = 1/1 volume ratio) at 800°C. In the initial dry-reforming using DC current, the flow rates of H\(_2\) and CO gases were 6.4–7.3 and 7.7–8.1 ml/min, respectively. The flow rates of CH\(_4\), CO\(_2\), H\(_2\) and

![Table 1. Compositions of the biogases used](image)

![Fig. 2. Microstructures of (a) 20 vol% Ni–GDC cathode, (b) 30 vol% Ni–GDC cathode, (c) 20 vol% Ru–GDC anode and (d) 30 vol% Ru–GDC anode, sintered at 1200°C in air. RD: relative density, OP: open porosity, CP: closed porosity.](image)
CO gases slightly increased at 0.1 Hz of pulsed current. However, the flow rates of H2 and CO gases decreased gradually at a higher frequency pulsed current or a longer reforming time. After the experiment at 100 Hz of pulsed current, DC current was again flowed through the cell but no significant recovery of the flow rates of H2 and CO gases was measured. The conversion rate (CR) of CH4 or CO2 gas was calculated from the difference in the inlet and outlet gas flow rates by Eq. (8).

\[
\text{CR (\%)} = \frac{\text{inlet gas flow rate} - \text{outlet gas flow rate}}{\text{inlet gas flow rate}}
\]

The CR values in Fig. 3(a) were 80.6–60.8% for CH4 gas and 85.9–71.8% for CO2 gas, respectively, and decreased at a longer reforming time.

Figure 3(b) shows the gas composition of the outlet gas during the dry-reforming of biogas No. 1 with CO2 gas at 800°C. The initial compositions of H2 and CO gases were 29.6 and 32.9%, respectively. Theses compositions decreased gradually to 8.9 and 17.4%, respectively, after the dry-reforming for 12 h. The H2/CO volume ratio was in the range of 0.899–0.511, and decreased gradually at a longer reforming time. The result measured in Fig. 3 is discussed in a later part of this section.

Figure 4 plots the relationship between the pulsed frequency and the gas composition of the outlet gas at 800°C. The error bars indicate the change of gas compositions of H2, CO, CH4 and CO2 gases within 2 h. Figure 4 shows two factors of applied frequency and reforming time for the compositions of the outlet gases. As seen in Fig. 4, the gas compositions depend greatly on the applied frequency rather than the reforming time at a given pulsed frequency. The increased frequency of pulsed current reduced the formation rates of H2 and CO gases. This result may be related to the slower electrochemical reaction rate as compared with the supplied rate of electrons in the electrodes, because the higher frequency of pulsed current shortens the supplied time of electrons.

3.1.2 Current density during electrochemical reforming

The current density during the dry-reforming shown in Fig. 5(a) was almost constant (0.853–0.910 A/cm²) for 0–8 h (DC ~ 10 Hz) but decreased gradually for 8–10 h at 100 Hz of pulsed current (0.883–0.554 A/cm²). In the dry-reforming for 10–12 h at DC current, the current density was significantly small (0.554–0 A/cm²). After the experiment for 12 h in Fig. 5(a), the exfoliation of the cathode
from the electrolyte and carbon deposition on the cathode were observed. This deformation of electrode and carbon deposition may be responsible for the decreased current density. The detail was discussed in section 3.1.4.

The electrochemical dry-reforming is composed of the CO₂ reduction at the cathode (CO₂ + 2e⁻ → CO + O₂⁻) and CH₄ oxidation at the anode (CH₄ + O₂⁻ → 2H₂ + CO + 2e⁻) as shown in Fig. 1(b). Two mole electrons are used to the formations of two mole H₂ molecules and two mole CO molecules. On the other hand, the mole number of electrons (n) passing the electrochemical cell per one second is expressed by Eq. (9),

\[ n = \frac{1}{F} \]  

where I and F are the electric current (A) and Faraday constant, respectively. The n value, which is equal to the mole number of H₂ molecules formed, is converted to the flow rate (V, m³/s) by Eq. (10),

\[ V = \frac{nRT}{P} \]  

where R, T and P are the gas constant [8.314 J/(K·mol)], absolute room temperature (298.15 K) and gas pressure (1.01325 × 10⁵ Pa), respectively. Figure 5(b) shows the ratio of flow rates of H₂ gas between Faraday’s law and the composition of the outlet gas during the dry-reforming.

Figure 6 shows the appearance of the electrochemical cell after the dry-reforming experiment at 800°C. Ru–GDC was lifted up after the experiment. Carbon deposition was observed in the cathode side. The carbon deposited during the dry-reforming reaction pushed up the electrochemical cell in the Al₂O₃ holder and caused the exfoliation between the Ni–GDC cathode and Pt current collector. This change of the cell structure may be responsible for the decreased current density after 10 h of reforming time [Fig. 5(a)].

Figure 7 shows the X-ray diffraction patterns of (a) Ni–GDC cathode and (b) Ru–GDC anode after the dry-reforming experiment in Fig. 3. The carbon deposition (graphite) in the Ni–GDC cathode was confirmed by the X-ray diffraction pattern. However, no graphite peak was observed in the Ru–GDC anode. According to the XRD measurement, deposition of carbon was accelerated in the Ni–GDC cathode and caused the reduced flow rate of outlet gas measured in Fig. 3.

Figure 8 shows the elementary distribution of C, Ni and Ce elements in the cathode. The distribution of Ce element [Fig. 8(d)] overlapped the light gray region of the microstructure [Fig. 8(a)]. The carbon was formed in the region without Ce element. The distribution of carbon deposited in the Ni–GDC cathode overlapped that of Ni element. Ni metal assisted the formation of carbon and the carbon deposited on the GDC particles was eliminated as CO gas by the reaction with oxide ions formed by the electrochemical reaction at the Ni–GDC cathode (CO₂ + Ni → NiO + CO, NiO + 2e⁻ → Ni + O²⁻, C + O²⁻ → CO + 2e⁻).
According to the semi-quantitative analysis of EMPA, the carbon content was 0.42 mass% in the Ru–GDC anode and 6.08–10.52 mass% in the Ni–GDC cathode.

3.1.4 Influence of pulsed current in the reforming of biogas

Figure 9 shows the Gibbs free energy change [$\Delta G$, Eq. (11)] of the dry-reforming reaction [Eq. (5)] at 800°C, calculated using the measured partial pressures of CH$_4$, CO$_2$, H$_2$ and CO of outlet gas.\(^{15}\)

$$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}$$  \hspace{1cm} (5)

$$\Delta G = \Delta G^\circ + RT \ln \frac{p^2(\text{H}_2)p^2(\text{CO})}{p(\text{CH}_4)p(\text{CO}_2)}$$  \hspace{1cm} (11)

The calculated $\Delta G$ values at $E = 0$ V were negative values, supporting the thermodynamic formation of H$_2$ and CO gases. When an external voltage ($E$) is applied to the electrochemical cell, the applied voltage causes the decrease of Gibbs free energy change ($\Delta G$) of the specified chemical reaction by Eq. (12).

$$\Delta G = -nFE$$  \hspace{1cm} (12)

where $n$ is the number of electrons required to complete the electrochemical reaction and $F$ is the Faraday constant ($9.6485 \times 10^4$ C/mol). The application of 0.5 V of external voltage for $n = 2$ mol in Fig. 1(b) causes the decrease of $\Delta G = -96.485$ kJ. As seen in Fig. 9, the $\Delta G$ value under the applied voltage decreases to more negative values, and the reforming reaction becomes easier to occur.

The deposition of carbon on the cathode is caused by the pyrolysis of CH$_4$ ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$) and the dispr-
portionation of CO (2CO → C + CO₂). The pyrolysis of CH₄ over Ni catalyst proceeds thermodynamically at 800°C. The disproportionation of CO gas is accelerated under the applied voltage. At the same time, the application of external voltage assists the elimination of carbon in the cathode as CO gas (C + O₂ → CO + 2e⁻).

3.2 Electrochemical reforming of biogas with air using pulsed current

3.2.1 Analysis of gas composition

Figure 10 shows (a) the flow rate of outlet gas and (b) gas composition during the dry-reforming of biogas No. 2 with air at 700–800°C. The stable flow rates of H₂ and CO gases were measured for 24 h at 700–800°C under the supply of air at 50 ml/min. The applied frequency of pulsed current gave little influence on the flow rates of H₂ and CO gases. The compositions of H₂ and CO gases were 34.5–40.9 and 16.7–20.6%, respectively, at 700–800°C. The H₂/CO volume ratio was 1.90–1.95 and 1.87–2.07 at 800 and 700°C, respectively. The conversion rates of CH₄ and CO₂ were 95.8–98.9 and 87.1–95.7%, respectively, at 700–800°C. When the amount of supplied air decreased from 50 to 0 ml/min at 800°C under the applied voltage of 0.5 V at 1 Hz, the measured H₂/CO volume ratio decreased from 1.9 to 1.4.

Tables 2 and 3 summarize the chemical reactions for electrochemical reforming of biogas No. 2 with air. In the case of (A) in Table 2, CO₂ is only used to oxidize CH₄, resulting in the constant H₂/CO molar ratio (=1) at 0–50 ml/min of the supplied air. In the case of (B), the remaining O₂ gas in the case (A) reacts with CH₄ to form H₂ and CO gas, resulting in the increase in the H₂/CO molar ratio (=1.19). In the case of (C) in Table 3, O₂ gas is only used to oxidize CH₄, resulting in the constant H₂/CO ratio (=2.0) at 10–50 ml/min of the supplied air. In the case of (D) in Table 3, the remaining CO₂ gas in the case (C) reacts with CH₄ to increase the formation rates of H₂ and CO gases, resulting in the increase in the H₂/CO molar ratio at a higher supplied rate of air.

Figure 11 shows the comparison between the measured and calculated values for (a) H₂ fraction, (b) CO fraction, (c) CO₂ fraction and (d) H₂/CO volume ratio as a function of the O₂/(O₂ + CO₂) volume ratio of the supplied gas. The measured tendency of H₂ and CO fractions was almost fitted by the B or D curve. The measured tendency of CO₂ fraction and H₂/CO volume ratio was also close to D curve. These results suggest that the dominant reaction with air proceeds along the D curve of O₂-preferred reactions in Table 3.

3.2.2 Analysis of current density during the dry-reforming with air

Figure 12 shows the current density and the ratio of formation rates of H₂ gas between Faraday’s law and the composition of outlet gas during the dry-reforming with air.
than that with CO2 oxidant shown in Fig. 5(b). As seen in during the dry-reforming shown in Fig. 12(b) was lower ratio of the amount of H2 gas calculated by Faraday Fig. 12(b), the formation of H2 and CO gases at 700°C was signifi-
cation between Fig. 10 with air oxidant and the previous studies with a direct current method, it was found that (1) the dry-reforming of CH4 with CO2 proceeded mainly thermodynamically at 800°C and (2) the ratio of the fraction of H2 gas formed from the electrochemical reforming increased at 700–600°C.11) The different observation between Fig. 10 with air oxidant and the previous experiment with CO2 oxidant reflects the higher reactivity of O2 gas rather than CO2 gas in the electrochemical reforming with electrons at 800°C (O2 + 4e⁻ → 2O2⁻) and in the thermodynamic oxidation with CH4 in the cathode at 700°C (CH4 + 5/2O2 → 2H2 + CO2, Table 1 and Fig. 11). The above mixing effect of air with a biogas decreased the influence of applied pulsed frequency, which was significant in Fig. 4 with CO2 oxidant.

3.2.3 Analysis of electrochemical cell after dry-reforming

The X-ray diffraction patterns of the electrochemical cell after the dry-reforming experiment with air in Fig. 10 showed the coexistence of Ni and GDC in the cathode and the coexistence of Ru and GDC in the anode, suggesting the high catalytic performance of the electrodes under the supply of air with the biogas.

**Table 2.** Possible CO2-selected or CO2-preferred reactions for electrochemical reforming of biogas No. 2 with air

| Air supplied (ml/min) | Chemical reaction | H2 fraction (vol%) | CO fraction (vol%) | H2/CO ratio |
|-----------------------|-------------------|-------------------|-------------------|-------------|
| 0                     | 3CH4 + 2.034CO2 → 4.068H2 + 4.068CO + 0.966CH4 | 43.23 | 43.23 | 1.00 |
| 10                    | 3CH4 + 2.034CO2 + 0.283O2 → 4.068H2 + 4.068CO + 0.283O2 + 0.966CH4 | 37.81 | 37.81 | 1.00 |
| 20                    | 3CH4 + 2.034CO2 + 0.567O2 → 4.068H2 + 4.068CO + 0.567O2 + 0.966CH4 | 33.60 | 33.60 | 1.00 |
| 30                    | 3CH4 + 2.034CO2 + 0.850O2 → 4.068H2 + 4.068CO + 0.850O2 + 0.966CH4 | 30.25 | 30.25 | 1.00 |
| 40                    | 3CH4 + 2.034CO2 + 1.133O2 → 4.068H2 + 4.068CO + 1.133O2 + 0.966CH4 | 27.47 | 27.47 | 1.00 |
| 50                    | 3CH4 + 2.034CO2 + 1.416O2 → 4.068H2 + 4.068CO + 1.416O2 + 0.966CH4 | 25.18 | 25.18 | 1.00 |

**Table 3.** Possible O2-selected or O2-preferred reactions for electrochemical reforming of biogas No. 2 with air

| Air supplied (ml/min) | Chemical reaction | H2 fraction (vol%) | CO fraction (vol%) | H2/CO ratio |
|-----------------------|-------------------|-------------------|-------------------|-------------|
| 0                     | 3CH4 + 2.034CO2 → 3.000CH4 + 2.034CO2 | 0.00 | 0.00 | — |
| 10                    | 3CH4 + 2.034CO2 + 0.283O2 → 1.133H2 + 5.067CO + 2.433CH4 + 2.034CO2 | 15.03 | 7.51 | 2.00 |
| 20                    | 3CH4 + 2.034CO2 + 0.567O2 → 2.266H2 + 1.133CO + 1.867CH4 + 2.034CO2 | 23.27 | 11.63 | 2.00 |
| 30                    | 3CH4 + 2.034CO2 + 0.850O2 → 3.399H2 + 1.708CO + 1.308CH4 + 2.034CO2 | 28.47 | 14.23 | 2.00 |
| 40                    | 3CH4 + 2.034CO2 + 1.133O2 → 4.532H2 + 2.266CO + 0.734CH4 + 2.034CO2 | 32.05 | 16.03 | 2.00 |
| 50                    | 3CH4 + 2.034CO2 + 1.416O2 → 5.656H2 + 2.833CO + 0.168CH4 + 2.034CO2 | 34.67 | 17.34 | 2.00 |

Air. The pulsed current density except for 100 Hz at 800°C was 0.86–0.92 A/m² and was comparable to that with CO2 gas as shown in Fig. 5(a). This result indicates that both the O2 and H2 gases produce oxide ions at cathode. The ratio of the amount of H2 gas calculated by Faraday’s law during the dry-reforming shown in Fig. 12(b) was lower than that with CO2 oxidant shown in Fig. 5(b). As seen in Fig. 12(b), the formation of H2 and CO gases at 700°C proceeded through the thermodynamic reactions. In our previous studies with a direct current method, it was found that (1) the dry-reforming of CH4 with CO2 proceeded mainly thermodynamically at 800°C and (2) the ratio of the fraction of H2 gas formed from the electrochemical reforming increased at 700–600°C.11) The different observation between Fig. 10 with air oxidant and the previous experiment with CO2 oxidant reflects the higher reactivity of O2 gas rather than CO2 gas in the electrochemical reforming with electrons at 800°C (O2 + 4e⁻ → 2O2⁻) and in the thermodynamic oxidation with CH4 in the cathode at 700°C (CH4 + 5/2O2 → 2H2 + CO2, Table 1 and Fig. 11). The above mixing effect of air with a biogas decreased the influence of applied pulsed frequency, which was significant in Fig. 4 with CO2 oxidant.
in Fig. 6, and guarantees the stable long-term formation of H₂ and CO gases.

4. Conclusions

The dry-reforming of a real biogas with CO₂ or air was examined at 700–800°C by pulsed current method (0.1, 1, 10, 100 Hz) using the electrochemical cell, which consisted of a gadolinium-doped ceria (GDC, Ce₀.₉Gd₀.₁O₁.₉₅) porous electrolyte, 20 and 30 vol % Ni–GDC bilayer cathode and 20 and 30 vol % Ru–GDC bilayer anode. In the dry-reforming of a mixed gas of CH₄/CO₂ = 1/1 (volume ratio) at 800°C, the formation rates of H₂ and CO gases decreased at a higher frequency because of the slower reaction rate of the electrochemical reactions as compared with the supplied rate of electrons in the electrodes. The H₂–CO mixed fuel was produced thermodynamically (44–81%) and electrochemically (19–56%) over the metal catalysts in the electrodes, depending on the applied frequency. Carbon was also deposited on the cathode by the

Fig. 11. Comparison between the measured and calculated values for (a) H₂ fraction, (b) CO fraction, (c) CO₂ fraction and (d) H₂/CO volume ratio as a function of the O₂/(O₂ + CO₂) volume ratio of the supplied gas.

Fig. 12. (a) Logarithmic current density and (b) ratio of flow rates of H₂ gas between Faraday’s law and the composition of outlet gas during the dry-reforming with air.

Fig. 13. (a) Microstructure and (b)–(e) elementary distributions of (b) O (K line), (c) C (K line), (d) Ni (K line) and (e) Ce (L line) of 30 vol % Ni–GDC cathode after the dry-reforming with air.
disproportionation reaction of CO and the thermal decomposition of CH₄. The application of external voltage reduced the Gibbs free energy change (ΔG) of CH₄ → CO₂ + 2H₂ + 2CO, giving the more spontaneous dry-reforming reaction. In the electrochemical reforming of a biogas with air, the stable formation of H₂ and CO gases, which was independent of the frequency of pulsed current, proceeded for 24 h at 700–800°C. The reforming of the biogas proceeded thermodynamically and electrochemically. The mixed air worked as an oxidant to produce a H₂–CO fuel and to eliminate carbon as a CO gas, leaving little carbon in the electrodes. The reactivity of the mixed O₂ gas with CH₄ gas was higher than that of CO₂ gas of the biogas. As a result, the influence of applied frequency in the dry-reforming with air became smaller than that in the dry-reforming with CO₂.

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