



Hydrogen formation from a real biogas using electrochemical cell with gadolinium-doped ceria porous electrolyte



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ABSTRACT

The electrochemical cell consisting of a gadolinium-doped ceria (GDC, Ce_{0.9}Gd_{0.1}O_{1.95}) porous electrolyte, Ni–GDC cathode and Ru–GDC anode was applied for the dry-reforming (CH₄+CO₂→2H₂+2CO) of a real biogas (CH₄ 60.0%, CO₂ 37.5%, N₂ 2.5%) produced from waste sweet potato. The composition of the supplied gas was adjusted to CH₄/CO₂=1/1 volume ratio. The supplied gas changed continuously into a H₂–CO mixed fuel with H₂/CO=1/0.949–1/1.312 vol ratios at 800 °C for 24 h under the applied voltage of 1–2 V. The yield of the mixed fuel was higher than 80%. This dry-reforming reaction was thermodynamically controlled at 800 °C. The application of external voltage assisted the reduction of NiO and the elimination of solid carbon deposited slightly in the cathode. The decrease of heating temperature to 700 °C reduced gradually the fraction of the H₂–CO fuel (61.3–18.6%) within 24 h. Because the Gibbs free energy change was calculated to be negative values at 700–600 °C, the above result at 700–600 °C originated from the gradual deposition of carbon over Ni catalyst through the competitive parallel reactions (CH₄→C+2H₂, 2CO→C+CO₂). The application of external voltage decreased the formation temperature of carbon by the disproportionation of CO gas. At 600 °C, the H₂–CO fuel based on the Faraday's law was produced continuously by the electrochemical reforming of the biogas.

1. Introduction

Currently, 90% of industrial hydrogen gas has been produced through a steam-reforming process of naphtha (C_mH_n+mH₂O→(m+n/2)H₂+mCO), followed by a water-gas shift reaction (mCO+mH₂O→mH₂+mCO₂). The reformed gas contains hydrogen and carbon dioxide. To suppress the consumption of fossil fuels and to decrease the concentration of carbon dioxide in atmosphere, renewable energies have been developed to produce an electric power or converted to a hydrogen gas. One possible renewable energy source for the production of hydrogen is a biogas from waste foods or drainage. The dry-reforming of CH₄ gas (~60 vol%) with the included CO₂ gas (~40 vol%) yields a mixed fuel of H₂–CO gas system (CH₄+CO₂→2H₂+2CO), which can be supplied to a solid oxide fuel cell. Many catalysts have been investigated to accelerate the dry-reforming of a biogas [1,2] and to suppress the carbon deposition due to the decomposition of methane (CH₄→C+2H₂) or disproportionation of carbon monoxide (2CO→C+CO₂) [1–3]. Noble metals such as ruthenium or rhodium are reported to possess the above catalytic properties [1], but nickel metal causes the carbon deposition from CH₄ gas [1]. On the other hand, the separation of the formed H₂ gas using a

membrane reactor [4,5] has been studied to shift the reversible reforming reaction to the fuel side or to suppress the consumption of hydrogen gas in the reversible water-gas shift reaction (H₂+CO₂→CO+H₂O). The standard Gibbs free energy changes of the above reactions are calculated using the data base by National Institute of Standards and Technology [6] and are presented in Fig. 1. It is understood that both the dry-reforming reaction (Eq. (a)) and decomposition of methane (Eq. (b)) proceed above 642 °C and the disproportionation of carbon monoxide (Eq. (d)) is suppressed above 700 °C.

To produce a hydrogen gas from a biogas, we have reported the dry-reforming of CH₄ with CO₂ using a porous electrochemical cell with a porous oxide ion electrolyte [7–11]. By applying 1–2 V of external voltage to a gadolinium-doped ceria (GDC) porous electrolyte with Ni–GDC cathode and Ru–GDC anode, the mixed gas of 50 vol% CH₄–50 vol% CO₂ was continuously converted to the H₂–CO mixed fuel at 800 °C for 13 h [7]. Although the flow rate of outlet gas fluctuated in the range from 10 to 80 ml/min, no gas blockage due to the carbon deposition occurred [7]. The conversion ratio of the supplied CH₄–CO₂ gas was higher than 90%. In this porous electrochemical cell, the carbon deposited partially in the cathode is easily removed by reaction with O²⁻ ions (C+O²⁻→CO+2e⁻) [9]. The produced CO and electrons at

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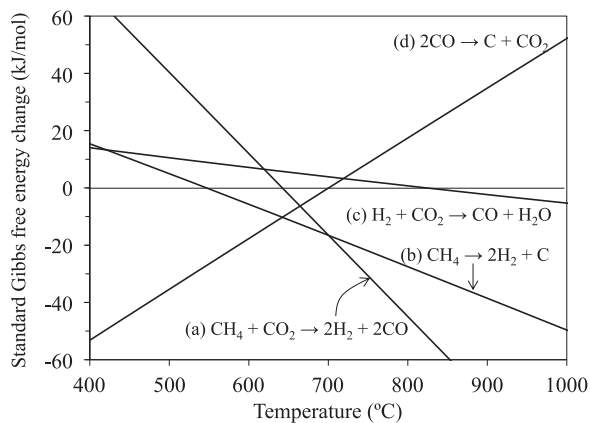


Fig. 1. Standard Gibbs free energy changes of (a) methane dry-reforming reaction and (b–d) possible competitive reactions.

Table 1

Composition of the biogas used in this study.

Analytical method	Gas	Concentration (vol%)
Gas chromatography	CH ₄	60.0
	CO ₂	37.5
	N ₂	2.5
	O ₂	0.1
	H ₂	<0.1
	CO	<0.1
	H ₂ S	2.1ppm(0.00021%)
	NH ₃	< 0.1
Absorptiometric	NH ₃	< 0.1
Gas chromatography–mass spectroscopy	Cyclasiloxane	
	[(CH ₃) ₂ SiO] ₃	<0.001 ppm
	[(CH ₃) ₂ SiO] ₄	<0.001 ppm
	[(CH ₃) ₂ SiO] ₅	0.0027 ppm
	[(CH ₃) ₂ SiO] ₆	<0.001 ppm

the cathode are transported to the anode through the porous GDC electrolyte of a mixed conductor of oxide ions and electrons in the O₂-poor atmosphere. In this paper, the developed electrochemical cell was applied for the dry-reforming of a real biogas to produce a H₂ fuel. Table 1 shows the composition of the biogas produced by CH₄ fermentation using waste sweet potato in Kagoshima, Japan (Sei-Satsu Clean Sunset Cooperative Association, Ichiki-Kushikino, Kagoshima 896-0046, Japan). The biogas contained 60.0% CH₄ and 37.5% CO₂. The included N₂ gas (2.5%) may provide no significant influence on the reforming of the biogas. The small amount of O₂ gas (0.1%) is to be changed to O²⁻ ions at the cathode (O₂+4e⁻→2O²⁻). The formed O²⁻ ions oxidize CH₄ to produce a H₂ gas at the anode (CH₄+O²⁻→CO+2H₂+2e⁻). The concentrations of hydrogen sulfide and cyclasiloxane which degrade the cell performance, were significantly low, and 2.1 ppm and less than 0.0027 ppm, respectively. This paper reports the reforming results of the real biogas at 600–800 °C for 72 h and discusses the potential ability of the developed cell.

2. Experimental procedure

2.1. Fabrication of electrochemical cell

A gadolinium-doped ceria (GDC, Ce_{0.9}Gd_{0.1}O_{1.95}) porous electrolyte, Ni–GDC cathode and Ru–GDC anode were fabricated to make the porous electrochemical cell. The GDC powder was prepared by a coprecipitation method reported in detail elsewhere [12,13]. The aqueous solutions of 0.2 M-Ce(NO₃)₃ and Gd(NO₃)₃ were mixed and then dropped into an 0.4 M oxalic acid to coprecipitate the oxalate solid solution, (Ce_{0.9}Gd_{0.1})₂(C₂O₄)₃. The oxalate solid solution was calcined at 600 °C in air for 1 h to produce the GDC powder. The calcined powder was milled with alumina balls for 24 h to obtain the fine GDC

powder. The obtained GDC powder was dispersed at the solid content of 25 vol% in an organic solution with 67 vol% isopropanol and 33 vol% toluene. Polyvinyl butyral as a binder and polyethylene glycol as a plasticizer were added at 5% and 9%, respectively, against the mass of GDC powder. 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 the thickness of 100 μm. In the fabrication of the Ni–GDC cathode, the GDC powder was mixed with a 0.4 M Ni(NO₃)₂ aqueous solution at the volume ratio of GDC/Ni=70/30. The obtained suspension was freeze-dried and then calcined at 600 °C in air for 1 h to form a NiO–GDC mixed powder. To fabricate the Ru–GDC anode, the GDC powder and RuCl₃ solution were mixed at the volume ratio of GDC/Ru=70/30 at pH 10 with an NH₄OH aqueous solution. The obtained suspension was freeze-dried and then calcined at 800 °C in air for 1 h to form a RuO₂–GDC mixed powder. The GDC electrolyte film, NiO–GDC cathode powder and RuO₂–GDC anode powder were laminated in a stainless mold with the diameter of 10 mm and then pressed uniaxially at 80 MPa. The obtained three-layered compact was co-sintered at 1200 °C in air for 2 h. The diameter of the sintered electrochemical cell was about 9 mm and the thickness of cathode or anode was 4.9 mm. The open porosities of the cathode and anode were 23.2% and 39.8%, respectively.

2.2. Electrochemical reforming of biogas

Each surface of cathode and anode was attached to a Pt mesh connected to a Pt lead wire using a Pt paste. The electrochemical cell was set in an alumina holder, and the alumina holder was sandwiched between upper and lower 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 of the cell were reduced to Ni and Ru metals, respectively, in a H₂ atmosphere with 3 vol% H₂O at 800 °C for 12 h. Then the supplied H₂–H₂O gas was purged by an Ar gas and the electrochemical reforming of a biogas was carried out at 800, 700 and 600 °C. Since the used biogas contained 60.0% CH₄ and 37.5% CO₂ (Table 1), a high purity CO₂ gas (purity > 99.99%) was mixed to the biogas to adjust the volume ratio of CH₄/CO₂ = 1/1 for the stoichiometric chemical reaction. The flow rates of biogas and CO₂ gas were 40 and 10 ml/min, respectively. The external voltage by a potentiostat (HAL-3001, Hokuto Denko Corp., Japan) was applied to the cell in the range from 1.0 to 2.0 V. The composition of the outlet gas was measured by a gas chromatograph equipped with an active carbon column and a thermal conductivity detector (GC7100T, J-Science Lab Co. Ltd., Japan) using an Ar carrier gas. The temperatures of the column and detector were 70 and 100 °C, respectively. The electric current supplied to the detector was 60 mA. The flow rate of the outlet gas was measured by a flow meter (Soapfilm Flow Meter, 3001-11002, GL Science Inc., Japan). After the dry-reforming experiment, the phases of constituent materials of the cell were identified by an X-ray diffraction equipment (RINT2200 PCH/KG, Rigaku Co., Japan). The carbon deposition in the cell was analyzed by an electron-probe microanalyzer (EPMA, JXA-8230, JEOL Ltd., Japan).

3. Results and discussion

3.1. Electrochemical reforming of biogas

Fig. 2(a)–(c) shows the fraction and flow rate of the outlet gas and electric current density with heating time, respectively. Under the conditions of 800 °C and 1.0 V, the gas composition was almost constant for 12 h and consisted of 45.4–47.1% H₂, 43.6–46.8% CO, 1.1–3.6% CH₄, 4.2–6.0% CO₂, 1.3–1.9% N₂ and 0–3.2×10⁻³% O₂. The volume ratio of H₂/CO was close to unity, suggesting the stoichiometric dry-reforming reaction proceeded (CH₄+CO₂→2H₂+2CO). The flow rate of the outlet gas increased initially for 4 h and then decreased with

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