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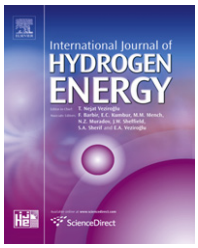

Internal reforming SOFC running on biogas

Y. Shiratori [a,*], T. Ijichi [b], T. Oshima [a], K. Sasaki [a,c]

[a] Department of Mechanical Engineering Science, Faculty of Engineering, Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan

[b] Tosu Kankyo Kaihatsu Ltd., Todoroki-machi 929-2, Tosu-shi, Saga 841-0061, Japan

[c] International Research Center for Hydrogen Energy, Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan

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ABSTRACT

Direct feeding of biogas to SOFC, which is derived from municipal organic wastes, has been investigated as a carbon-neutral renewable energy system. CH_4/CO_2 ratio in the actual biogas fluctuated between 1.4 and 1.9 indicating biogas composition is strongly affected by the kinds of organic wastes and the operational conditions of methane fermentation. Using anode-supported button cells, stable operation of biogas-fueled SOFC was achieved with the internal reforming mode at 800 °C. Cell voltage above 0.8 V was recorded over 800 h at 200 mA cm^{-2}. It has been revealed that air addition to actual biogas reduced the risk of carbon formation and led to more stable operation without compromising cell voltage due to the lowering of anodic overvoltage.

1. Introduction

Active use of municipal organic wastes (bio-wastes) as an alternative to fossil fuels such as petroleum, coal, propane and natural gas will reduce the net increase in CO_2 emission as well as the amount of wastes (see Fig. 1). Moreover, the use of bio-wastes is a cost-effective approach in comparison to using a newly-produced biomass. CH_4 is also known as a major greenhouse gas, and the contributing rate of CH_4 to the green house effect is considered to be around 20% of the total emissions. Because 70% of atmospheric CH_4 is derived from anthropogenic emissions from landfill site and livestock, etc., the energy use of these CH_4 should be quite effective to suppress the greenhouse effect [1,2]. In using garbage and cattle manure as energy resources, they are first of all metabolized by bacteria under anaerobic conditions producing a biogas mixture consisting of 60% CH_4 and 40% CO_2. In the presence of air, namely aerobic process, the organic matters are decomposed to H_2O and CO_2, and useful lower hydrocarbon cannot be obtained. Anaerobic fermentation which proceeds in reducing atmosphere enables us to extract chemical energy of bio-wastes as CH_4-rich biogas.

The application of fuel cell instead of heat engine will lead to 10–20% higher efficiency of electrical power generation [3]. Generation of electricity from biogas using low temperature phosphoric-acid, alkaline-based, and polymer-electrolyte fuel cells (PAFC, AFC, and PEFC) has been considered [4–6]. However, biogas must be converted to H_2-rich gas by using a gas processor (reformer and CO-removal system) prior to feeding into fuel cell anodes. Besides, precious metal catalysts are required resulting in a quite costly system. The most attractive feature of solid oxide fuel cells (SOFCs) is their flexibility in selecting types of fuels due to the high operating temperatures (700–1000 °C) [7–9]. Biogas contains natural

* *Corresponding author*. Tel.: +81 92 802 3094; fax: +81 92 802 3094.
E-mail address: y-shira@mech.kyushu-u.ac.jp (Y. Shiratori).

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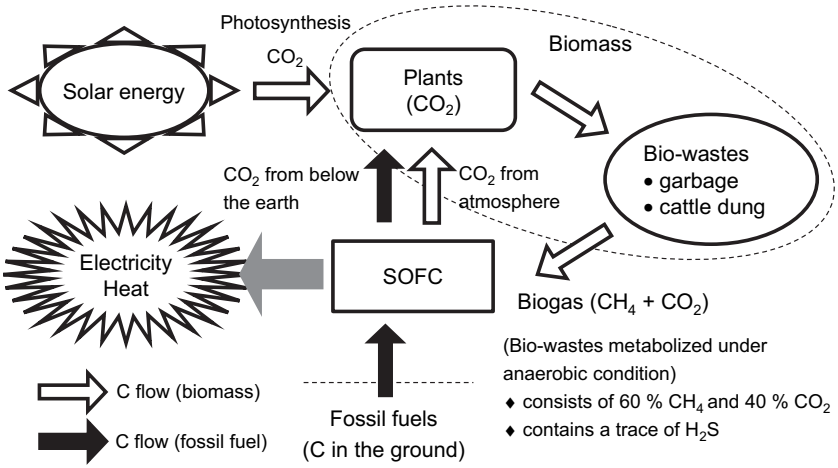

Fig. 1 – Generation of electricity and heat from bio-wastes using SOFC technology. The use of bio-wastes as energy resources contributes to the reduction of CO_2 and CH_4 emissions.

reforming agent (CO_2) and therefore can be directly fed into SOFC without humidifier. In principle, biogas-fueled SOFC can be operated with internal reforming mode. In this case, facilities of hydrogen production, purification and storage can be eliminated from an energy conversion system leading to cost cutback and enhancement of overall system efficiency. The advantage of SOFC over gas engine is that an auxiliary fuel to compensate the insufficient calorie of biogas is not necessary, and NOx and SOx emissions are negligibly small during operation. It has been reported that SOFCs can generate considerable power even at 20% CH_4 to CO_2 while the combustion engines cannot be applicable under this condition [10].

Internal reforming SOFC running on biogas (hereafter sometimes called as direct-biogas SOFC) is an environmental-friendly, compact and cost-effective energy conversion system in which internal dry reforming of CH_4 (reaction (1)) proceeds on Ni-based anode using CO_2 inherently included in biogas without an external reformer and precious metal catalysts. Then, the produced H_2 and CO are electrochemically oxidized to produce electricity (reactions (2,3)).

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

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (2)$$

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

Only a few reports have been found, providing the performance of internal reforming SOFCs running on biogas [11–14], because carbon formation thermodynamically can take place on the anode material. Kendall et al. has reported the results of direct-feeding of landfill biogas (general CH_4-rich biogas). However, that was only 6.5 h level short-term experiment and not continuous feeding of as-produced real biogas [11]. To avoid coking pre-reforming of biogas is generally required [3]. Recently, development of new fermentation path producing H_2-rich biogas [15] and highly active catalysts to assist biofuel reforming [16–18] has been reported. In this study, mixture of cattle manure and garbage has been directly fed into SOFC as a gaseous fuel (biogas) via a series of fermentation processes. Heretofore, we have succeeded in stable operation of SOFC running on actual biogas produced in waste treatment center using Ni–ScSZ cermet as an anode material without any support catalysts [12]. During the test, fluctuation of cell voltage was observed. This may be due to the fluctuation of biogas composition which depends on the kinds of bio-wastes and the conditions of methane fermentation. Therefore, monitoring of the composition of actual biogas has been performed by introducing an automatic gas chromatograph. Based on the electrochemical properties of internal reforming SOFC operated with simulated and actual biogases, feasibility of direct-biogas SOFC will be discussed focusing especially on the following three issues, fuel impurity poisoning, fluctuation of gas composition, and carbon deposition.

2. Experimental

2.1. *Single cell fabrication*

Anode-supported half cells with a diameter of 20 mm (purchased from Japan fine ceramics) in which 10 mol% Sc_2O_3-1 mol% CeO_2-89 mol% ZrO_2 (scandia-stabilized zirconia, abbreviated by ScSZ) electrolyte with a thickness of 30 μm was sintered on a porous anode support (mixture of NiO and ScSZ (NiO:ScSZ = 5.6:4.4)) with a thickness of 800 μm were used to fabricate single cells. A mixture of NiO (>99.9%, Kanto Chemical, Japan) and ScSZ (Daiichi Kigenso Kagaku Kogyo, Japan) powders with a weight ratio of 8:2 was screen-printed and subsequently sintered on the anode support at 1200 °C for 3 h which acts as an anode current collector with the area of 8×8 mm^2. A mixture of $(La_{0.8}Sr_{0.2})_{0.98}MnO_3$ (>99.9%, Praxair, USA, abbreviated by LSM) and ScSZ with a weight ratio of 1:1