7-14. Process development of hydrogenous gas production for PEFC from biogas -Demonstration of producing hydrogen powering a 50W class PEFC stack-

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バイオガスを原料とするPEFC用水素の製造プロセスの開発
-生成水素による50W級PEFCの実証運転-

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1. Introduction
A three years laboratory-scale technical research project had been carried out to convert biogas to hydrogen-rich gas and to demonstrate the possibility of applying the acquired hydrogenous gas to polymer electrolyte full cell (PEFC) to co-generate electricity and heat. The biogas was processed in two steps, successively in a desulfurizer that removes the H₂S in biogas down to ppb levels and in a hydrogenous gas producer that converts the desulfurized biogas to hydrogen-rich gas containing CO less than PEFC-tolerable value of, say, 10 ppm. Without removing its CO₂ and residual CH₄ components the acquired hydrogenous gas was then fueled to a 50-watt model PEFC stack to demonstrate its fuel applicability. This paper reports the result of a final demonstration test on the proposed system using an actual biogas formed from anaerobic digestion of cattle excreta.

2. Experimental
The experimental system used for the demonstration test consisted mainly of three parts: a bio- and chemical-combined desulfurizer, a four fixed-bed reactors hydrogenous gas producer and a 50-watt model PEFC unit. The biogas feed was taken from an anaerobic digestion plant in Rakuno Gakuen University with cattle excreta as feed, and its CH₄ content was slightly time-dependent, varying around 56 vol% in the test period. About 1.0 L/min of the biogas was first pumped into a semi-transparent plastic column sizing 90 mm in diameter and 2000 mm in height from its bottom section and bubbling through the photosynthetic sulfur bacteria-containing digester fluid phase in the column for reducing its H₂S content. To have a good contact between the biogas and the fluid three glass beads beds of 50 mm in height were fixed at the different sections inside the column serving as biogas distributors. The volume of the fluid in the column was about 11 L and its temperature was maintained at 303 ± 1 K by circulating it through a temperature-controlled fluid container that possessed about 40 L of the same bacteria-containing fluid. After being out of the column and passing a water condenser, three fourth of the biogas was slightly pressured by a micro gas pump to flow through a ZnO packed column for removing the residual H₂S and then enter the producer for its conversion to hydrogenous gas.

The biogas conversion process in the producer involved four successive catalytic reactions and they took place in a steam reformer (SRr), high and low temperatures shifters (HTSr and LTSr) and a selective CO oxidizer (SLOXr), respectively. Kinds of the catalysts for the reactions, sizes of the corresponding reactors and their appropriate operating conditions as well as other necessary conditions all were detailed in a pair of the paper [1]. How to activate the catalysts and start the biogas conversion was also described there. As done in running the producer with a clean model biogas, the dry product composition at each reactor exit was continuously monitored by a two channels micro gas chromatograph during the test.

After confirming CO content in the final hydrogenous gas stream out of the producer being less than 10 ppm, the stream was allowed instead of purging gas of N₂ to enter the anode chamber of the PEFC stack. The stack was operated at a temperature of 353 K and with 4.0 L/min of pure O₂ as oxidant. A galvanostat was used to regulate the current imposed on the stack and also to measure the stack voltage. Detail operation procedure of the stack and its particular feature were given somewhere else [2]. Presently, the current was increased from 0 to 4.4 A step by step to pursue its maximum power output on the acquired hydrogenous gas fuel. Variation of the hydrogenous gas flow rate through the stack was also

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measured by two gas flow meters before and after the stack to estimate its hydrogen unitizing efficiency.

3. Results and Discussion
3.1. H2S removal

H2S content in the original biogas in the 8 hrs test period was almost constant at around 2100 ppm. After the biogas bubbled through the bacteria-containing digester fluid in the plastic column, it was measured to fall to around 1200 ppm levels, about 43% H2S being removed by the photosynthetic sulfur bacteria in the fluid. This H2S removal ratio was lower than what we observed at the same time using a much smaller bottle type bubbling reactor, might indicating a worse contact between biogas and the fluid in this large scale reactor. To prevent any H2S from entering the producer and deactivating the catalysts there, the ZnO pellets packed column reactor was followed to completely remove the residual H2S chemically. Preliminary tests had shown that using the ZnO pellets at an appropriate space velocity could ensure the H2S level in the off-stream not higher than 30 ppb. In fact, no H2S was detected from the biogas after the chemical desulfurization.

3.2. Conversion of biogas to hydrogenous gas

Due to an abrupt introduction of the desulfurized biogas via a four-way valve between the desulfurizer and the producer, all working temperatures of the reactors in the producer, particularly that of SRr where the highly endothermic reforming took place, were unstable in the first 50 min. After that, both the reaction temperatures and the dry gas compositions at all reactor exits indicated the stability of the whole producer to the time to end the test. Limited to the gas compositions, the only difference observed between the present test and that using a clean mode biogas was that CH4 contents started to increase slightly with time from 320 min. For SRr the maximum CH4 increase to the end was about 0.7 vol%, high enough to completely rule out the cause of measurable errors. Thus, the catalyst slightly losing its activity with the steam reforming of the biogas proceeding was ascribed reasonably to the increase. Since no such phenomenon was observed in preliminary condition-determining tests using the mode biogas, trace S-containing species in the desulfurized biogas might be responsible for the gradual deactivation of the catalyst. Confirmed by S deposition over the spent SR catalyst is under way. As shown in Xu's work, the used model PEFC stack allowed CH4 content in its fuel to be as high as 4 vol% as long as the feed hydrogen was sufficient. The content of H2 in the final stream out of the producer was stable at around 69 vol% and its rate was about 1.6 L/min against the biogas feed of 0.75 L/min.

3.3. Applicability of the hydrogenous gas to PEFC

The hydrogenous gas stream was introduced to the stack at about 50 min from the start after its CO content was confirmed to be allowable to PEFC. As shown in Fig. 1, 50 W output from the stack was achieved at the imposed current of 4.0 A. The stack also showed a long period of stability in power output at this high current, indicating applicability of the acquired hydrogenous gas without removing its CO2 as high as 30 vol%. To examine the effect of CO2 on performance of the stack a comparative test was also conducted with pure H2 of 1.5 L/min. It was found that CO2 in the hydrogenous gas indeed reduced the power output at the imposed currents over 1.2 A, and the higher the current, the larger the degree of the output reduction. In fact, due to low voltages near the limit one observed at 4.0 A for some cells, no current higher than 4.4 A was imposed on the stack in the test. It seems that CO2-tolerant cells are essential for the fuel containing high CO2. From the measured variations of the gas flow rate through the stack its hydrogen utilizing efficiency was also estimated. At 4.0 A it was about 48%, much lower than the generally expected level of 80%, leaving a challenging task ahead for PEFC development.

In summary the present work has demonstrated that the proposed biogas processing system is capable to convert actual biogas to a hydrogenous gas for directly fueling the PEFC stack. Simultaneously, the technical problems requiring to be overcome are also clarified.

![Fig 1 Performance of the 50-W PEFC stack running on the hydrogenous gas from biogas.](image)

Acknowledgment

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References