Ceramic-supported Pd Membrane Module for On-site Hydrogen Production from Natural Gas

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ABSTRACT

A large number of hydrogen refueling stations is necessary for quick spread of fuel cell vehicles (FCVs). In Japan, a hundred hydrogen refueling stations will be in business by 2015 and FCVs will be introduced into the market in 2015. One of the most promising pathways to produce hydrogen for FCVs is on-site hydrogen production from natural gas. Now hydrogen production systems with $\underline{S}$team $\underline{M}$ethane $\underline{R}$eforming (SMR) and $\underline{P}$ressure $\underline{S}$wing $\underline{A}$dsorption (PSA) technologies are commonly introduced into the stations. However, they are too expensive and too large to spread quickly.

To solve these issues and support the quick spread of FCVs, we have been developing a hydrogen production system with a ceramic-supported palladium membrane module. This system can produce and separate hydrogen simultaneously in a single reactor. Compared with the previous membrane module with metal support, the manufacturing cost of the ceramic-supported module will be significantly reduced by well-established mass production technologies for the ceramic products. Therefore the ceramic-supported membrane module has a possibility to realize a compact and low-cost hydrogen production system. In our past work, we evaluated the hydrogen production performance and long-term durability of the module. However, it is still necessary to increase the hydrogen production performance per module and decrease the total number of modules per system in order to commercialize a compact and low-cost hydrogen production system. It is known that one of the biggest inhibition factors for hydrogen permeation across palladium membrane is concentration polarization. It is also known that raising linear velocity of feedstock gas is effective to suppress the concentration polarization.

In our present research, we performed reforming tests to evaluate the effect of the linear velocity on the concentration polarization and hydrogen production performance. The reforming tests were carried out with different inside diameters (16-24 mm) of reactor vessel at different feedstock gas flow rates (3.0-6.0 $Nmlmin^{-1}cm^{-2}$). In the tests, excessive amount of catalyst for reforming was set around the module. The processed gas was analyzed with gas chromatography to calculate the methane conversion and the hydrogen concentration at outlet of reactor vessel. By comparing the hydrogen concentrations among different diameters of reactor vessels at different feedstock gas rates, we evaluated the suppressing effect of concentration polarization.

As a result of the performance test, it was confirmed that hydrogen production amount increased by 1.2 times by changing reactor vessel inside diameter from 24 mm to 16 mm at reaction temperature of 550 °C. This result suggests that increase of the linear velocity with narrow reactor vessel suppressed the concentration polarization and promoted the hydrogen permeation. In addition, when the reaction temperature was raised from 550 to 600 °C, the hydrogen production amount increased by 1.4 times while heating energy of reactor vessel increased only 1.1 times. We also confirmed the effect of linear velocity and reaction temperature on the hydrogen production performance by Computational Fluid Dynamics (CFD) simulation.

TABLE OF CONTENTS

2.BODY OF PAPER

2.1. INTRODUCTION

A large number of hydrogen refueling stations is necessary for quick spread of fuel cell vehicles (FCVs). In Japan, a hundred hydrogen refueling stations will be in business by 2015 and FCVs will be introduced into the market in 2015. One of the most promising pathways to produce hydrogen for FCVs is on-site hydrogen production from natural gas. Now hydrogen production systems with Steam Methane Reforming (SMR) and Pressure Swing Adsorption (PSA) technologies are commonly introduced into the stations because it is a mature and commercial technology. However, the commercial SMR+PSA systems are not compact enough to be used in urban areas and the hydrogen production efficiency is insufficient. To solve these issues of the present system, we have been developing a hydrogen production system with membrane reactor.

Membrane reactors are hydrogen production systems using hydrogen permeable membrane, and are compact in size and highly efficient in the hydrogen production. In general, a membrane reactor consists of catalysts for the SMR and metallic membranes which separate the produced hydrogen. The membrane reactor can produce and separate hydrogen simultaneously [1-2]. The following two chemical reactions: steam reforming reaction and CO shift reaction, proceed in the membrane reactor.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2, \Delta H_o = 206.2 kJ/mol \cdot \cdot \cdot (1)$$
$$CO + H_2O \leftrightarrow CO_2 + H_2, \Delta H_o = -41.2 kJ/mol \cdot \cdot \cdot (2)$$

The characteristic feature of the membrane reactor is that the produced hydrogen is removed from the reformed gas, and as a result, the reactions shown as Eqs. (1) and (2) shift toward the hydrogen production side. Consequently high methane conversion rate can be obtained even at a low temperature

of around 500-550℃. This temperature is lower than that of SMR+PSA system, 700-800 ℃.

At Tokyo Gas, we have researched and developed membrane reactors since 2000. In our previous work, we have developed a 40 Nm³/h class Membrane Reformer (MRF) system for hydrogen production from natural gas and have demonstrated that the system is more compact, more highly efficient, and simpler than the conventional SMR+PSA system [3-4].

Although the MRF system has demonstrated high hydrogen production efficiency, two significant issues must be solved for commercialization. One is the durability of the membrane for several years. Another issue is the system cost, mainly from the material cost of Pd-alloy. To reduce the membrane cost, we have been developing a hydrogen production system with a ceramic-supported palladium membrane module [5]. This system can produce and separate hydrogen simultaneously in a single reactor. Compared with the previous membrane module with metal support, the manufacturing cost of the ceramic-supported module will be significantly reduced by use of well-established mass production technologies for ceramic products. Furthermore, plating technologies can be applied to produce a thin membrane on the ceramic support. Therefore the membrane module has a possibility to realize a compact and low-cost hydrogen production system. In our past work, we evaluated the hydrogen production performance and the long-term durability of the module. However, it is still necessary to increase the hydrogen production performance per module and decrease the total number of modules per system in order to commercialize a compact and low-cost hydrogen production system. It is known

that one of the biggest inhibition factors for hydrogen permeation across palladium membrane is concentration polarization. It is also known that raising the linear velocity of feedstock gas is effective to suppress the concentration polarization. Therefore, in this paper, we planned to decrease the influence of concentration polarization and evaluated the effect.

2.2. Concentration polarization

In the case of hydrogen separation through the membrane, it is well known that the hydrogen permeation amount is controlled by the membrane thickness, the permeability of membrane, and the pressure difference between a process side and a permeation side. However, in the past researches, it was cleared that the concentration polarization, which is concentration changes adjacent to the membrane surface caused by hydrogen permeation through the membrane, also affects to the hydrogen permeation through the membrane [6-7]. It was reported that the membrane permeability, separation factor, membrane thickness, boundary layer mass transfer coefficient, and Henry's law coefficient are the factors that determine the extent of polarization [6]. Furthermore it was also cleared that higher temperature and thinner membrane have a bigger influence on the concentration polarization from the computational fluid dynamics (CFD) simulation [7]. As shown in Fig. 1, it is important to decrease the thickness of the boundary layer to improve the hydrogen production performance.
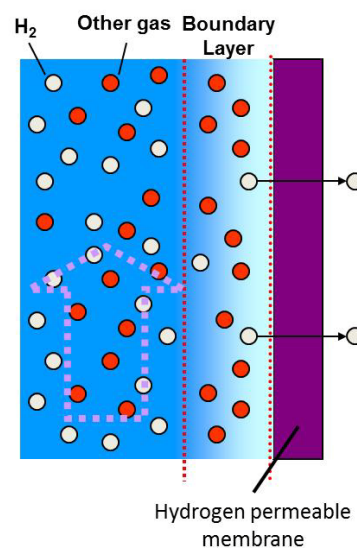

Fig.1 Illustration of concentration polarization

In this study, the suppressing effect of the concentration polarization was evaluated with reducing a diameter of reactor vessel and increasing a linear velocity of feedstock gas. The reason why we chose the diameter of the reactor vessel as a parameter is that we want to keep high hydrogen production amount and hydrogen purity. It is supposed that the hydrogen production amount is decreased by the reducing reaction temperature and the reaction pressure.

2.3. CFD simulation

We employed CFD simulations of the membrane module to predict the hydrogen production performance and influence of the concentration polarization. Computer simulations are suitable for

parametric studies supposing many kinds of experimental conditions, such as temperature, pressure and flow rate of the feedstock gas. The detail of calculation condition has been already reported in [6], therefore, the difference of the calculation condition is mainly explained here. The dimension of the model used for the simulation was the same as that used for the practical performance tests. The conditions used for the simulation are as follows. 1) The temperature is assumed to be uniform over the membrane module. 2) The reaction rates of the SMR and CO shift reactions are infinite. 3) The hydrogen permeation rate in the membrane follows the Sievert's law. 4) Gas flux follows the Darcy's law. The porosity of the support tube and hydrogen permeability was measured by the experiments. On the basis of the above assumptions, the pressure and concentration of the chemical species contained in processed gas under the SMR and CO shift reactions were calculated. Thereby, the amount of permeated hydrogen through the membrane and the methane conversion ratio were estimated at each temperature, flow rate, and diameter of the reactor vessel. The computer and the software used for the simulations were HP Z800 WorkStation and ANSYS FLUENT 14, respectively.

2.4. Experimental
2.4.1. Apparatus used for reforming test
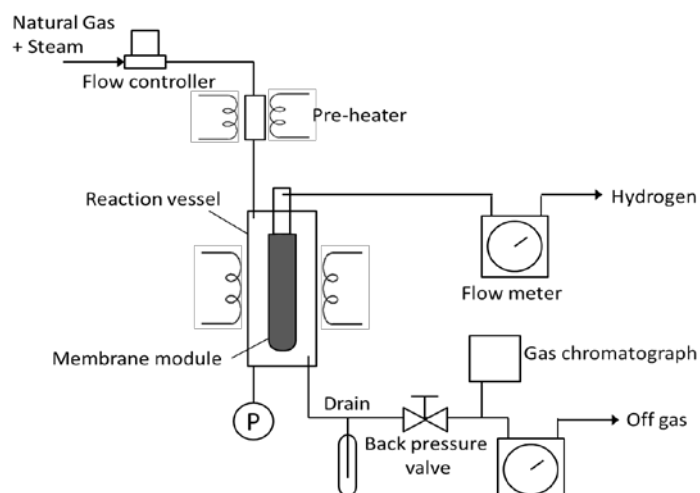The configuration of the apparatus used for the reforming test was shown in Fig.2.

Fig.2 Schematic flow diagram of the experimental apparatus for reforming tests.

In the reforming test, the flow rates of water and a natural gas were controlled with chemical pumps and mass flow controllers. The city gas (CH_4: 89.6 vol%, C_2H_6: 5.6 vol%, C_3H_8: 3.4 vol%, and C_4H_{10}: 1.4 vol%) was desulfurized and then introduced at a S/C (Steam/Carbon) ratio of 3.0. The water was vaporized at a vaporizer, and then mixed with the fuel, and the mixed gas was pre-reformed at pre-reforming catalysts. Next the pre-reformed gas was introduced into the outside of the membrane module. The pre-reforming catalysts have a role of preventing a thermal shock at the module, carbon deposition and a reverse permeation of hydrogen from the permeation side. The Pressures of process side and permeation side were set at 0.8 MPaG and 0.0 MPaG, respectively. The product hydrogen amount and the flow rate of off-gas were measured with the wet gas meter. The off-gas at the process side was analyzed with a Thermal Conductive Detector (TCD) gas chromatography to calculate the methane conversion ratio. A

reactor is composed of a stainless steel vessel and a membrane module with a catalyst inside the vessel as shown in Fig.3. The ceramic-supported Pd-Ag membrane module was used as the membrane module. A mechanical joint was attached to one end of the membrane module for connecting a stainless tube. The membrane module has about 10 mm outer diameter, 300 mm length, approximately 90 cm^2 membrane area. Enough amount of Ruthenium catalyst which has high activity for both SMR and CO shift reactions was fixed around the module via an alumina continuous fiber. Feedstock gas was introduced from the tip side of the membrane module. Produced hydrogen at outside of the module permeates the Pd-Ag membrane to inside the module. The temperature of the module top was measured with a thermo-couple and set as the representative temperature to be controlled in the measurement because the reforming reaction was most intensive there. Additionally, the two types of reactor vessel were used with different inside diameter (16.6 or 23.9 mm).
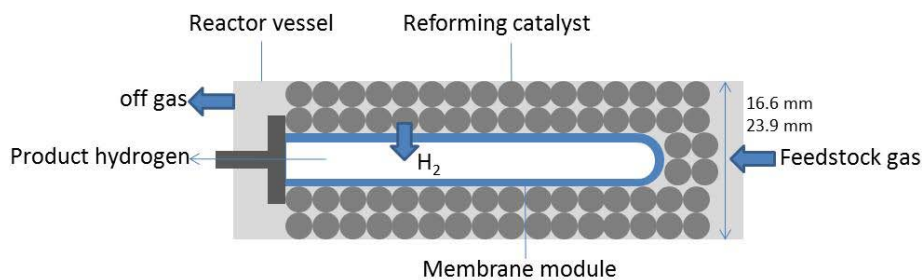

Fig.3 Schematic diagram of a reactor

2.4.2. Reforming test with different diameter of the reactor vessel

We performed reforming tests to evaluate the effect of the linear velocity on the concentration polarization and hydrogen production performance. Therefore, reforming tests were carried out with different diameters (16.6 and 23.9mm) of reactor vessel at different feedstock gas flow rates (3.0-6.0 Nmlmin^{-1}cm^{-2}). In the tests, 43 g and 70g of catalysts were set around the module at 16.6 mm and 23.9 mm reactor vessels. Reaction temperature and reaction pressure were set at 550 °C and 0.8 MPaG.

2.4.3. Evaluation of the reaction temperature on the hydrogen production performance with narrow reactor vessel

If the concentration polarization is suppressed by use of the narrow reactor vessel, it is expected that the hydrogen production performance will be maximized at higher reaction temperature. To confirm the maximum capability of the hydrogen production performance, reaction temperature was varied from 550 to 600°C. The flow rate of the feedstock gas was from 3.0 to 6.0 Nmlmin^{-1}cm^{-2}. . The pressure of process side was set at 0.8 MPaG.

2.5 Results and Discussion
2.5.1 Simulation result

The calculation conditions used in the simulation are listed in Table 1. The simulation results with different diameters of the reactor vessels are shown in Fig. 4.

Table 1 Calculation conditions of the CFD simulation.

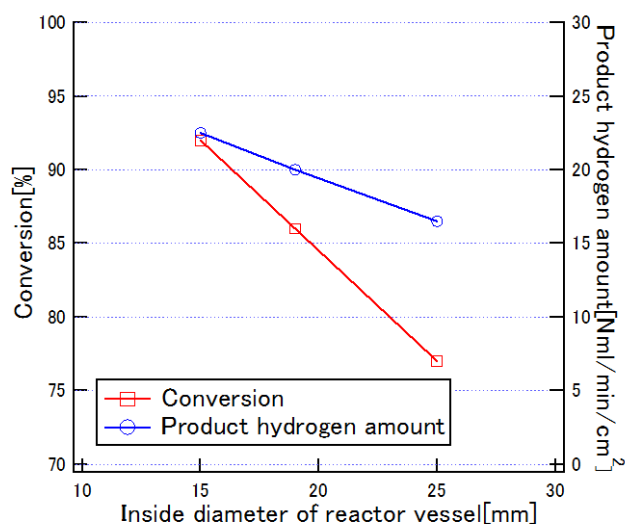| Feedstck gas rate [Nml/min/cm^2]	S/C	Temperature [℃]	Process side pressure [MPaG]	Permeation side pressure [MPaG]	Reactor vessel diameter [mm]
6.0	3.0	600	0.8	0.0	15-25

Fig. 4 Calculation result of the CFD simulation at 600 °C and 6.0 Nml/min/cm^2 of feedstock gas; open square:Conversion ,open circle:Product hydrogen amount

The result shows that the hydrogen production performance increases with decrease of the diameter of reactor vessel. From the simulation result, it was also confirmed that the hydrogen concentration was the highest at the tip of the module because pre-reformed gas was introduced from the tip of the module. By the hydrogen permeation along the module, the hydrogen concentration decreased gradually and the concentration of other gas such as CO_2 and CO increased. At the part of module end, the boundary layer arised and hydrogen permeation through the membrane was prevented though hydrogen was still existed. With reduction of the diameter of reactor vessel, the linear velocity of feedstock gas became high and the boundary layer along the membrane surface became thin. Thereby, it is thought that the influence of the concentration polarization is suppressed and product hydrogen amount increases. This result means that the diameter of reactor vessel is important factor for improving the hydrogen production performance.

2.5.2 Experimental result
2.5.2 .1. Reforming performance with different diameters of reactor vessels and flow rates of feedstock gas

Fig.5 shows the results of the performance tests with different diameters of reactor vessels at 550 °C. The product hydrogen amount with 16.6 mm diameter of reactor vessel was more than that with 23.9 mm diameter of reactor vessel with higher flow rate of feedstock gas. These trends corresponded to the results of simulation. This phenomenon is explained as follows: The total amount of produced hydrogen increased with increasing flow rate of feedstock gas. Besides, the process of hydrogen permeation through the membrane is not rate-determining in these flow rates. Therefore, the product hydrogen

amount increased. From the results of the CFD simulation and experiments, the concentration polarization was suppressed by using the narrow reactor vessel and it suppression resulted in improvement of the hydrogen production performance.
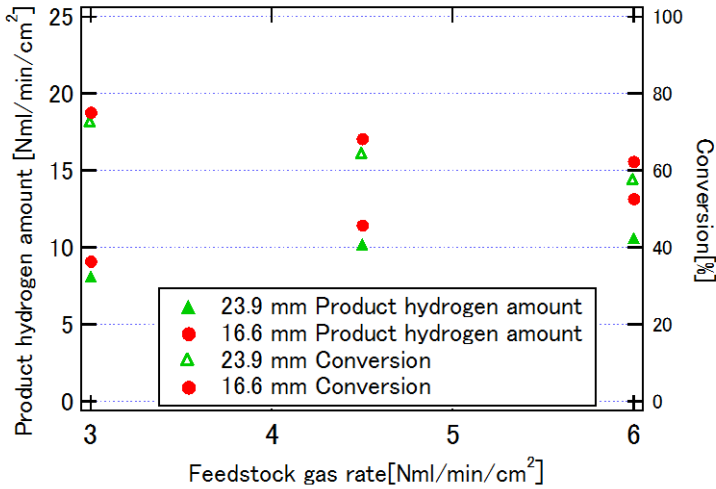

Fig. 5 Effect of the feedstock gas rate on the hydrogen production amount with different inside diameter of reactor vessel;circle:16.6mm,triangle:23.9mm

2.5.2 .2. Reforming performance with different reaction temperatures

The results of reforming tests at different reaction temperatures with narrow reactor vessel are shown in Fig. 6.
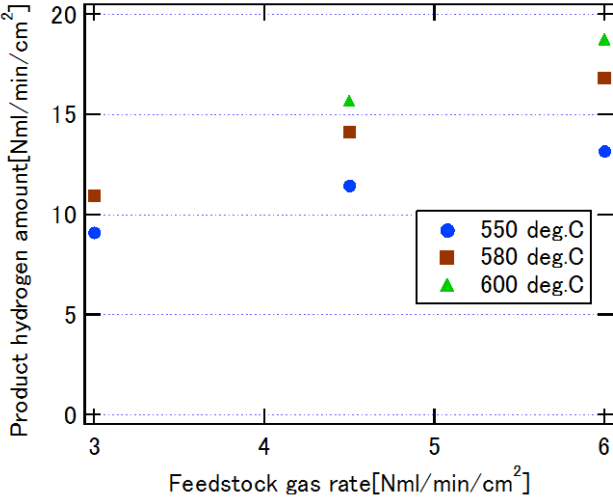

Fig. 6. Effect of the flow rate of feedstock gas on the product hydrogen amount with narrow reactor vessel at 550 °C (solid circle), 580 °C (solid square), and 600 °C (solid triangle).

The product hydrogen amount increased with the increase of the reaction temperature. The results of the experimental results are in good agreement with the simulation results. Furthermore, the flow rate of feedstock gas had a high impact on the performance of the membrane module at high temperature. In the flow condition of 6.0 Nml/min/cm^2, the product hydrogen amount at 600 °C was 1.4 times higher than that at 550 °C, despite only for 50 °C increase in temperature.

2.6. Conclusion

We investigated the influence of the concentration polarization by changing the diameter of the reactor vessel by CFD simulation and experiment. As a result of CFD, the concentration polarization decreased and the hydrogen production performance was improved by use of the narrow reactor vessel. Experimental results, using the ceramic-supported Pd-Ag membrane module, also indicated that the performance was improved with the narrow reactor vessel. These results means that the boundary layer along the membrane became thin and the concentration polarization was suppressed with decreasing the diameter of the reactor vessel.

3. Acknowledgement

4. Reference

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5. List of Tables

Table 1. Calculation conditions of the CFD simulation.

6. List of Figures

Fig. 1 Illustration of concentration polarization.

Fig. 2 Schematic flow diagram of the experimental apparatus for reforming tests.

Fig. 3 Schematic diagram of a reactor.

Fig. 4 Calculation result of the CFD simulation at 600 °C and 6.0 Nml/min/cm^2 of feedstock gas; open square:Conversion ,open circle:Product hydrogen amount

Fig. 5 Effect of the feedstock gas rate on the hydrogen production amount with different inside diameter of reactor vessel;circle:16.6mm,triangle:23.9 mm

Fig. 6 Effect of the flow rate of feedstock gas on the product hydrogen amount with narrow reactor vessel at 550 °C (solid circle), 580 °C (solid square), and 600 °C (solid triangle).