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Highly Efficient Hydrogen Production System with Membrane Reformer for Hydrogen Refueling Station

Main author

Yuudai Kaneko

Coauthors

H. Kurokawa, H. Yakabe, and T. Tokumoto

Tokyo Gas Co., Ltd.

JAPAN

ABSTRACT

Long-term durability of a Pd-based membrane module used in a membrane reformer was improved. The improved membrane module with higher-purity membrane material was fabricated and the long term durability was evaluated. From the evaluation test it was found that purifying the membrane material is effective to increase the long term durability of the membrane module.

A membrane reformer is a hydrogen production system using the Pd-based membrane and has been expected as a next generation hydrogen production system in hydrogen refueling stations as well as on-site hydrogen generators for other purposes. The membrane reformer is a non-equilibrium reformer in which steam reforming reaction of natural gas, CO shift reaction and hydrogen separation occur at the same time. Owing to its low-temperature operation range of 500 to 600 °C, thermal loss from the reactor can be mitigated and high hydrogen production efficiency can be achieved. We have already developed a $40Nm^3/h$-class membrane reformer system and demonstrated the world-highest hydrogen production efficiency of 81.4% HHV. We have also showed that the membrane reformer system can be more compact than conventional systems because steam reforming and hydrogen separation process proceeds simultaneously in a single reactor.

The main issues in the development of the membrane reformer system are to improve the durability and to reduce the cost of the membrane modules. Especially to obtain the long term durability of the membrane module is the current issue. Our previous measurement showed that the purity of the produced hydrogen using the membrane reformer system decreased significantly after 3000 h operation. The detailed research revealed that some inclusions exist in the membrane module and they cause a leakage of impurity gases into the produced hydrogen. Purifying the membrane material is very important to obtain the long term durability of the module. Accordingly we manufactured the membrane module with the higher-purity membrane material and carried out a long term durability test. As the results, the improved membrane module demonstrated that the purity of the hydrogen produced with the improved module has maintained over 99.99% (4N) for more than 13000 h. This result is much higher than the Japanese national project’s target of 8000 h durability. Thus this study has made clear that purification of the membrane material is effective for the membrane module to increase the durability.

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1. Introduction

For prevention of global warming and realization of sustainable societies, various technical researches on reducing CO_2 emissions have been done. Improvement of the energy efficiencies for various kinds of equipment and promotion of renewable energy utilizations have been expected as effective ways for the reduction of the use of fossil fuels and resulting CO_2 emissions. Presently thermal electric power plants with More Advanced Combined Cycle have already achieved high efficiency of over 55% HHV [1-2], and replacing conventional thermal plants with such high energy efficient systems can help to mitigate the use of fossil fuels and reduce the CO_2 emissions. Researches of intensive use of renewable energies, such as hydroelectric power, solar energy, wind power and biomass energy have been also carried out in many universities and research institutes [3-5]. Moreover, carbon capture and sequestration (CCS) is considered as a key technology to reduce CO_2 emissions drastically, and related fundamental researches have been conducted in many research institutes all over the world [6-8].

In addition to the above-mentioned technologies, hydrogen energy and its utilization technologies have been receiving much attention as effective key-technologies for CO_2 reduction. Hydrogen is expected to be a clean energy carrier since no CO_2 is emitted during combustion or power generation, and can be used efficiently in co-generation systems, stationary fuel cells, and fuel-cell vehicles (FCVs). The other attractive feature of hydrogen is that hydrogen can be produced from various resources, such as wind power, solar power and other renewable powers. Hydrogen can also be produced efficiently from fossil fuels such as petroleum or natural gas. On-site hydrogen production from natural gas is one of the most promising pathways to hydrogen society since we can use the existing natural gas pipeline networks. Thus many hydrogen refueling stations for FCVs have been constructed and the feasibility has been evaluated in the world. The combination of steam methane reforming (SMR) and pressure swing adsorption (PSA) is typically used for hydrogen production from natural gas in the hydrogen refueling stations. However, the hydrogen production efficiency for the SMR+PSA system is not so high, and as a result, the Well to Wheel (WtW) efficiency of FCVs is not enough to be advantageous over other clean car technologies. Thus highly efficient hydrogen production system is desired to achieve higher WtW efficiency for FCVs. In addition, a more compact package is required for the on-site hydrogen production systems in urban areas.

A membrane reformer system has been expected as a new technology to solve these issues. The membrane reformer system is a hydrogen production system using a hydrogen-permeable Pd-based membrane. Since in the membrane reactor the methane reforming reaction, CO shift reaction, and separation of hydrogen occur simultaneously, the reforming and CO shift reactions can proceed under a non-equilibrium state. This promotes both the reaction and thus the hydrogen production. Because the membrane reformer can be operated at a low-temperature of 500 to 600°C, the thermal loss from the reformer can be mitigated and high hydrogen production efficiency can be achieved. We have already developed a 40 Nm^3/h-class membrane reformer system and demonstrated the highest hydrogen production efficiency of 81.4% HHV from natural gas [9]. We have also shown that the membrane reformer system can be more compact than the conventional PSA systems because the fuel reforming reaction, the CO shift reaction and the post-refinement process are conducted in a single reactor. Currently our main issue in the development of the membrane reformer system is to improve the durability of the membrane itself. Long term durability of hydrogen production systems enables us to operate hydrogen refueling stations for a prolonged period and it contributes to the reduction of the cost of produced hydrogen. Regarding the long term durability of the membrane reactor, we must consider both the performance of the hydrogen production and the purity of the produced hydrogen. We have carried out the durability tests using a single membrane reactor and obtained fundamental data for the single membrane reactor to increase system durability.

In our previous research [10], serious leakage occurred in the membrane, and the purity of the produced hydrogen decreased rapidly after the hydrogen production test of 3000 h. The detailed investigation on the membrane module after the test revealed that some impurities exist at some leak points on the membrane surface which was considered to have caused the leakage. Hence for the improvement of the durability of the membrane itself, the preparation method was modified and a membrane module with higher-purity membrane material was manufactured. The improved module was expected to achieve longer durability than the conventional module because reduction of impurities in the membrane would suppress the occurrence of leakage in the membrane.

2. Outline of membrane reformer

2.1. Principle of membrane reactor

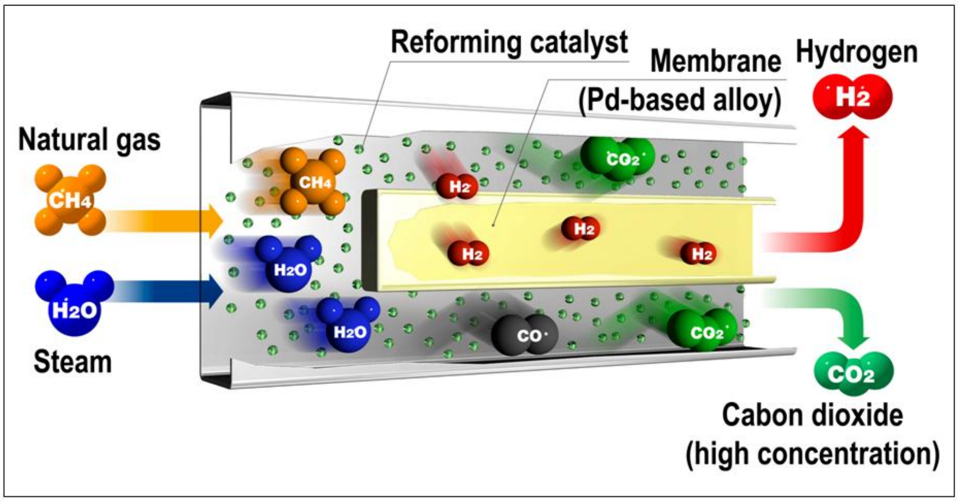

Fig. 1. Principle of membrane reactor.

The schematic diagram of a membrane reactor is illustrated in Fig. 1. The membrane reactor consists of a catalyst part and a Pd-based membrane module. Introduced fuel is reformed to hydrogen rich gas at the catalyst part and the produced hydrogen selectively permeates the Pd-based membrane. The following two chemical reactions: steam methane reforming reaction and CO shift reaction, proceed in the membrane reactor.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (2)$$

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 in Eqs. (1) and (2) shift toward the hydrogen production side. Consequently a high methane conversion rate can be obtained even at a low temperature of around 550 °C. The low operating temperature can reduce the heat loss and thus high hydrogen production efficiency can be obtained.

2.2. Configuration of membrane reformer

Figure. 2 shows the configuration of the membrane reactor. Two modules of Pd-based membrane with a thickness of around 20 μm, primary catalysts and catalysts for SMR are mounted in a reactor tube of stainless steel. A fuel feeding pipe is also inserted into the reactor tube and a mix of fuel and steam is introduced using the fuel feeding pipe. The introduced fuel through the pipe turns its flow at the bottom of the reactor tube and is firstly pre-reformed to methane-rich gas by the primary catalysts. Then most of the methane is reformed at the catalysts part as the process gas flows along the length of the module. Hydrogen in the reformed gas selectively permeates the membrane module and the pure hydrogen goes outside through collection pipes.

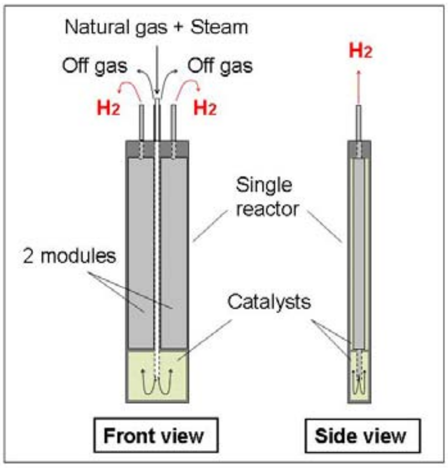

Fig. 2. Configuration of membrane reactor.

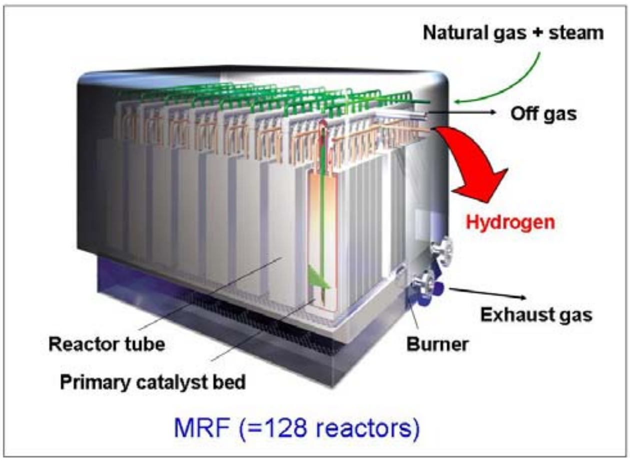

Fig. 3. Schematic diagram of 40 Nm^3/h-class membrane reformer (model).

The 40 Nm^3/h-class membrane reformer consists of 128 membrane reactors and other balance of plants such as a burner, a boiler and an air blower. A burner is located under an assembly of the membrane reactors and heat energy necessary for the endothermic reforming reaction is supplied with the burner. The schematic diagram of the membrane reformer is displayed in Fig. 3.

2.3. New improved module

In our previous study, we have tested the long term durability of the membrane module which is the same as that used in the 40 Nm^3/h-class membrane reformer [9)]. After 3000 h test, serious leakage occurred at the membrane part, and the purity of the produced hydrogen decreased rapidly. Then we analyzed the membrane module used in the durability test in detail and it was found that some inclusions containing Al or Si exist at some leaking points on the membrane surface. These impurities are considered to have caused some micro cracks of the membrane or micro pores in the membrane and finally induced the leakage. To prevent the occurrence of the cracks and the micro pores in the membrane, it is important to reduce the amount of impurities in the membrane. Hence to obtain a higher-purity membrane material, we employed a cold crucible process. A cold crucible process is used for the manufacturing of alloys requiring a high-purity materials that are free from contamination due to contact with the crucible [11)]. Using the cold crucible process, we can obtain the improved module of the Pd-based membrane with higher purity. Except for the preparation method, the configuration and the size of the improved module are the same as those of the conventional module.

3. Experimental

3.1. Placement of membrane reactor

The membrane reactor was set in an electric furnace and the performance of the membrane reactor was measured. Figure. 4 shows the cross sectional diagram of the equipment. Three heaters at the top, middle, and bottom in the furnace control the temperature of the module independently and the temperature distribution over the module is kept within 2 °C. Thermo-couples placed at 5 different points at the reactor outside, top of the reactor, and 2 different points inside the reactor monitor the temperature distribution under the measurements.

3.2. Experimental configuration

The schematic flow diagram of the performance tests for single reactors is shown in Fig. 5. Natural gas with steam or pure hydrogen was pre-heated with a pre-heater and then injected into the reactor through the fuel feeding tube. Off-gas (for natural gas with steam case) or the rest of hydrogen (for pure hydrogen case) after the hydrogen separation went into the drain pot for condensing

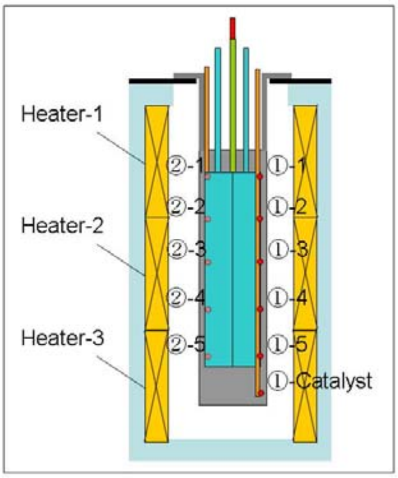

Fig. 4 Cross sectional diagram of the equipment.

the water and then the flow rate was measured with a wet type gas meter (SHINAGAWA W-NK Da-1A). In the process side, the pressure was controlled by using a back pressure valve located downstream of the exit port of the membrane reactor. The composition of the off-gas was analyzed with a gas chromatograph (Agilent micro GC 3000). Pure hydrogen separated at the membrane part was removed through a nozzle connected to the membrane module and the flow rate was measured with the wet type gas meter. A gas chromatograph (GC-FID, GL Science GC-4000) and an infrared gas analyzer (IR, HORIBA GA-360E and VIA-510) were set for analyzing the concentration of impurities: CO, CO_2 and CH_4, in the produced hydrogen. Only the concentration of CH_4 was measured with GC-FID after 9000 h performance test.

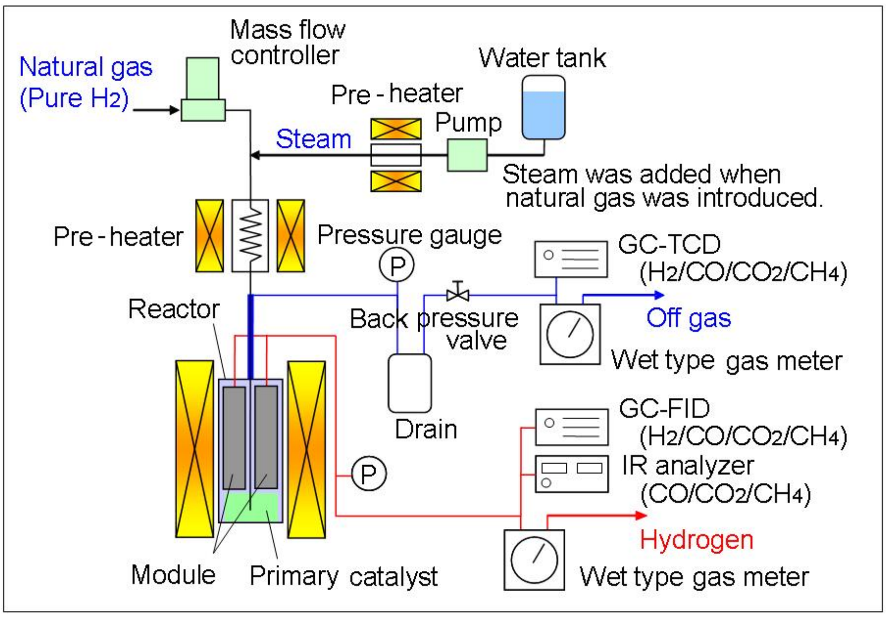

Fig. 5. The schematic flow diagram of the performance tests for single reactors.

3.3. Hydrogen permeability test

The hydrogen permeability of the membrane module was measured using the membrane reactor with pure hydrogen. The module is kept at 550 °C and pure hydrogen is introduced to the process side of the membrane at 0.1 MPaG. Under a condition of abundant hydrogen flow, the flow rate of the permeating hydrogen was measured. The measurement conditions are listed in Table 1. The hydrogen permeability test was carried out before the long term durability test to confirm the initial performance. Then the hydrogen permeability was measured periodically under the long term durability test to check the performance of the module.

3.4. Leakage check test

We measured the leakage from the module before the long term durability test to confirm the initial condition of the membrane module. Pure N_2 of 1.0 MPaG was introduced to the process side of the module at a flow rate of 1.0 NL/min and the volume of the leaking N_2 at the permeation side of the module was measured with a soap bubble flow meter. If the membrane is damaged, the amount of the leaking N_2 increases and thus we can confirm the damage of the membrane. The long term durability test was interrupted periodically and the leakage check test was carried out at room temperature to investigate the degradation of the module under the long term durability test.

3.5. Long term durability test

The long term durability of the module was evaluated through the measurement of the hydrogen production rate from natural gas. The hydrogen production rate from the natural gas was measured continuously for the membrane reactor and the change of the hydrogen production rate with time was investigated. The test condition is listed in Table 2. The natural gas with steam was introduced into the membrane reactor at 0.8 MPaG and the flow rate of the produced pure hydrogen from the permeation side of the module was measured with a wet gas meter.

Flow rate of Pure hydrogen	Operation temperature	Pressure (process side)	Pressure (permeation side)
20.0 NL/min	550°C	0.1 MPaG	0 MPaG

Table 1. The measurement condition for hydrogen permeability test.

Flow rate of Natural gas	Operation temperature	S/C	Pressure (process side)	Pressure (permeation side)	Operation
1.53 NL/min ($10.6\ Nm^3/h$)	550°C	3.0	0.8 MPaG	0 MPaG	Continuous

Table 2. The measurement condition for long term durability test.

The reforming reaction is an endothermic reaction and a temperature distribution occurs at the module. To minimize the temperature distribution, three heaters were controlled carefully and the temperature at the reactor top was controlled to be 550 °C over the whole test period.

4. Results and discussion

Figure 6 shows the results of the hydrogen permeability measurements for the conventional and the improved modules. These modules were operated at 550 °C during the measurements, which is almost the same operating temperature as in the 40 Nm^3/h-class reformer system. From the test, it was found that the hydrogen permeability of the improved module is 3% lower than that of the conventional module at the beginning of the tests. We consider that the difference is just within the individual difference of the module and is not due to the different preparation method. Both the modules show the same decreasing curve in view of hydrogen permeability in the initial period of the measurement. As mentioned below, for the conventional module, the leakage increased seriously when 3000 h passed and thus we stopped the measurement. As a result there are no data plotted after 3000 h. On the contrary, for the improved module, we could continue the measurement to 13000 h because no serious leakage was detected. Although the hydrogen permeation decreased rapidly with time at the begging of the measurement, the decreasing rate became gradual after 3000 h operation. Thus it was found that the degradation rate on the hydrogen permeation is almost the same for both the modules and it is steep only in the initial period**.**

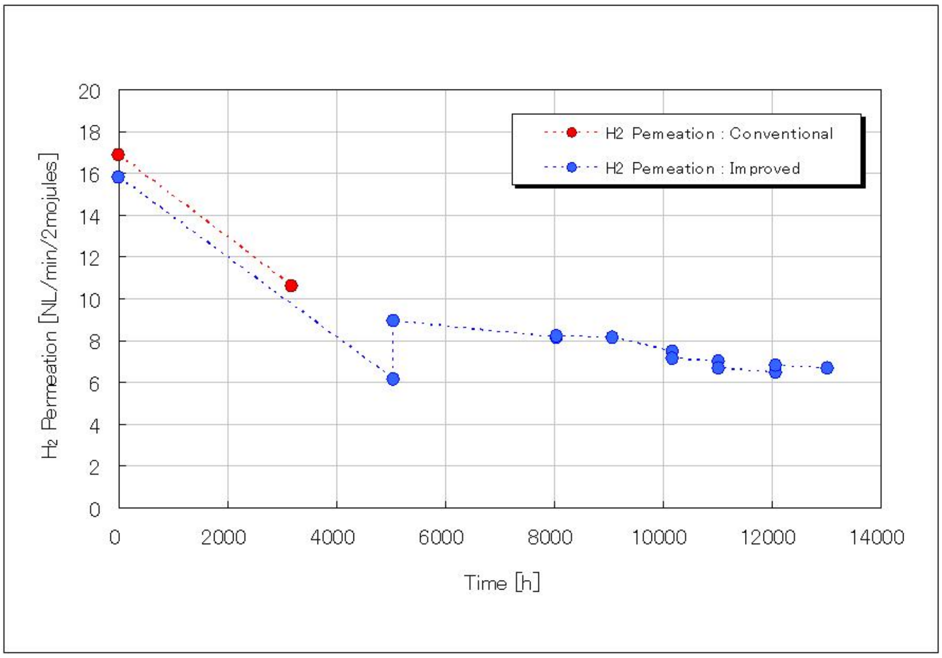

Fig. 6. The results of hydrogen permeability measurement.

Next, we present the results of the long term hydrogen production tests for both modules. The leakage tests were also carried out periodically during the long term test. Before the long term test, no leakage was detected for both modules, indicating that there were no damages or pin holes in the modules. Fig. 7 shows the change of the hydrogen production rate and leakage with time for both modules. The change of the measured concentration of the impurity gases in the produced hydrogen is also shown in Fig. 8. For the conventional module, a leakage of 0.5 Ncc/min was already detected after 958 h hydrogen production test and it increased to 8.8 Ncc/min at 3167 h. The purity of the produced hydrogen was lower than 99.99% (4N) at that time, and thus we gave up continuing the measurement. For the improved module, the initial hydrogen production rate is 10% lower than that of the conventional module. As mentioned above, we also consider that this difference is within the individual difference for the modules.

The hydrogen production rates for both modules decreased similarly with time. At 1500 h the hydrogen production rates were almost 10% lower than those of the initial values for both modules. After 1500 h hydrogen production tests, the decreasing curve of the hydrogen production rate became gradual and at 13000 h the hydrogen production rate was about 72% of the initial value. Although the reason of the degradation of the performance on the hydrogen production is not clear now, it would be related to the degradation of the hydrogen permeability of the membrane. The reason is that the hydrogen permeability directly affects the hydrogen production rate and the hydrogen permeability of the membrane also decreased with time as shown in Fig. 6. We are now investigating the mechanism of the decrease of hydrogen permeability in the membrane modules.

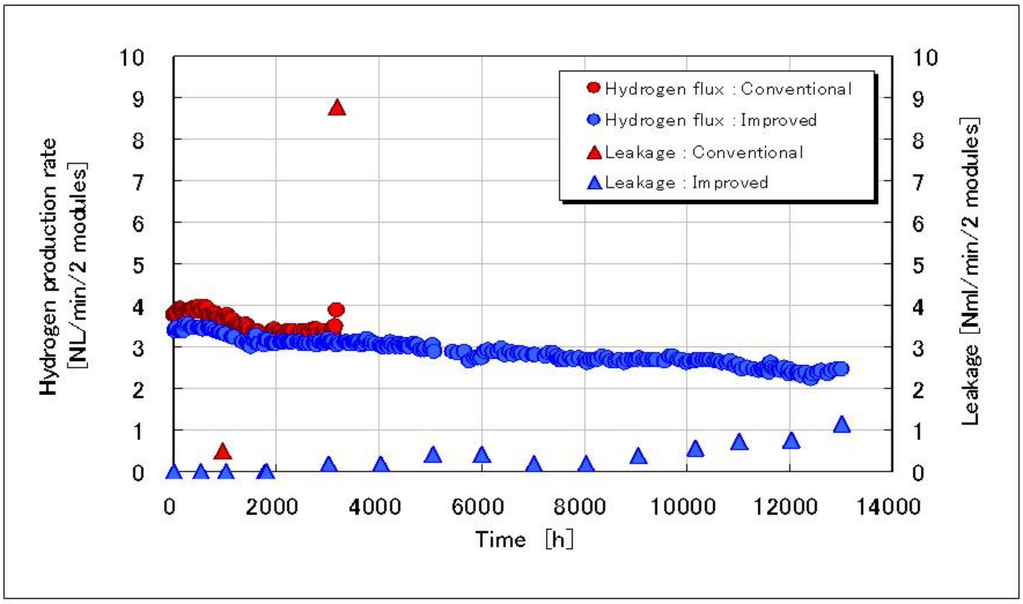

Fig.7. The change of hydrogen production rate and leakage.

From our past researches on the conventional module it was revealed that the concentrations of CO and CO_2 in the produced hydrogen increased significantly after 3000 h hydrogen production test. The increase of the impurity gases lowered the purity of the produced hydrogen and the purity of the hydrogen was less than 4N at 3000 h. To the contrary, for the improved module no impurity gases were detected even at 4000 h. Only after 4000 h operation, a minor leakage was detected and then the concentrations of CO and CO_2 increased gradually. After 13000 h operation, the leakage from the module was 1.14 Ncc/min and the amount of the impurities in the produced hydrogen was 19.7 ppm. These values were low enough and the purity of the produced hydrogen could be still maintained over 4N. Accordingly durability of the improved module in terms of the purity of the produced hydrogen was increased remarkably and it was confirmed that reduction of the impurities in the membrane is effective to improve the module durability.

5. Conclusion

We have been developing a membrane reformer which is a next-generation hydrogen production system. One of the important issues in the development of the membrane reformer is the durability of the membrane module. To obtain membrane modules with high durability, we fabricated the improved membrane module with higher-purity membrane material using the cold crucible process. From the long term durability test for the improved module, it was found that the purity of the produced hydrogen using the improved module maintained over 4N for 13000 h. Thus it was made
clear that purifying the membrane material is very effective to prevent the occurrence of leakage in the

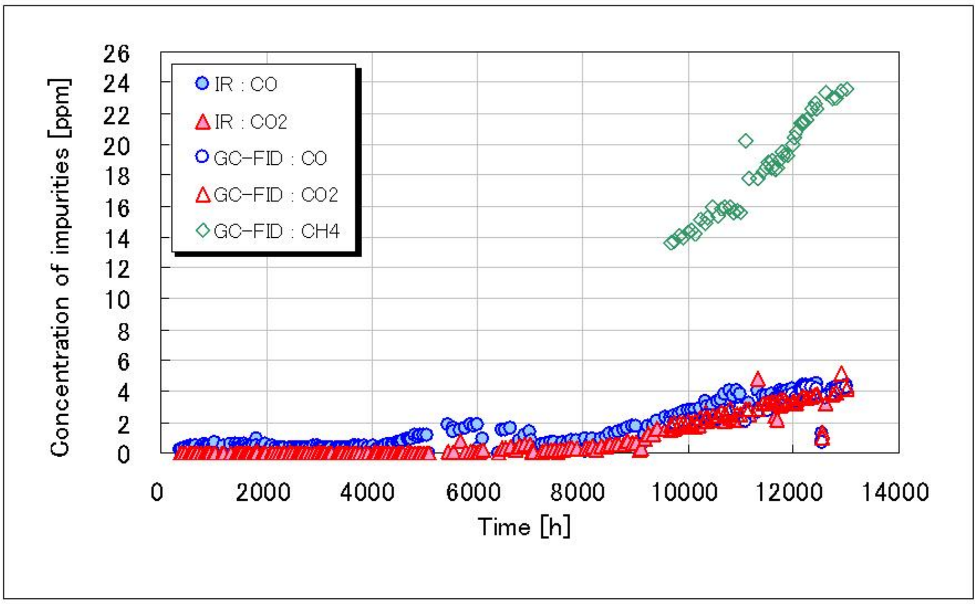

Fig. 8. The change of the measured concentration of the impurity gases in the produced hydrogen

membrane. On the other hand for both the conventional and the improved modules, it was revealed that the hydrogen production rate decreases with time. The decrease of the module performance would be related to the degradation of the hydrogen permeability and we are now investigating the mechanism of the decrease of the hydrogen production rate. We will obtain the prospect for the long term durability of the membrane module as soon as possible and will commercialize the membrane reformer system.

6. Acknowledgement

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