

## **Development of Compact and Efficient Hydrogen Production Module with Membrane on Catalyst**

### **Main author**

T. Kume  
Tokyo Gas Co., Ltd.  
Japan  
kume@tokyo-gas.co.jp

### **Co-author**

Y. Ikeda  
T. Iseki  
H. Yakabe  
H. Tanaka  
H. Hikosaka  
Y. Takagi  
M.Ito

## **ABSTRACT**

A new module of Pd-based membrane on catalyst (MOC) for hydrogen production has been developed. The MOC is based on a unique concept of combining the Pd-based membrane and catalysts for steam methane reforming (SMR). A thinner Pd-based membrane is fabricated on a catalytic substrate, and it is possible to lower the module cost by reducing the amount of Pd and applying the well-established mass-production technology.

The MOC module showed hydrogen production capability as high as the conventional hydrogen production membrane module, however, the purity of the produced hydrogen decreased rapidly in several ten hours. The main reason of the decrease of the hydrogen purity in a short time is an increase of leakage of the reformed gas into the permeated hydrogen. To improve the durability of the MOC and maintain the purity of the produced hydrogen, we modified the MOC manufacturing process to prevent the leakage. The 3 points were improved, (i) supporting tube structure and the production method (ii) sealing materials (iii) membrane penetration depth into the support. As a result of the improvement, the durability of the MOC is improved drastically and the purity of the produced hydrogen has been maintained over 99.99% for 1000 hours. The influence of the improvements against the hydrogen production capability of MOC was also discussed.

## **TABLE OF CONTENTS**

1. Abstract
2. Body of Paper
  - 2.1. Introduction
  - 2.2. MOC module
    - 2.2.1. Configuration of a MOC module
    - 2.2.2. Manufacturing method of the MOC module
    - 2.2.3. Configuration of a reactor
  - 2-3. Experimental
    - 2.3.1. Structural analysis of MOC
    - 2.3.2. Performance tests of the module
    - 2.3.3. Test of hydrogen permeability
    - 2.3.4. Test of reforming performance
  - 2.4. Results and Discussion
    - 2.4.1. Results of structure analysis for the MOC
    - 2.4.2. Hydrogen permeability
    - 2.4.3. Reforming performance
  - 2.5. Improvements of the durability of the MOC
    - 2.5.1. Improvement of the MOC module
    - 2.5.2. Change of the manufacturing method for supporting tube
    - 2.5.3. Improvement of the adhesion strength between membrane and porous support
    - 2.5.4. Coating of a blocking layer on the reactor vessel
    - 2.5.5. Performance of the improved MOC module
  - 2.6. Conclusion
3. Acknowledgements
4. Reference
5. List Tables
6. List of Figures

## 2.BODY OF PAPER

### 2.1. INTRODUCTION

Hydrogen is clean and environmentally friendly energy, and expected as a future alternative to fossil fuels. Though hydrogen can be produced from various resources, the hydrogen production using renewable energy will be general in the future. However, currently most hydrogen is produced from fossil fuels such as natural gas because it is a mature and cost effective technology [1]. Although CO<sub>2</sub> is emitted during the hydrogen production, in a transition phase to low carbon society, the hydrogen production from natural gas, because of lower CO<sub>2</sub> emission among fossil fuels, would be a main hydrogen production method.

Hydrogen is mainly used for transportation and stationary applications [2], [3]. On site hydrogen production from natural gas by steam reforming of methane is one of the most promising processes to produce hydrogen at hydrogen refueling stations. A combination of steam methane reforming (SMR) and purification with a pressure swing adsorption (PSA) is a typical hydrogen production system. In the early stage of the introduction of hydrogen refueling stations, the SMR+PSA system would be employed firstly because it had been 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. Hence more compact and highly effective hydrogen production systems used in urban areas are required.

Membrane reactors are hydrogen production systems using hydrogen permeable membrane, and are compact in size and highly efficient in the hydrogen production. Membrane reactors have been studied intensively as excellent apparatus for the production of hydrogen from hydrocarbon and alcohols [4], [5]. 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 [6-8]. The following two chemical reactions: steam reforming reaction and CO shift reaction, proceed in the membrane reactor.



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 a high methane conversion rate can be obtained even at a low temperature of around 550°C.

For these few years, laboratory tests of membrane reactors have been carried out in several institutes [9-11]. For example, Falco et al. developed a 20 Nm<sup>3</sup>/h prototype reformer and modules (RMM) plant where the reformer works at 550-650°C [9]. They showed that the methane conversion rate was approximately 57.3 % in the system. At Tokyo Gas, we have researched and developed

membrane reactors since 2000. In our previous work, we have developed a 40 Nm<sup>3</sup>/h class membrane reformer (MRF) system for pure hydrogen production from natural gas and have demonstrated that the system is more compact, more highly efficient, and simpler than the conventional hydrogen production systems with SMR+PSA. The detail of the MRF system has been reported elsewhere [11], [12].

Although the MRF system has demonstrated a high hydrogen production efficiency of 81.4%HHV, two significant issues must be solved for commercialization of the system. One is the durability of the membrane itself. For commercial MRF systems, a lifetime over several years is necessary. Both the hydrogen production rate and the purity of the produced hydrogen must be maintained at a high level over several years, and thus the membrane must be also durable over the lifetime. For these few years we have concentrated on establishing the long term durability of the membrane.

Another issue is the cost of the system. The main material of the membrane is a Pd-based alloy. Pd is a precious metal and thus the material cost of the membrane becomes expensive. For the reduction of the material cost, using other alternative materials to Pd or decreasing the amount of the Pd is effective. Yukawa et al. have been researching Nb-based hydrogen permeable membranes and shown that the Nb-based membranes exhibit excellent performance in the hydrogen permeability [13]. However, the stability and the durability of the Nb-based membrane under a high temperature reformed gas has not been proved yet and it will take further several years to apply the Nb-based membranes to a practical system. Accordingly, for early commercialization of the MRF system, the reduction of the amount of Pd used for the membrane is a realistic solution.

To reduce the membrane cost, we have started researches and developments of a hydrogen production module based on a new idea. Membrane on catalyst (MOC) is a unique concept of the combination of catalysts and a membrane, and has a potential to reduce the membrane cost significantly. In the present paper, we report the development of the MOC with focusing on the long term durability.

## **2.2. MOC module**

### **2.2.1. Configuration of a MOC module**

A thin membrane of a Pd-based alloy is fabricated on the porous support. In the MOC concept, the porous support itself has catalytic activity for the SMR reaction while the conventional MRF requires separated catalysts. The difference of the configuration between the conventional MRF module and the MOC module is illustrated in Fig. 1.

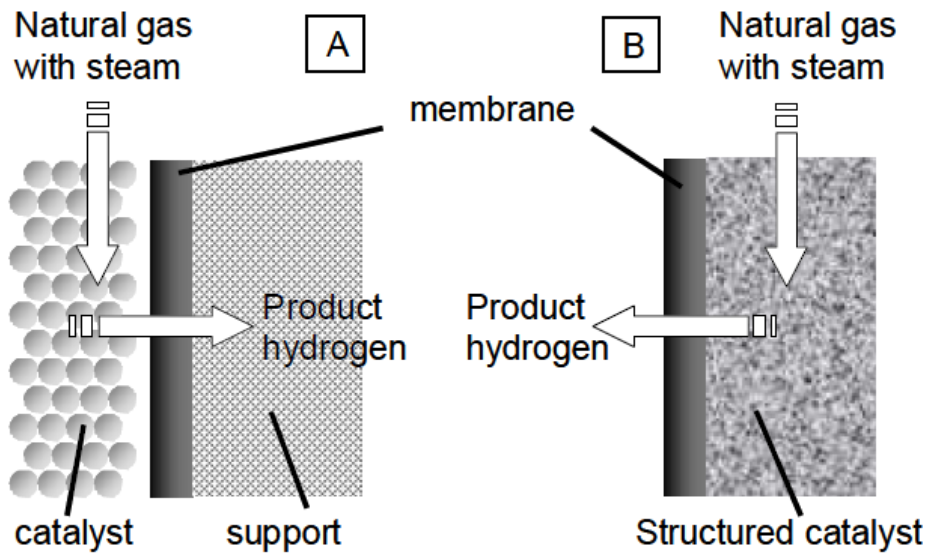


Fig.1 Configuration of the conventional MRF module and MOC module.

A: Conventional MRF module, B: MOC module.

The MOC has four advantageous features. Firstly, the membrane can be thinner by an excellent plating technique, resulting in a reduction of the amount of Pd and the module cost. Secondly, the support also works as catalysts and thus the module becomes more compact. Thirdly, the thin membrane can enhance the hydrogen permeability and the resulting hydrogen production performance. Fourthly, well-established mass production technologies can be applied for the production of the MOC, and thus the fabrication cost can be also reduced.

### 2.2.2. Manufacturing method of the MOC module

The typical manufacturing method of the MOC is as follows. Firstly, a one end closed tubular porous support is composed of Ni and 8YSZ (8 mol% Ytria- stabilized Zirconia). After NiO and 8YSZ raw powders are blended, the tubular support is molded with extrusion and then is sintered in air at 1400°C. Secondly, a barrier layer which prevents the inter-diffusion between Ni in the support and Pd in a hydrogen permeable membrane is formed on the surface of the porous support with dip coating of 8YSZ slurry and sintered in air at 1300°C. Thirdly, the Pd-alloy membrane is formed on the barrier layer with electro-less plating of Pd and Ag and alloying through subsequent heat treatment. Fourthly, the module is heat-treated in H<sub>2</sub> atmosphere at 600°C for 3 hours to reduce NiO in the support to Ni. Finally, a mechanical joint was attached to one end of the tubular module for connecting to a stainless pipe the module. The appearance of the MOC module is shown in Fig. 2.



Fig.2 Appearance of the extrusion-molded MOC module.

The fabricated MOC module has about 10 mm outer diameter, 100 mm or 300 mm length, approximately 30 cm<sup>2</sup> or 90 cm<sup>2</sup> membrane area, and 6 – 10 μm membrane thickness. The cross-sectional diagram of the MOC is indicated in Fig.3.

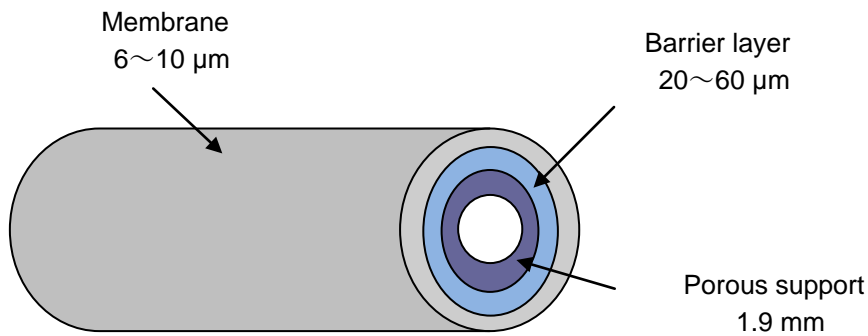


Fig.3 Structure of the MOC module.

### 2.2.3. Configuration of a reactor

A fuel-feeding tube is inserted into the MOC for introducing fuel. A reactor is composed of a stainless steel vessel and the MOC module inside the vessel as shown in Fig. 4.

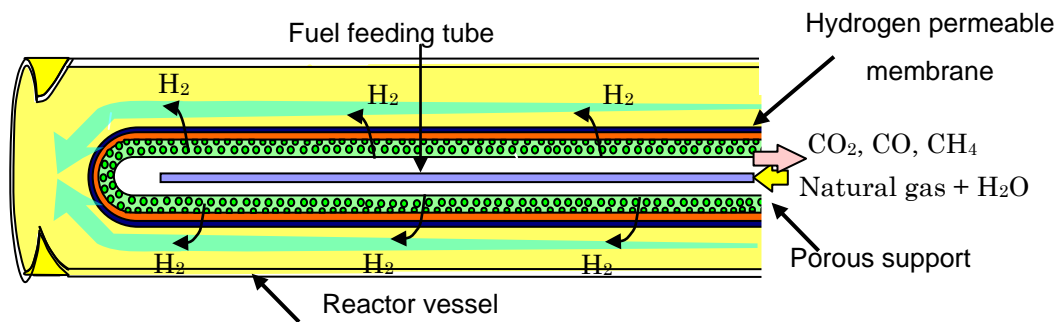


Fig.4 Schematic diagram of a reactor.

The introduced fuel through the fuel-feeding tube turns the flow at the closed end of the MOC, as being reformed inside the porous support along the stream. Hydrogen produced inside the porous support permeates the Pd-Ag membrane to the outside of the MOC module, passes between the module and the reactor vessel, and then is collected using a manifold. The off-gas inside the MOC module also goes out through the outlet manifold.

## 2.3. Experimental

### 2.3.1. Structural analysis of MOC

The structure of the fabricated MOC module was analyzed using analysis devices. The thickness of the membrane and the Ag ratio in the membrane was measured with the fluorescent X-ray membrane thickness meter at several points on the module. The thickness of the support, Pd-Ag membrane and Pd-Ag penetration into the porous ceramic support were measured using the scanning electron microscope (SEM) with the cross section of MOC module.

### 2.3.2. Performance tests of the module

The configuration of the apparatus used for performance tests is shown in Fig.5.

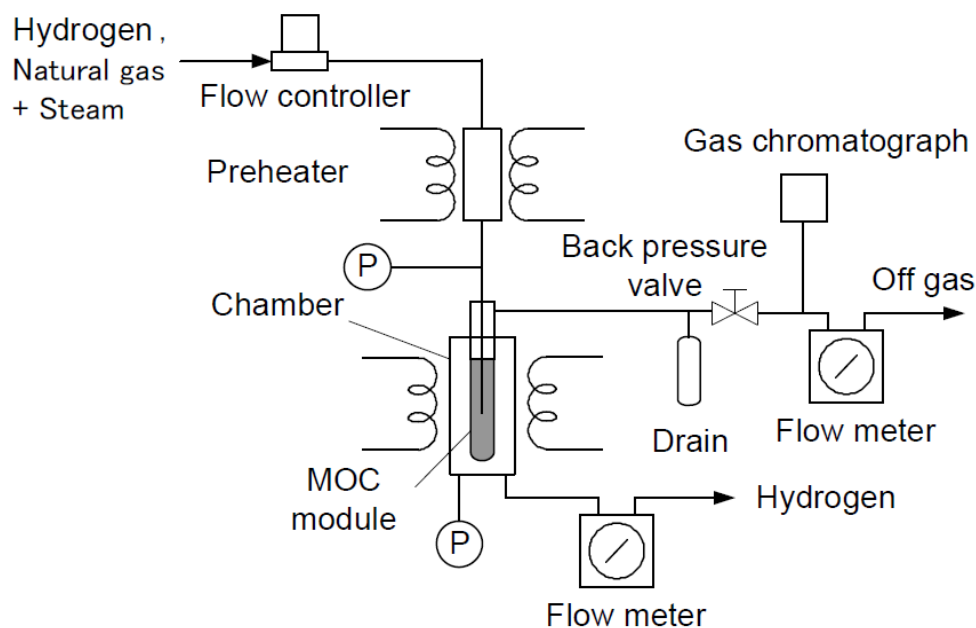


Fig.5 Schematic flow diagram of the experimental apparatus for hydrogen permeability and reforming performance tests for the MOC modules.

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. In the hydrogen permeation test, hydrogen flow was controlled with a mass flow controller and introduced inside the MOC module. The amount of the permeated hydrogen was measured with a wet gas meter. In the tests of fuel reforming, the flow rates of water and city gas were controlled with chemical pumps and mass flow controllers. The water was vaporized at a vaporizer, 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 inside of the MOC module. The pre-reforming catalysts prevents (i) a thermal shock at the module caused by the intensive endothermic reaction, (ii) carbon depositions coming from hydro carbons with more C<sub>2</sub> components, and (iii) a reverse permeation of hydrogen from the permeation side to the process side.



### 2.3.3. Test of hydrogen permeability

The temperature at the top of the MOC module was kept 550°C, and pure hydrogen was introduced into the inside of the MOC module at a pressure of 0.1 MPaG. The pressure at the permeation side of the MOC was set at 0.0 MPaG. The flux of hydrogen permeating through the membrane was measured by using the wet gas meter.

### 2.3.4. Test of reforming performance

In the test of reforming performance, 0.28 NLmin<sup>-1</sup> of natural gas was introduced into the pre-reforming catalysts at a S/C (Steam/Carbon) ratio of 3.0 and then the subsequently reformed gas was introduced into the inside of the MOC module. The reforming side pressure, permeation side pressure, and reaction temperature were set at 0.8 MPaG, 0.0 MPaG, and 550°C, respectively. The off gas at the reforming side was analyzed with a TCD (Thermal Conductive Detector) gas chromatography, and then the methane conversion ratio was calculated. The methane conversion was calculated with Eq.(3).

$$Conversion(\%) = \frac{C_{CO_2} + C_{CO}}{C_{CH_4} + C_{CO_2} + C_{CO}} \times 100 \dots (3)$$

The permeated gas was analyzed with an FID (Flame Ionization Detector) gas chromatography and thus the purity of the produced hydrogen was evaluated. The amount of the produced hydrogen was measured with the wet gas meter.

## 2.4. Results and Discussion

### 2.4.1. Results of structure analysis for the MOC

Membrane thickness of the MOC module was measured to verify the uniformity of the membrane. The measuring points are indicated in Fig.6 and the corresponding measured thickness and the Ag ratio of the fabricated membrane are shown in Table.1.

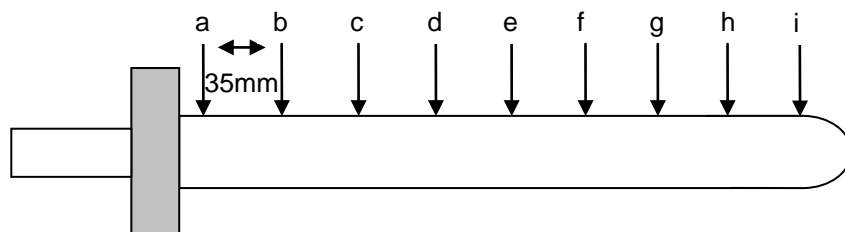


Fig.6 Measuring points at the membrane for thickness and Ag ratio.

Table.1 Measurement result of a fabricated module.  
(PdAg membrane thickness and Ag ratio in membrane)

Position	a	b	c	d	e	F	g	h	i	average
membrane thickness* ( $\mu\text{m}$ )	10.9	10.3	10.4	10.4	10.4	10.1	10.0	9.7	8.4	10.1
Ag ratio (wt%)	12.7	14.6	13.1	11.8	12.2	11.9	13.2	12.8	15.6	13.1

\*the thickness is the averaged value of those at circumferentially different 4 points.

The thickness of the membrane and the ratio of Ag in the membrane are around 10  $\mu\text{m}$  and 13%, respectively and uniform over the MOC. The other fabricated modules show almost the same values. From this measurement, it was proved that the fabricated membrane is homogeneous over the MOC.

#### 2.4.2. Hydrogen permeability

The specification of the module used for the hydrogen permeation test is listed in Table.2.

Table.2 Specification of the extrusion molded type MOC module used for  
the hydrogen permeability test.

Length of the hydrogen permeation part	88.1 mm
Outer diameter	9.95 mm
Averaged membrane thickness	6.1 $\mu\text{m}$
Averaged Ag ratio	15.1 wt%

Before the performance tests, the amount of the leakage from the MOC module was measured with He for all the specimens. From the leakage test, it was found that each module show no measurable He leakage (the leakage is less than 0.2 Nmlmin<sup>-1</sup> at an inside pressure of 0.8 MPaG).

The result of the hydrogen permeability test for the extrusion-molded module is shown in Fig.7.

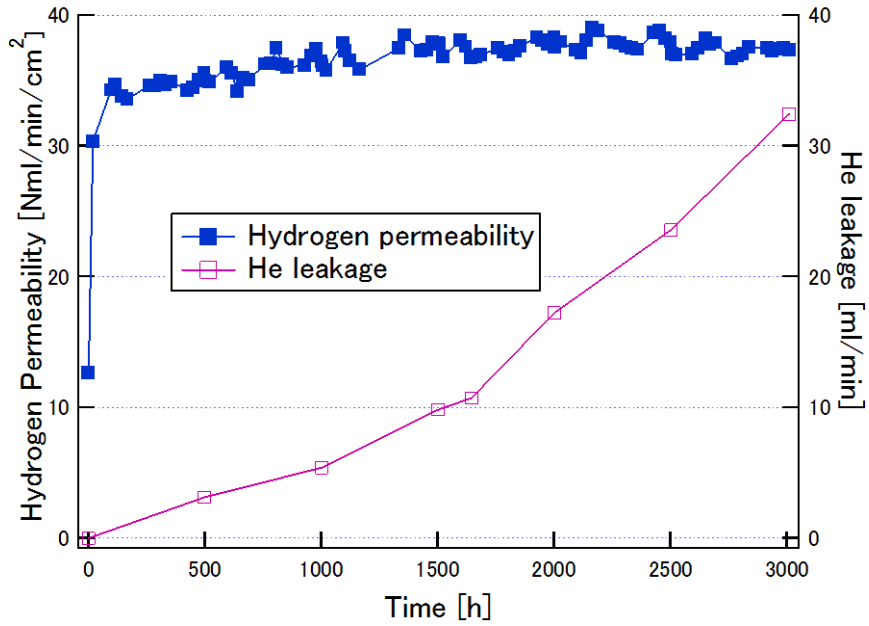


Fig.7 Hydrogen permeability for the extrusion-molded module and the He leakage from the module.

(Module : length is 100 mm、membrane thickness is 10.1 μm).

The hydrogen permeability is 35~40 Nmlmin<sup>-1</sup>cm<sup>-2</sup> and it is close to that of the conventional module used in the 40 Nm<sup>3</sup>/h class MRF system [11]. The permeability increases slightly with time at the beginning of the test and then maintains the same value for 3000 hours without significant changes. On the contrary to the stable hydrogen permeability, the He leakage increases gradually with time. After the 3000 hours test, we checked the He leakage from the module in water. From the leak check, it was found that there are many pin-holes over the membrane and He leaks through the pin-holes.

### 2.4.3. Reforming performance

The specification of the module used for the reforming test was listed in Table.3.

Table.3 Specification of the extrusion-molded MOC module used for the reforming test.

Length of the hydrogen permeation part	298.4 mm
Outer diameter	9.88 mm
Averaged membrane thickness	10.1 μm
Averaged Ag ratio	13.1 wt%

The result of the reforming test for the extrusion-molded module is shown in Fig.8.

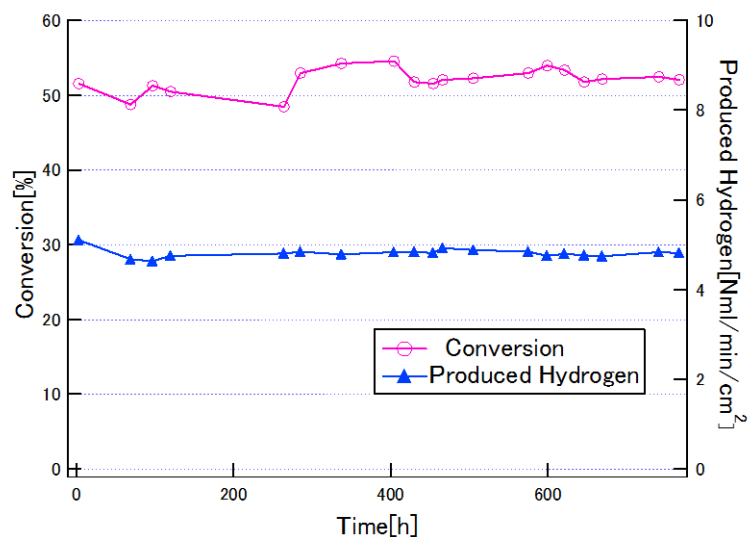


Fig.8 Reforming performance of the extrusion-molded module; squares: conversion, diamonds: produced hydrogen.

The extrusion-molded MOC module shows a hydrogen production capability over  $6.5 \text{ Nmlmin}^{-1}\text{cm}^{-2}$  and it can be increased to  $10 \text{ Nmlmin}^{-1}\text{cm}^{-2}$  by decreasing the pressure of the permeated side to  $-0.06 \text{ MPaG}$ . Moreover the conversion was approximately 50% while calculated equilibrium conversion without hydrogen separation is only 28% in this condition. The higher conversion is owing to shift equilibrium in the reforming reaction by separating hydrogen out of the reaction system, which is the advantage of the membrane reactor. This reforming performance is almost the same as that of the module used in the MRF system. The performance has not changed for 767 hours, suggesting that the Ni catalyst in the support and the membrane itself do not deteriorate during the test. On the contrary to the stable hydrogen production performance, the purity of the produced hydrogen decreases with time as shown Fig.9.

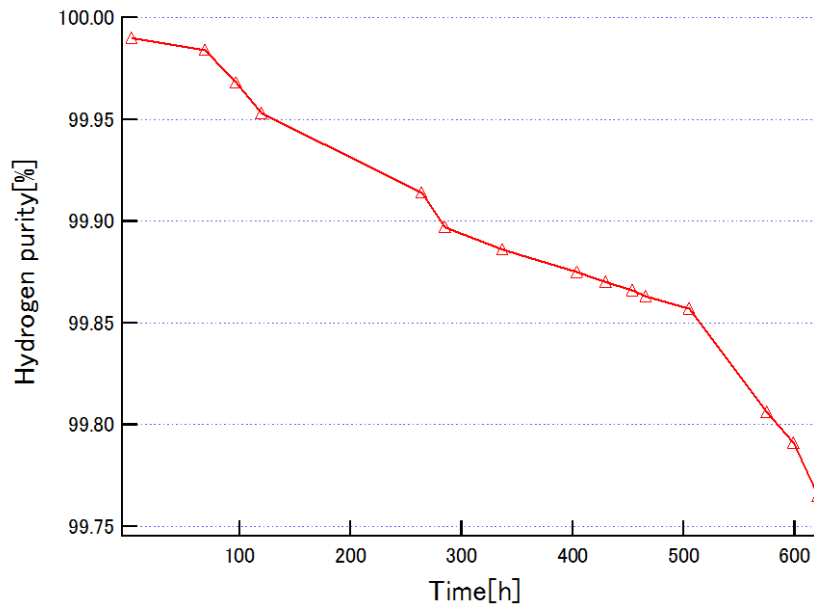


Fig.9 Change of the purity of the produced hydrogen for the MOC module.

From Fig. 9, we can see that the purity of the produced hydrogen over 99.99% is maintained only for several tens hours. The required criteria for the hydrogen purity is over 99.99% because the impurities such as carbon mono-oxide or carbon dioxide involved in the produced hydrogen damage cells in fuel cell vehicles (FCVs) [14-16]. Hence our current target value for the produced hydrogen purity is over 99.99 %. One reason for the poor durability of the extrusion-molded MOC module on the hydrogen purity is the weakness of the mechanical joint part. The other reason is that the depth of the penetration part of the membrane inside the porous support (2~4  $\mu\text{m}$ ) is insufficient and not uniform. The penetration depth is small at some points and this causes a de-lamination of the membrane from the support.

## 2.5. Improvements of the durability of the MOC

### 2.5.1. Improvement of the MOC module

In the early stage of the MOC development, we have demonstrated the high performance on the hydrogen production for the MOC. The present most significant issue is to establish the long term durability of the MOC. Especially, maintaining the high purity of the produced hydrogen for a long time is a serious problem. A leakage of the off gas into the produced pure hydrogen lowers the purity of the hydrogen. The main causes of the gas leakage are an insufficient connection between the MOC and the manifold pipe, a damage of the membrane, and a pin-hole in the membrane. In order to solve these problems, we have improved the MOC itself, the manufacturing method, and coated a blocking layer on the surface of the reactor vessel.

### 2.5.2. Change of the manufacturing method for supporting tube

The MOC is connected with the manifold pipe by the stainless joint using with compression fitting.

Because the support of the MOC is a porous tube and the mechanical strength is not so high, it is difficult to tighten the nut sufficiently. As a result, under thermal cycles, the fitting of the joint loosens and it leads to gas leakage. To clear this problem, we have changed the structure of the supporting tube and the production method from the extrusion molding to the press molding.

The purpose of the change is to increase the mechanical strength of the connection part. The press molding method enables to vary the composition of the support along the longitudinal direction. Thus the support of the press-molded MOC has three parts: a hydrogen permeation part, a functional gradient part, and a dense connection part as shown in Fig.10.

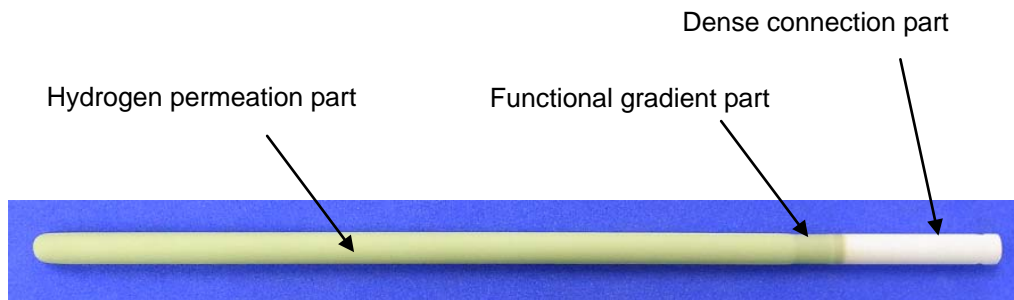


Fig.10 Appearance of the porous support fabricated by the press molding.

The hydrogen permeation part is a porous substrate and consists of NiO and 8YSZ similarly to the extrusion-molded MOC. The dense connection part is only made of YSZ and not porous. The composition of the functional gradient part is the mixture of the hydrogen permeation part and the dense connection part. This part has a role to connect the hydrogen permeation part and the dense part smoothly, and reduce thermal stresses due to a difference of the thermal expansion behavior of the both parts. The dense part has a high mechanical strength and it is possible to tighten the nut more strongly, compared to the case of using the extrusion-molded support. Besides, a glass is newly placed between compression materials as a sealing assistant material. The glass transition of this is nearly the operation temperature and its viscosity assists the sealing performance. Figure 11 shows the image of the modified MOC module manufactured by the press-molding.



Fig.11 Appearance of the press-molded MOC module.

To verify the sealing performance of the new supporting tube and the glass seal, we carried out a gas leakage test using the dense 8YSZ tube fabricated by press-molding. Because the dense 8YSZ does not permeate any gas, only the sealing performance at the connection part is examined. The

specification of the used test module is listed in Table 4.

Table.4 Specification of the module used to evaluate sealing performance.

Module length	215.7 mm
Outer diameter	10mm
Length of the 8YSZ part	126.3mm

In this test, pre-reformed gas at 600°C was introduced into the inside of the test module at 0.8 MPaG, and the pressure of the outside was set at -0.06 MPaG. At the outside of the test module pure nitrogen was flowed at a flux rate of 1.0 Lmin<sup>-1</sup> as a carrier gas. The test module temperature was kept at 550°C and the gas composition outside was measured with an FID gas chromatography. The result of analysis on the gas composition outside the module is shown in Fig. 12.

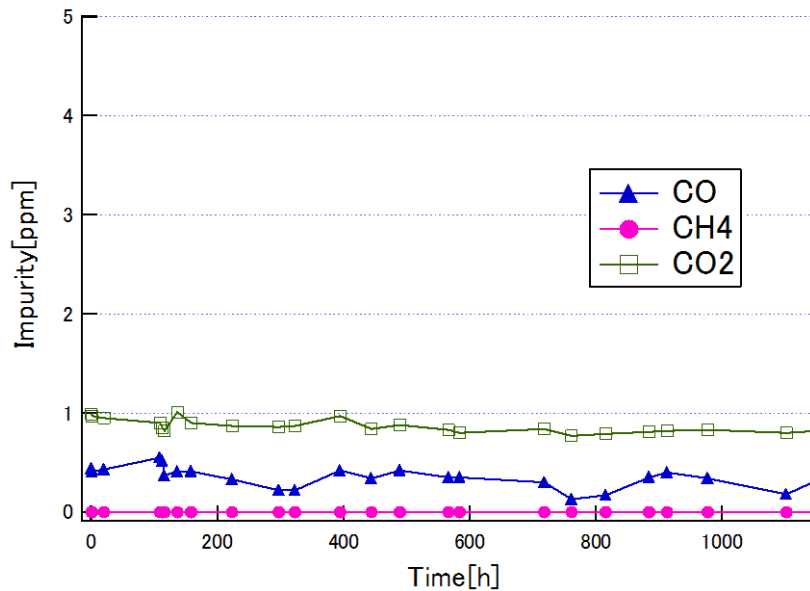


Fig.12 Evaluation test for the sealing performance.

Leaking gas composition at the outside of the module was analyzed.

This result shows that there is no significant change of the impurity concentration in the nitrogen over 1000 h and the effectiveness of the new support and joint is proved.

### 2.5.3. Improvement of the adhesion strength between membrane and porous support

A thin membrane is fabricated outside the supporting tube and under usual operations of the MOC, a high pressure is applied inside the supporting tube. The pressure would peel the membrane off the support. To avoid the de-lamination of the membrane, a part of the membrane was penetrated into the porous support deeply. Such structure enhanced the anchor effect. Figure 13 displays the comparison of the developed structure and the previous one.

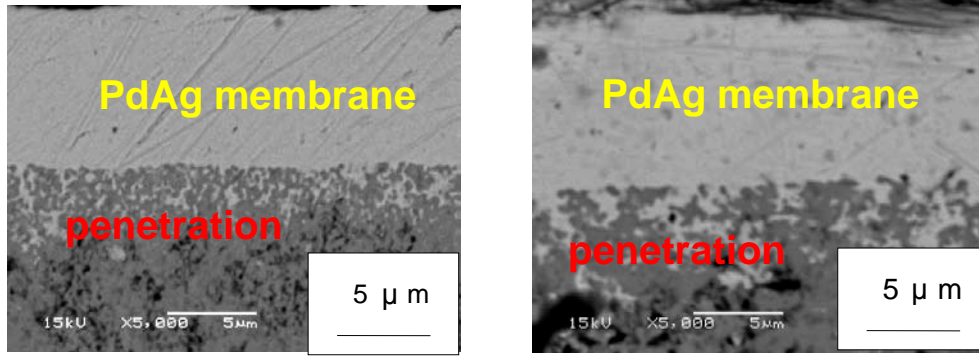


Fig.13 Increase of the anchor depth. (left : previous support, right : modified support)

The penetration depth of the membrane metal is increased from 2~4 μm to 5~10 μm and the membrane was not peeled off under usual operations.

#### 2.5.4. Coating of a blocking layer on the reactor vessel

David et al. [17] clarified that the Kirkendall void is one of the main reasons which cause a pin-hole in the membrane. If some metal impurities are put on the surface of the membrane, the metal impurities and Pd counter-diffuse each other under a reforming condition. The difference in diffusion rates of the impurity metal and Pd causes Kirkendall voids. The impurities, in the present case, are Fe, Cr, or Ni contained in the vessel and the joint.

In order to prevent the emissions of impurity particles from the reactor vessel or mechanical joints, Ag or Al was coated on the surfaces of the reactor vessel and the joint with a plating method. For example, Al, plated at 700°C, was heated at 1500°C to be alloyed with the stainless steel of vessel or joint, subsequently was did at 800°C to be converted to Al<sub>2</sub>O<sub>3</sub>. By these treatments, the resistance of the stainless steel against heat, corrosion and abrasion is enhanced.

The effect of the surface treatments for the vessel on blocking the emission of impurities from the vessel was evaluated through a hydrogen permeation test. The specification of the used MOC module is listed in Table 5.

Table.5 Specification of the module used for the test to evaluate the coating effect for the reactor vessels.

Specification	Reactor vessel		
	no coating	Ag-coating	Al-coating
hydrogen permeation part	297.5 mm	297.7 mm	271.2 mm
Outer diameter	9.94 mm	10.04 mm	10.37 mm
averaged membrane thickness	9.4 μm	9.3 μm	9.4 μm
averaged Ag ratio	16.6 wt%	16.8 wt%	15.4 wt%

H<sub>2</sub>/He (0.9Lmin<sup>-1</sup>, 0.6Lmin<sup>-1</sup>) mixed gas was introduced into the outside of the MOC module at a



pressure of 0.8 MPaG and the inside pressure was set at 0.0 MPaG. In this test, we controlled the operation temperature at 600°C which was higher than that of the reforming performance test to accelerate the degradation of the membrane. The hydrogen permeation test was carried out continuously, and periodically a He leak check was conducted. In the He leak check, pure He was introduced outside the MOC at 0.8 MPaG and the flow rate of leaking He inside the MOC was measured at 0.0 MPaG with a film flow meter. If the membrane is damaged by emissions of the impurities from the reactor vessels, the amount of the leaking He increases.

Figure 14 shows the results of the He leak tests conducted with three different vessels: no-coating, Ag-coating and Al-coating.

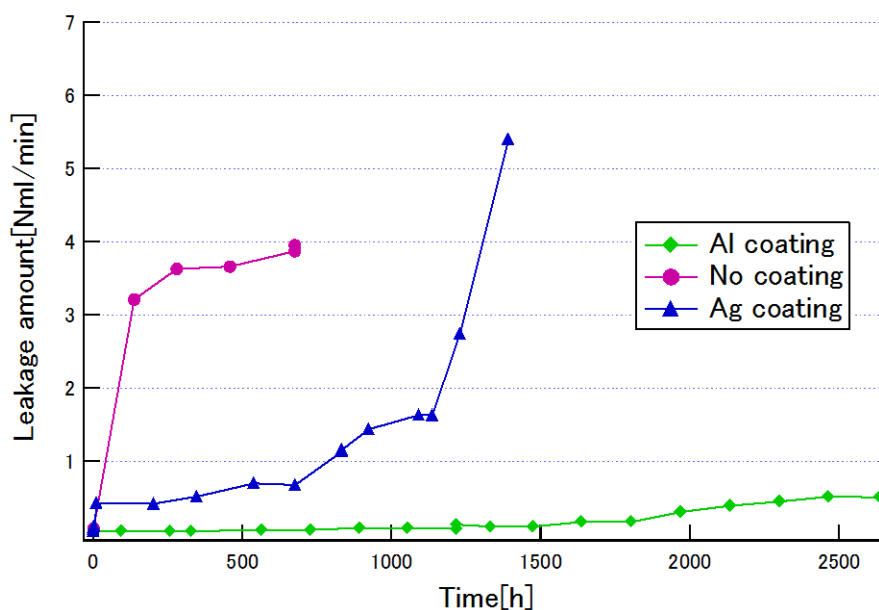


Fig.14 Results for the leak check test of the effect of coating on the vessels. 3 different vessels: no-coating, Ag-coated , and Al-coated were evaluated.

We can see that the leakage of He increases drastically in 1000 hours for no coating and Ag-coated vessels. SEM measurement carried out after the leakage tests revealed that the main reason of the increase of the leakage is pin-holes on the surface of the membrane. These pin-holes are caused by the adhesion of Fe and Cr particles flying from the reactor vessel to the membrane surface. For the Al-coated vessel, the He leakage does not increase over 2000 hours. This means that the Al-coating (result in alumina coating) prevented the emission of the impurity particles from the surface of the vessel. Hence we could confirm the effectiveness of the Al-coating and the relating surface treatment for the vessel on the prevention of the Kirkendall void, and hereafter all the tests are performed using the MOC modules with the Al-coated reactor vessels.

### 2.5.5. Performance of the improved MOC module

The hydrogen permeability of the new module was examined. The specification of the module is listed in Table.6.

Table.6 Specification of the improved press-molded module used for the performance test.

Length of the hydrogen permeation part	272.3 mm
Outer diameter	10.43 mm
Averaged membrane thickness	9.4 $\mu\text{m}$
Averaged Ag ratio	17.4 wt%

The measured hydrogen permeability of the module was less than  $17 \text{ Nmlmin}^{-1}\text{cm}^{-2}$ . This value was lower than that of the extrusion-molded module. One reason of this low permeability would be the deeper penetration depth of the membrane in press-molded module than that of the extrusion-molded module. Because the deeper penetration is necessary to avoid the de-lamination of the membrane, it is better to make the membrane thin except the penetration part. The hydrogen pathway through the membrane in the press-molded module was longer than that of the extrusion-molded module due to the deeper penetration

Next, the reforming performance of the press-molded module was evaluated under the same condition as the test for the extrusion-molded module. The same module used for the permeability test was employed in the present test. The result of the test is shown in Fig. 15.

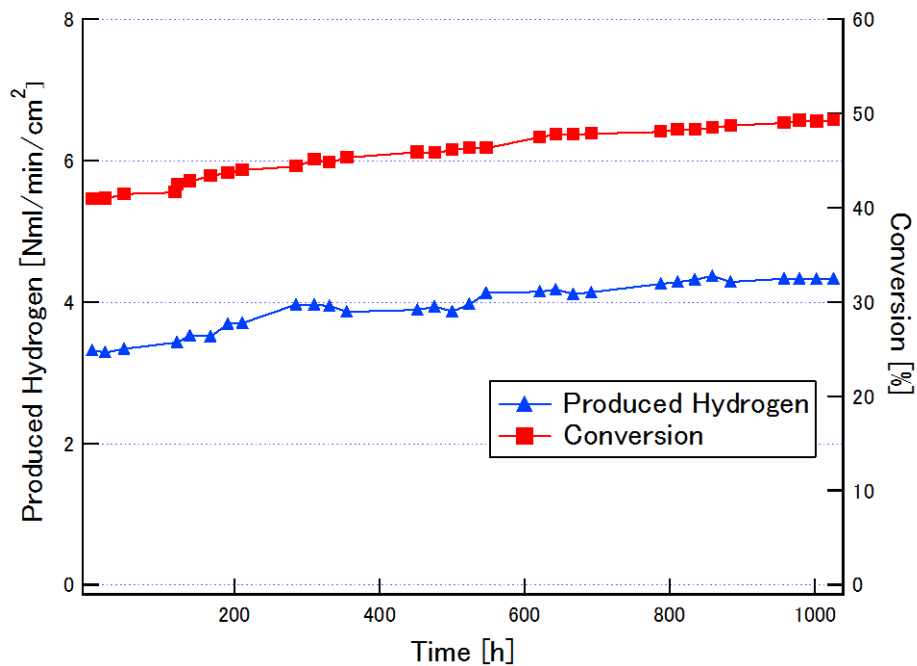


Fig.15 Result of the reforming test with the press-molded module;  
 Square: Conversion, Diamond : produced hydrogen

The amount of the produced hydrogen is less than that of the extrusion-molded module. In addition, the fuel conversion rate is also lower than that of the extrusion-molded module. One reason of

this low performance is the low permeability of the membrane coming from the deeper penetration. Another reason is a low catalytic activity of the support. For the press-molded module, NiO content in the support was reduced from 60 wt% for the extrusion-molded module to 20 wt% to suppress a sintering of Ni under hydrogen atmosphere at high temperature. However, the less volume of Ni would have caused the lower performance on the reforming reaction. To obtain high catalytic activity of the support, it is better to reconsider the Ni content again, change the particle size of the raw powder, and optimize the microstructure of the support.

From Fig. 15, it is found that the hydrogen production rate and the fuel conversion rate increase gradually with time. Although the exact reason has been unclear yet, it must be related to the increase of the hydrogen permeability of the membrane with time. Because, after the reforming test, we confirmed that the hydrogen permeability also increased to 26.5 Nml/min/cm<sup>2</sup> from 23.5 Nml/min/cm<sup>2</sup> at the beginning. We consider that the increase of the hydrogen permeability with time is due to a release of residues in the membrane with time. After the plating, some residues stay in the membrane and they inhibit the hydrogen permeation. The residues would be removed during the long term reforming test and as a result the hydrogen permeability increases. We will analyze the membrane part in detail to clear the reason of the increasing of the performance.

The change of the purity of the produced hydrogen with time is shown in Fig.16.

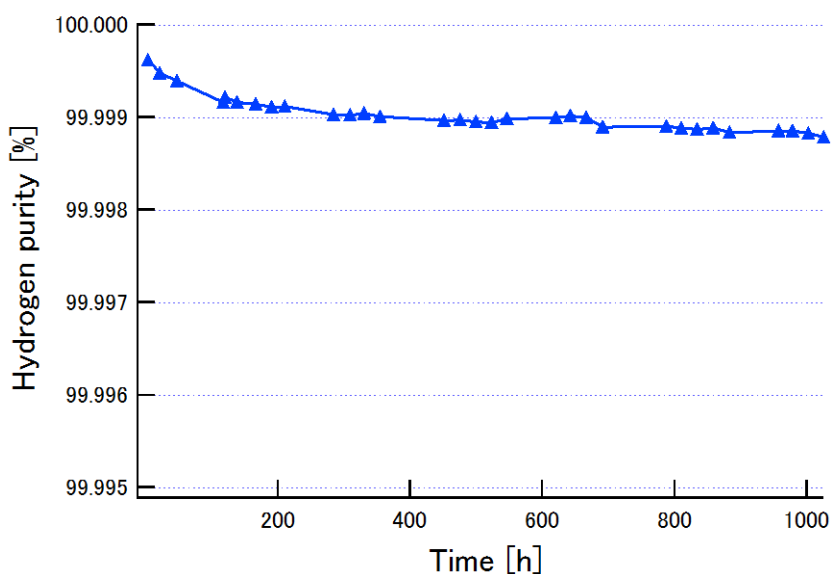


Fig.16 Change of the purity of the produced hydrogen using the press-molded module.

This measurement made clear that the purity of the produced hydrogen was over 99.999% at the beginning of the test and maintained over 99.99 % for 1000 hours. Hence we could confirm that the durability of the module concerning the hydrogen purity is indeed improved by the present modifications of the MOC. We will continue the long term test over 8000 h.

As mentioned above, the durability of the MOC was remarkably improved, but the reforming performance of the MOC decreases. It is required to satisfy both the performance and the durability,

and thus we will modify the MOC module more. Preparing thinner membrane enhances the hydrogen permeability, and increasing NiO in the support encourages the catalytic activity. We will try these two methods as a next step. In addition, to accelerate the development of the membrane reactor, we will prepare a small size reformer with the modified MOC modules, and evaluate the performance and the durability of the reformer as soon as possible.

## 2.6. Conclusion

We have developed a new concept hydrogen production module of membrane on catalyst (MOC) to reduce the module cost. The characteristic of the MOC is that the Pd-based membrane is fabricated on the catalytic support. Although the MOC module fabricated by the extrusion molding method had enough hydrogen production capability as high as the conventional module used in the MRF, the long term durability of the module was not enough. To improve the durability of the MOC on the hydrogen purity we changed the configuration of the support and the relating fabrication method, strengthened the connection between the support and the membrane, employed a glass sealing at the joint, and coated the barrier layers on the surface of the reactor vessel. Consequently the durability of the module has been increased significantly. The high purity of the hydrogen produced by new concept hydrogen production module over 99.99% has been maintained over 1000 h. The performance of hydrogen producing had decreased although the hydrogen purity in the long term increased. Both the performance and the durability must be satisfied, and thus we will modify the MOC module more.

## 3. Acknowledgement

This work was supported by the New Energy and Industrial Technology Development Organization (NEDO). The authors acknowledge their financial and technical supports. The authors are also very grateful to coworkers at Tokyo Gas Co., Ltd.; Dr. Isamu Yasuda of the former manager and Mr. Yoshinori Shirasaki of the former leader for their energetic promotion of the MOC development in the early stage of the development, Mr. Tsutomu Tokumoto of the current manager for his appropriate management, Mr. Tatsuya Tsuneki and Mr. Takumi Nishii for their helpful support and advice.

## 4. Reference

- [1] Nobuhiro Iwasa, Toshiyuki Yamane, Masaaki Takeji, Jun-ichi Ozaki, Masahiko Arai, Hydrogen production by steam reforming of acetic acid: Comparison of conventional supported metal catalysts and metal-incorporated mesoporous smectite-like catalysts, *International Journal of Hydrogen Energy*, Volume 35, Issue 1, January 2010, Pages 110-117.
- [2] J. Lu, Z.Z. Fang and H.Y. Sohn, A hybrid method for hydrogen storage and generation from water, *J Power Sources* **172** (2007), pp. 853–858.
- [3] Richard Toonssen, Nico Woudstra, Adrian H.M. Verkooyen, Exergy analysis of hydrogen production plants based on biomass gasification, *International Journal of Hydrogen Energy*, Volume 33, Issue 15, August 2008, Pages 4074-4082.

- [4] Silvano Tosti, Overview of Pd-based membranes for producing pure hydrogen and state of art at ENEA laboratories, *International Journal of Hydrogen Energy*, Volume 35, Issue 22, Bio-Ethanol and Other Renewable Sources and Reforming Process for Sustainable Hydrogen Production, November 2010, Pages 12650-12659.
- [5] P. Ferreira-Aparicio, M. Benito, K. Kouachi, S. Menad, Catalysis in membrane reformers: a high-performance catalytic system for hydrogen production from methane, *Journal of Catalysis*, Volume 231, Issue 2, 25 April 2005, Pages 331-343.
- [6] M.L. Bosko, J.F. Munera, E.A. Lombardo, L.M. Cornaglia, Dry reforming of methane in membrane reactors using Pd and Pd-Ag composite membranes on a NaA zeolite modified porous stainless steel support, *Journal of Membrane Science*, Volume 364, Issues 1-2, 15 November 2010, Pages 17-26.
- [7] Alexander S. Augustine, Yi Hua Ma, Nikolaos K. Kazantzis, High pressure palladium membrane reactor for the high temperature water-gas shift reaction, *International Journal of Hydrogen Energy*, Volume 36, Issue 9, May 2011, Pages 5350-5360.
- [8] L. Coronel, J.F. Munera, E.A. Lombardo, L.M. Cornaglia, Pd based membrane reactor for ultra pure hydrogen production through the dry reforming of methane. Experimental and modeling studies, *Applied Catalysis A: General*, In Press, Accepted Manuscript, Available online 30 April 2011.
- [9] M. De Falco, G. Iaquaniello, A. Salladini, Experimental tests on steam reforming of natural gas in a reformer and membrane modules (RMM) plant, *Journal of Membrane Science*, Volume 368, Issues 1-2, 15 February 2011, Pages 264-274, ISSN 0376-7388.
- [10] Angelo Basile, Stefano Campanari, Giampaolo Manzolini, Adolfo Iulianelli, Tiziana Longo, Simona Liguori, Marcello De Falco, Vincenzo Piemonte, Methane steam reforming in a Pd-Ag membrane reformer: An experimental study on reaction pressure influence at middle temperature, *International Journal of Hydrogen Energy*, Volume 36, Issue 2, The 3rd Annual Korea-USA Joint Symposium on Hydrogen & Fuel Cell Technologies, January 2011, Pages 1531-1539.
- [11] Y. Shirasaki, T. Tsuneki, Y. Ota, I. Yasuda, S. Tachibana, H. Nakajima, K. Kobayashi, Development of membrane reformer system for highly efficient hydrogen production from natural gas, *International Journal of Hydrogen Energy*, Volume 34, Issue 10, 2nd World Hydrogen Technologies Convention, 2nd World Hydrogen Technologies Convention, May 2009, Pages 4482-4487, ISSN 0360-3199.
- [12] Shirasaki Y, Tsuneki T, Yasuda I, Tachibana S, Nakajima H, Kobayashi K. Development of membrane reformer system for highly-efficient hydrogen production from natural gas. *Proceedings of HYPOTHESIS VII*, CD-ROM, Media, Mexico, March 27-29, 2007.
- [13] Y. Awakura, T. Nambu, Y. Matsumoto, H. Yukawa, Hydrogen solubility and permeability of Nb-W-Mo alloy membrane, *Journal of Alloys and Compounds*, In Press, Corrected Proof, Available online 4 November 2010, ISSN 0925-8388.
- [14] Ahluwalia RK, Wang X. Effect of CO and CO<sub>2</sub> impurities on performance of direct hydrogen polymer-electrolyte fuel cells. *J Power Sources* 2008;180:122–31.
- [15] Thampan T, Rocheleau R, Bethune K, Wheeler D. Effect of trace contaminants on PEM fuel cell

performance. In: 2005 MRS Fall Meeting. Boston, MA, United States: Materials Research Society, Warrendale, PA 15086, United States; 2006, pp. 21–31.

[16] Hajbolouri F, Andraus B, Scherer GG, Wokaun A. CO Tolerance of commercial Pt and PtRu Gas diffusion electrodes.

[17] David J. Edlund, Jack McCarthy, The relationship between intermetallic diffusion and flux decline in composite-metal membranes: implications for achieving long membrane lifetime, *Journal of Membrane Science*, Volume 107, Issues 1-2, 15 November 1995, Pages 147-153

## 5. List Tables

Table 1 Measurement result of a fabricated module. (PdAg membrane thickness and Ag ratio in membrane)

Table 2 Specification of the extrusion molded type MOC module used for the hydrogen permeability test.

Table 3 Specification of the extrusion-molded MOC module used for the reforming test.

Table 4 Specification of the module used to evaluate sealing performance.

Table 5 Specification of the module used for the test to evaluate the coating effect for the reactor vessels.

Table 6 Specification of the improved press-molded module used for the performance test.

## 6. List of Figures

Fig.1 Configuration of the conventional MRF module and MOC module. (A: Conventional MRF module, B: MOC module)

Fig.2 Appearance of the extrusion-molded MOC module.

Fig.3 Structure of the MOC module.

Fig.4 Schematic diagram of a reactor.

Fig.5 Schematic flow diagram of the experimental apparatus for hydrogen permeability and reforming performance tests for the MOC modules.

Fig.6 Measuring points at the membrane for thickness and Ag ratio.

Fig.7 Hydrogen permeability for the extrusion-molded module and the He leakage from the module. (Module : length is 100 mm, membrane thickness is 10.1  $\mu\text{m}$ ).

Fig.8 Reforming performance of the extrusion-molded module; squares: conversion, diamonds: produced hydrogen.

Fig.9 Change of the purity of the produced hydrogen for the MOC module.

Fig.10 Appearance of the porous support fabricated by the press molding.

Fig.11 Appearance of the press-molded MOC module.

Fig.12 Evaluation test for the sealing performance. Leaking gas composition at the inside of the module was analyzed.

Fig.13 Increase of the Pd-Ag penetration depth. (left : previous support, right : modified support).

Fig.14 Results for the test of the effect of coating on the vessels. 3 different vessels: no-coating, Ag-coated , and Al-coated were evaluated.

Fig.15 Result of the reforming test with the press-molded module; Square : conversion, Diamond : produced hydrogen.

Fig.16 Change of the purity of the produced hydrogen using the press-molded module.