1. Introduction

Infrastructures supplying large amount of hydrogen at low cost are essential to realize hydrogen society. At present, on-site hydrogen production from natural gas is one of the most promising pathways to supply hydrogen. As a matter of fact, Tokyo Gas Co., Ltd. and Taiyo Nippon Sanso Corporation have been demonstrating a 50 Nm³/h-class hydrogen refueling station for fuel cell vehicles in Tokyo (“JHFC Senju Hydrogen Station [1]”), which is based on SMR (Steam Methane Reforming) and PSA (Pressure Swing Adsorption). Although the SMR-PSA system is a proven technology, a more compact and more efficient system is required for commercial hydrogen refueling stations.

To meet these requirements, Tokyo Gas Co., Ltd. and Mitsubishi Heavy Industries, Ltd. have jointly developed a 40 Nm³/h-class MRF (Membrane Reformer) system [2-3]. Figure 1 shows the principle of the MRF system. In the MRF system, hydrogen generated by SMR of natural gas permeates through a hydrogen separation membrane module made of Pd-based alloy and a porous support. Since hydrogen generation and separation proceed simultaneously in a single reactor, the MRF system is simpler and more compact than the conventional SMR-PSA system. In addition, the MRF system can provide higher efficient and can lower reaction temperature down to 500–550 °C, since it is free from
limitations by chemical equilibrium. The 40 Nm$^3$/h-class MRF system has a package volume of only one-third of the conventional system, and it has 10-15 percentage points higher hydrogen production energy efficiency than the conventional system [2-3]. However, the 40 Nm$^3$/h-class MRF system has challenges to be overcome such as durability and facility cost. Especially, cost reduction of the hydrogen separation membrane module is the main challenge for the current system. In the present work, we have developed a new-concept hydrogen production module with membrane on catalyst (MOC) [4-8] for a compact and low-cost MRF system.

2. Advantages of the MOC module

The MOC module has two advantages over the current hydrogen separation module. One is its compactness. As shown in Figure 2, a porous support itself has the activity of reforming catalyst as well as a role of membrane support, and no separate reforming catalyst is required in a reactor. The other is that it is potentially low cost. The fabrication process of the MOC module is basically based on plating on a porous ceramic tube, and is suitable for mass production.

To be more specific, the fabrication process of the MOC module is roughly divided into three steps: 1) production of a porous support, 2) coating a barrier layer and 3) plating Pd-Ag alloy membrane. Firstly, 60 mass% NiO and 40 mass% YSZ (Yttria-Stabilized Zirconia) powders were blended and formed into a tube by extrusion or press molding. The porous support was produced by sintering the tube in air. Secondly, slurry of YSZ was dip-coated on the outer surface of the porous support and fired to form the barrier layer. The barrier layer is 20-60 $\mu$m in thickness and prevents interdiffusion between Pd-Ag in the membrane and Ni in the catalytic porous support. Thirdly, Pd and Ag films were electroless-plated on the barrier layer and subsequently heat-treated for alloying. The Pd-Ag membrane is 6-10 $\mu$m in thickness. Lastly, the MOC module is heat-treated in hydrogen atmosphere to reduce NiO in the porous support into Ni.

![Figure 2. Schematic Diagram of the MOC Module.](image-url)
Figures 3(a) and 3(b) are photographs of two types of the finished MOC module. One has the length of about 100 mm and the membrane area of about 30 cm$^2$, and the other has the length of about 300 mm and the membrane area of about 90 cm$^2$. Both types have the outer diameter of about 10 mm.

3. Project Target

We are developing new-type membrane reformer with the MOC module (MOC reformer) under a NEDO (New Energy and Industrial Technology Development Organization) project during fiscal year 2008-2012 (April 1, 2008 to March 31, 2013). This project is targeted at demonstrating over 8000 hours of durability with product hydrogen purity of more than 99.99 vol % by the end of fiscal year 2012 (March 31, 2013).

Cost of the MOC reformer depends on the sales volume. Figure 4 shows diffusion scenario on hydrogen refueling station and fuel cell vehicle in Japan. In this scenario, installations of commercial hydrogen refueling stations will start at 2015. The MOC reformer project targets facility cost of less than 300,000 JPY (3,000 USD) per Nm$^3$/h-H$_2$, and the MOC reformer is expected to be applied to commercial hydrogen refueling station after 2015.

Figure 4. Diffusion Scenario of Hydrogen Refueling Station and Fuel Cell Vehicle Roll-out [9].
4. Experiments

4.1 Experimental Setup

Hydrogen permeation performance and reforming performance of the MOC module were measured in an electrically heated chamber. Figure 5 shows the experimental setup for these tests.

In the hydrogen permeation performance test, we measured durability for long-term hydrogen permeation at 550 °C of the MOC module. The sample used in the test was 100 mm in length, 31.01 cm² in membrane area and 6.1 µm in membrane thickness. We supplied pure hydrogen into the MOC module at the pressure of 0.1 MPaG and measured the flow rate of the permeated hydrogen at 0.0 MPaG (ambient pressure). During this test, helium was introduced instead of hydrogen to check the leakage in the MOC module.

In the reforming performance tests, we measured temperature dependence of the reforming performance and durability for long-term reforming at 550 °C of the MOC module. The sample used in the tests was 300 mm in length, 93.34 cm² in membrane area and 7.3 µm in membrane thickness. The natural gas we used in the tests was composed of methane (89.6 vol %), ethane (5.6 vol %), propane (3.4 vol %) and butane (1.4 vol %). We supplied the natural gas at the flow rate of 280 Nm³/min (3.0 Nm³/min/cm²) with S/C (Steam to Carbon ratio) of 3.0. Since the MOC module requires a pre-reformer for ethane, propane, butane and higher hydrocarbons as most SMR reactors do, we introduced pre-reformed natural gas, not natural gas and steam, into the MOC module. The process side pressure was set at 0.8 MPaG, and the permeate side pressure was set at 0.0 MPaG or -0.06 MPaG. The flow rates of off-gas and product hydrogen were measured by gas meters, and the composition of off-gas and the purity of product hydrogen were measured by gas chromatograph.

![Figure 5. Experimental Setup for Performance Tests.](image-url)
4.2 Experimental Results

Figure 6 shows the experimental result of the hydrogen permeation test. The red diamond plots the permeated hydrogen flux vs. total permeation time, and the yellow triangle plots the leaked helium flux vs. total permeation time. As shown in the figure, hydrogen permeation performance was stable over 3000 hours. However, leakage increased as time.

Figures 7(a) and 7(b) show the experimental results of the temperature dependence of the reforming performance at the permeate side pressure of 0.0 MPaG (a) and -0.06 MPaG (b). The reforming performance is plotted in terms of the product hydrogen flux (red diamonds), the hydrogen recovery (orange open squares) and the conversion (green open diamonds). The conversion is much higher than the equilibrium conversion shown in the green curve. This means the membrane reformer functioned successfully in producing hydrogen without limitation of chemical equilibrium. In the best case where the permeate side pressure was -0.06 MPaG and the temperature was 546.5 °C, the product hydrogen flux was as high as 11.3 Nml/min/cm$^2$ (excluding leakage), and the conversion was as high as 87.8%.

Figure 8 shows experimental results of the durability test for long-term reforming at 550 °C. The red diamond plots the product hydrogen flux vs. total reforming time, the

![Figure 6. Results of Long-Term Hydrogen Permeation Test.](image)

![Figure 7. Temperature Dependence of the Reforming Performance](image)

(a) Permeate side pressure of 0.0 MPaG

(b) Permeate-side Pressure of -0.06MPaG

(Figure 7. Temperature Dependence of the Reforming Performance
(Natural gas input: 3.0 Nml/min/cm$^2$, S/C: 3.0)
green open diamond plots conversion vs. total reforming time, and the yellow triangle plots impurity level in the product hydrogen vs. total reforming time. As shown in the figure, the product hydrogen flux was stable for almost 800 (767.5) hours. However, the product hydrogen purity was over 99.99 vol % only for a few hours. We put an end to the long-term reforming test at the total reforming time of 767.5 hours when the impurity level increased dramatically. The impurity was composed of carbon mono-oxide, carbon dioxide and methane which were leaked from the process side through the membrane. By careful inspection after the long-term reforming test, it was found that leakage occurred in the membrane and the mechanical joint between the MOC module and an outer pipe fitting. Durability of the membrane and the mechanical joint against leakage is now the main challenge for the MOC module.

5. CFD simulation

We performed CFD (Computational Fluid Dynamics) simulation for optimizing the shape design and operating conditions of the MOC module. The detailed conditions of the simulation were as follows:

1. Commercially available CFD software FLUENT® was used.
2. Two-dimensional (2D) rotationally symmetric model with mesh size of 0.2 mm x 0.2 mm was adopted.
3. A uniform temperature distribution was assumed.
4. Reforming reaction with infinite reaction rate was assumed.
5. Hydrogen permeation was assumed to follow the Sievert’s law.
   Hydrogen permeation flux is proportional to the difference of the square root of hydrogen partial pressures across the membrane.
6. Permeability of the Pd-Ag membrane was set at $2.3 \times 10^{-8}$ mol/sec/m$^2$/Pa$^{1/2}$.
7. Gas phase resistance in the porous support was determined by the hydrogen permeation test in advance.

Figure 9 shows comparison of the CFD simulation and experimental results for the reforming performance test. The experimental conditions for Figure 9 are the same as that
for Figure 7(a). As shown in Figure 9, the CFD simulation results of the product hydrogen flux (red curve), the hydrogen recovery (orange curve) and the conversion (green curve) are in good agreement with the experimental results of the product hydrogen flux (red diamonds), the hydrogen recovery (orange open squares) and the conversion (green open diamonds), respectively.

Figure 10 shows the CFD simulation result of hydrogen concentration distribution in the 100 mm long MOC module. Note that the hydrogen concentration is already high in the insert tube, because pre-reformed gas is introduced into the MOC module. As shown in the figure, the hydrogen concentration in the porous support adjacent to the membrane is lower than that in the free space between the insert tube and the porous support.

Figure 9. Comparison of the CFD Simulation and Experimental Results.

Figure 10. Hydrogen Concentration Distribution in the 100 mm Long MOC Module.

Figure 11 shows the hydrogen partial pressure profiles in the 100 mm long MOC module at the end point (red circles), the middle point (orange squares) and the root point (blue triangles), the positions of which are shown in Figure 10. The vertical axis indicates hydrogen partial pressure while the horizontal axis indicates radial position (mm) in the direction vertical to the module surface. Note that the hydrogen pressure is shown in
terms of differential root pressure (Pa$^{1/2}$). Differential root pressure in this case means the difference between the square root of hydrogen partial pressure inside the module (that depends on position) and the square root of partial hydrogen pressure outside the module (0.1013 MPa). The product hydrogen fluxes at different points are proportional to the differential root pressure at the position of 1.9 mm in Figure 11. As shown in the figure, the hydrogen partial pressure is dramatically lowered by the existence of the porous support. In other words, significant concentration polarization occurs in the porous support. To overcome this problem, we have a possibility to enhance the hydrogen production of the MOC module by optimizing its shape design and operating conditions to reduce the gas phase resistance of the porous support.

6. Summary and Future Work

The major contribution of this work is summarized as follows:

1. A new-concept hydrogen production module with Membrane On Catalyst (MOC) was developed.
2. High reforming performance was demonstrated. The product hydrogen flux was as high as 11.3 Nml/min/cm$^2$ (= 0.084 mol/sec/m$^2$), and conversion was as high as 87.8 %.
3. Almost 800 hours (767.5 hours) of stable hydrogen production was demonstrated.
4. It is found that durability of the membrane and the mechanical joint is the main challenge for the MOC module.
5. The CFD simulation showed that significant concentration polarization occurred in the porous support.

In the future work, we are going to:

1. Improve the durability of the MOC module,
2. Build up a small-scale (ex. 5 Nm3/h-class) prototype of the MOC reformer,
3. Demonstrate over 8000 hours of durability with product hydrogen purity of over 99.99 vol %.
7. Acknowledgements

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8. Terms Definitions

**Hydrogen Production Energy Efficiency**

\[
\frac{F_p(H_2) \times Q(H_2)}{F_c(NG) \times Q(NG) + W(AUX)} \times 100
\]

- \(F_p(H_2)\): production rate of \(H_2\) (Nm\(^3\)/h)
- \(Q(H_2)\): heat value of \(H_2\) (J/Nm\(^3\))
- \(F_c(NG)\): consumption rate of natural gas (Nm\(^3\)/h)
- \(Q(NG)\): heat value of natural gas (J/Nm\(^3\))
- \(W(AUX)\): electric power consumed by the auxiliary equipment (J/h)

**Conversion**

\[
\frac{F_{off} (CO) + F_{off} (CO_2)}{F_{off} (CH_4) + F_{off} (CO) + F_{off} (CO_2)} \times 100
\]

- \(F_{off} (CH_4)\): flow rate of \(CH_4\) in off-gas (Nm\(^3\)/h)
- \(F_{off} (CO)\): flow rate of \(CO\) in off-gas (Nm\(^3\)/h)
- \(F_{off} (CO_2)\): flow rate of \(CO_2\) in off-gas (Nm\(^3\)/h)

**Hydrogen Recovery**

\[
\frac{F_{off} (H_2)}{F_p(H_2) + F_{off} (H_2)} \times 100
\]

- \(F_p(H_2)\): production rate of \(H_2\) (Nm\(^3\)/h)
- \(F_{off} (H_2)\): flow rate of \(H_2\) in off-gas (Nm\(^3\)/h)

9. References


