Experimental Study on a Compact Methanol Steam Reformer with Pd/Ag Membrane*

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Abstract
The performance of high purity hydrogen production from methanol for a compact steam reformer with a hydrogen purification membrane was investigated experimentally. A 77 wt.% Pd/23 wt.% Ag membrane with 25µm thickness and CuO/ZnO/Al2O3 catalyst were used. Heating was performed by a Bunsen type burner using City Gas 13A. The methanol reforming and purification of H2 were investigated at different reference catalyst zone temperatures (589-689K), pressures at the retentate side (0.2-0.5MPa), steam to methanol(S/C) ratios (0.8-1.6) and reactant flow rates (1.7×10⁻⁴ to 4.4×10⁻⁴ mol/s). The results show that at high reference temperature, high pressure and certain points of the reactant flow rate, the maximum hydrogen permeation rate is obtained when the S/C ratio is around 1. The modified Sieverts’ equation which considers the decrease in H2 concentration at the membrane surface, was proposed. The experimental result was lower than the permeation rate estimated by the modified Sieverts’ equation, which is probably caused by the adsorption of non-H2 species during permeation. It is further demonstrated that the modified Sieverts’ equation is able to estimate a more reasonable hydrogen permeation rate in comparison to the estimation by the ordinary Sieverts’ equation. In addition, it is shown that the compact methanol steam reformer with a Pd/Ag membrane is able to produce high purity hydrogen with very low CO concentration, which fulfills the Polymer Electrolyte Fuel Cell (PEFC) requirement (<10ppm).

Key words: Hydrogen, Methanol, Compact Steam Reformer, Pd/Ag Membrane, Sieverts’ Equation, PEFC, Fuel Cell

1. Introduction
The compact reformer in connection with Polymer Electrolyte Fuel Cell (PEFC) is an attractive option for supplying hydrogen for light-duty vehicles and portable electronic devices such as cellular phones, tablet computers and laptop computers. The development of compact reformers started more than a decade ago, with the aim of setting a reformer, catalytic burner and hydrogen purification device in a single package for vehicle application (1). The integrated compact reformer is supposed to be a reliable solution compared to complex, high price and bulky designed reformer systems consisting of separated units (2). Due to the difficulty in transporting and storing hydrogen, the compact reformer which
utilizes alcohols as fuel seems to be more practical\(^3\). Methanol is suitable for steam reforming because of the high H/C ratio, high reactivity and moderate reforming temperature\(^2\)(\(^4\)). Compared to the other liquid fuels such as liquid hydrogen and ammonia, the cost of hydrogen generation from methanol is still relatively low\(^5\)(\(^6\)).

Based on the reaction formula, the endothermic steam reforming process is more preferable than exothermic partial oxidation due to the higher hydrogen production from one mole methanol. The commercial catalyst CuO/ZnO/Al\(_2\)O\(_3\) was widely used for methanol steam reforming at moderate temperature ranges from about 423K to 623K because a high conversion rate was obtained\(^7\)(\(^8\)). Through methanol steam reforming, gas species other than \(\text{H}_2\) such as \(\text{CO}_2\) and \(\text{CO}\) are also produced. Previous studies showed that \(\text{CO}\) causes a decrease in the reactive surface area of the electrode fuel cell for \(\text{H}_2\) dissociation\(^9\)(\(^10\)) while \(\text{CO}_2\)\(^11\) causes a decline in \(\text{H}_2\) partial pressure, which affects the fuel cell performance. It was shown that \(\text{CO}\) damages the PEFC if it is more than 10ppm\(^12\).

Experimental and theoretical studies related to methanol steam reformer integrated with a purification membrane were conducted under various operating conditions and different configurations\(^7\)(\(^13\)-(\(^15\))(\(^16\)). In previous studies, two types of membrane were used; tubular type\(^14\)(\(^16\)) and foil type\(^7\)(\(^13\))(\(^15\)). Generally, the foil type membrane is less expensive because less thickness of foil type membrane is sufficient for structural stability, and is supposed to be commercially useful\(^15\). A Pd or Pd/Ag alloy membrane was adopted in many hydrogen purification studies due to its ability to provide high fluxes and high permselectivity. Alloying Pd with Ag or Cu is necessary to prevent embrittlement when the membrane is exposed to hydrogen at temperatures below 573K (critical temperature), and at pressures below 2MPa (critical pressure)\(^2\). Nevertheless, for application in gas mixture, hydrogen permeation through both types of membrane deteriorates, which is caused by the competitive adsorption and resistance by other gas species such as \(\text{CO}\), \(\text{CO}_2\), excessive methanol and steam\(^17\)-(\(^18\)). The experimental and simulation studies that were conducted at moderate temperature (498-573K) and pressure (0.3-0.5MPa) ranges revealed that the decrease in transmembrane \(\text{H}_2\) flux through the Pd/Ag membrane is mainly caused by the competitive adsorption of \(\text{CO}\), followed by \(\text{CH}_3\text{OH}\), \(\text{CO}_2\) and \(\text{H}_2\text{O}\)\(^19\). The study also demonstrated that the surface poisoning effect due to all species, except \(\text{CH}_3\text{OH}\), weakened with an increase in membrane temperature\(^19\). Based on several previous studies, it seems necessary to maintain the hydrogen purification at a temperature of 553K and above when using the Pd or Pd alloy membrane to reduce the disturbance effect of these non-hydrogen species and to obtain higher hydrogen permeation flux\(^17\)(\(^19\)).

Hydrogen permeates the membrane due to a solution-diffusion transport and then hydrogen permeation through the membrane can be estimated by applying Sieverts’ equation with Fick’s First Law\(^20\). However, several studies have pointed out that the use of Sieverts’ equation could not make predictions with a reasonable accuracy in the case of hydrogen mixture\(^20\)(\(^21\)). Therefore, several methods such as constant concentration method\(^21\) and consideration of concentration polarization effect\(^20\) have been introduced to modify the Sieverts’ equation for hydrogen mixture application. In order to obtain hydrogen flux using the constant concentration method, the feed concentration of the binary hydrogen mixture remains constant during the experiment\(^21\). The latter study demonstrated the existence of concentration polarization at the retentate side, which means the concentration gradient near the membrane must be considered in Sieverts’ equation. Though semi-empirical equations were proposed to estimate the permeation rate of hydrogen, some experimental data is necessary in order to use it\(^20\).

In our study, the performance of a compact methanol steam reformer under various operating conditions was investigated experimentally. Additional power for pressurization of the retentate side was not necessary because the pressure was exerted by the vaporization
of methanol and water instead of using a compressor. In addition, the estimation method of the hydrogen permeation rate through the membrane based on Sieverts’ equation is reconsidered by taking into account the characteristics of the mixture.

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>effective membrane surface area, $m^2$</td>
</tr>
<tr>
<td>d</td>
<td>membrane thickness, m</td>
</tr>
<tr>
<td>$F$</td>
<td>estimated hydrogen permeation rate, mol/s</td>
</tr>
<tr>
<td>$F_{\text{per}}$</td>
<td>hydrogen permeation rate, mol/s</td>
</tr>
<tr>
<td>$F_{\text{all-off-gas}}$</td>
<td>total flow rate of off-gas, mol/s</td>
</tr>
<tr>
<td>$F_{\text{H}_2\text{-off-gas}}$</td>
<td>flow rate of hydrogen in off-gas, mol/s</td>
</tr>
<tr>
<td>$F_{\text{in}}$</td>
<td>inlet total gas flow rate, mol/s</td>
</tr>
<tr>
<td>$F_{\text{in,H}_2}$</td>
<td>inlet flow rate of hydrogen, mol/s</td>
</tr>
<tr>
<td>$F_{\text{unreacted}}$</td>
<td>total flow rate of unreacted methanol and steam, mol/s</td>
</tr>
<tr>
<td>$P_1$</td>
<td>pressure at retentate side, MPa</td>
</tr>
<tr>
<td>$P_2$</td>
<td>pressure at permeated side, MPa</td>
</tr>
<tr>
<td>$P_{\text{H}_2,1}$</td>
<td>primary partial pressure of hydrogen, MPa</td>
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<tr>
<td>$P_{\text{H}_2,1}(\text{ref})$</td>
<td>reference primary partial pressure of hydrogen, MPa</td>
</tr>
<tr>
<td>$P_{\text{H}_2,2}$</td>
<td>secondary partial pressure of hydrogen, MPa</td>
</tr>
<tr>
<td>q</td>
<td>hydrogen permeance coefficient, molm$^{-1}$sec$^{-1}$Pa$^{-0.5}$</td>
</tr>
<tr>
<td>T</td>
<td>temperature, K</td>
</tr>
<tr>
<td>$T_{\text{mem(ref)}}$</td>
<td>reference membrane temperature, K</td>
</tr>
<tr>
<td>$T_{\text{cat(ref)}}$</td>
<td>reference catalyst zone temperature, K</td>
</tr>
<tr>
<td>$x_{\text{H}_2\text{-off-gas}}$</td>
<td>mole fraction of hydrogen in off-gas</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>steam to methanol (S/C) ratio</td>
</tr>
<tr>
<td>$\dot{n}$</td>
<td>reactant flow rate, mol/s</td>
</tr>
</tbody>
</table>

**2. Experimental and Estimation Method**

**2.1 Reaction Formula of Steam Reforming**

The overall methanol steam reforming reaction model is shown in the following equation.

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2 - 49.5 \text{ kJ/mol} \quad (1)$$

In a real steam reformer, a small amount of CO is formed. As we mentioned in Chapter 1, CO damages the PEFC and reduces H$_2$ permeation even though the concentration of CO is as low as the order of magnitude of 10ppm. In this paper, CO formation is modeled using the following two-step equations:

- Methanol decomposition reaction: $\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2 - 90 \text{ kJ/mol} \quad (2)$
- Water-gas shift reaction: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 + 40.5 \text{ kJ/mol} \quad (3)$

**2.2 Experimental Setup and Procedures**

The experimental setup of the flow system and the compact reformer unit are shown in Figs. 1 and 2, respectively. For the reforming process, tablet type catalyst CuO/ZnO/Al$_2$O$_3$ (CuO 42 mass%, ZnO 47 mass% and Al$_2$O$_3$ 10mass%) with diameter and height of 3.2mm, was used. To obtain high purity hydrogen, a 25$\mu$m thickness 77 wt.% Pd/23 wt.% Ag foil type membrane with diameter of 0.068m and effective surface area of 3.63×$10^{-3} \text{m}^2$ was hold by copper gasket and was set downstream of the catalyst zone. The purification
membrane was supported by sintering porous stainless steel. For both measurements of reference catalyst zone temperature and reference membrane temperature, K-type thermocouples (sheath diameter 1.6mm, material SUS316) were used. For measurement of reference catalyst zone temperature, a hole with diameter of 0.002m (2mm) and depth of 0.045m (45mm) was made to locate the thermocouple, as shown in Fig. 2. The position for the measurement of the reference catalyst zone temperature was set at horizontal distance of ~0.005m (~5mm) next to the wall of catalyst zone. Meanwhile, the position for the measurement of the reference membrane temperature was set at vertical distance of ~0.01m (~10mm) below the purification membrane. A thermocouple was placed at the one of the outlets of off-gas for measuring the reference membrane temperature. The whole reformer body was insulated with insulation materials (asahi light caster 10 with water addition 80 mass%, and glass wool) to prevent heat loss.

As shown in Fig. 2, the heating was performed by a Bunsen type burner using City Gas 13A while the reformer was first purged with nitrogen. The purging process was stopped when the measurement value became close to desired reference catalyst zone temperature. Then, methanol and water pressurized by nitrogen were supplied to the catalyst zone through the piping which was heated by ribbon heater. The flow rate of methanol and water were set by mass flow controllers (Horiba STEC, model: LV-410). After vaporization of methanol and water by heat from ribbon heater, hydrogen then was formed at the catalyst zone by steam reforming. To keep the reference catalyst zone temperature, the heat from the Bunsen type burner was controlled by adjusting City Gas 13A flow rate. In this case, the reference catalyst zone temperature and respective reference membrane temperature were almost stable for sufficiently long time period, due to the high heat capacity of stainless steel and heat loss prevention by the insulation materials.

After the reference catalyst zone temperature was stable, a needle valve was controlled to pressurize the off-gas at the retentate side. When the pressure of the reformed gas was increased, hydrogen started to permeate the membrane. In this case, the pressure was carefully adjusted, observing the pressure reading. The flow rate of off-gas was measured by a high precision film flow meter (Horiba STEC, model: VP-4U) and its mole concentration was measured by a gas chromatograph (Shimazu, model: GC-2014ATE and C-R8A). The flow rate of the purified gas was measured by a soap-film flow meter (GL Sciences 50ml) and its mole concentration was measured by a gas chromatograph and a CO infrared instrument (Horiba, model VIA-510) with a range of 0ppm to 200ppm as well because CO concentration was usually lower than 200ppm.

![Fig. 1 Experimental setup](image-url)
Fig. 2 Compact reformer for methanol steam reforming

The effect of the reference catalyst zone temperature, reference purification membrane temperature, pressure at the retentate side, steam to methanol (S/C) ratio, and reactant flow rate on the reforming of methanol and purification of H\textsubscript{2} were investigated experimentally.

### 2.2.1 Experimental Conditions

It has been reported that performance of methanol steam reforming and H\textsubscript{2} purification were affected by temperature, pressure, S/C ratio and feed flow rate\textsuperscript{7,15}. In our study, the experiments were conducted under various experimental conditions as mentioned in Table 1. The reference catalyst zone temperature (T\textsubscript{cat(ref)}) was set from 589 to 689 K to obtain maximum methanol conversion rate. The pressure range was set from 0.2 to 0.5 MPa, to obtain high hydrogen flux and at the same time, to consider the mechanical strength of the membrane. In other words, the range of pressure difference between retentate side and permeated side was 0.1 MPa to 0.4 MPa and the permeated pressure was atmospheric in all series of experiment. Meanwhile, the S/C ratio was varied between 0.8 to 1.6, which was commonly used for reducing CO in the reformed gas while maintaining high methanol conversion rate. The reactant flow rate was set from 1.7 × 10^{-4} to 4.4 × 10^{-4} mol/s to supply around 5.6 × 10^{-4} mol/s (2 mol/h) highly purified hydrogen to a PEFC.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reference Catalyst Zone Temperature, T\textsubscript{cat(ref)} [K]</th>
<th>Pressure, P\textsubscript{1} [MPa]</th>
<th>S/C Ratio, (\alpha)</th>
<th>Reactant Flow Rate, (\dot{n}) [mol/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>589-689</td>
<td>0.4</td>
<td>1</td>
<td>2.8 × 10^{-4}</td>
</tr>
<tr>
<td>2</td>
<td>637</td>
<td>0.2-0.5</td>
<td>1</td>
<td>2.8 × 10^{-4}</td>
</tr>
<tr>
<td>3</td>
<td>637</td>
<td>0.4</td>
<td>0.8-1.6</td>
<td>2.8 × 10^{-4}</td>
</tr>
<tr>
<td>4</td>
<td>637</td>
<td>0.4</td>
<td>1</td>
<td>(1.7-4.4) × 10^{-4}</td>
</tr>
</tbody>
</table>

### 2.3 Hydrogen Purification

The hydrogen permeation rate of the hydrogen purification membrane is estimated by Sieverts’ Law, which is quantified with Fick’s First Law as mentioned in Eq. (4)\textsuperscript{20}:

\[
F = \frac{qA}{d} \left( \sqrt{P_{H_{2,1}}} - \sqrt{P_{H_{2,2}}} \right)
\]  

(4)

The hydrogen permeance coefficient (q) for the Pd/Ag membrane is estimated using Fig. 3 as a function of membrane temperature.
Figure 3 shows that the hydrogen permeance coefficient is around 1.0 x 10^{-8} to 2.0 x 10^{-8} molH_2·m^{-1}·s^{-1}·Pa^{-0.5} and increases with an increase in temperature. The values of the coefficient, however, are different quantitatively in Refs. 22 and 23. It is not clear the difference in the present study, but it can be supposed that the characteristics of the membrane is sensitive to the manufacturing process, the condition to be used and so on. Thus, we used two values in Fig. 3 in the analysis of the present study.

As described in previous studies (20)-(21), Eq. (4) does not estimate the permeation rate with good accuracy for a hydrogen mixture even though the pressure terms are adjusted to the partial pressure of hydrogen. Catalano, et al. (20) mentioned that the hydrogen concentration decreases towards the membrane surface, and this is the reason why Sieverts’ Law is unable to give an accurate H_2 permeation rate for the hydrogen mixture. In order to compensate for the hydrogen concentration difference between the bulk gas phase and membrane surface, semi-empirical equations were proposed.

Figure 4 shows a schematic of the hydrogen concentration profile near the membrane. As shown in Fig. 4, Line 1 represents the hydrogen concentration profile based on the ordinary Sieverts’ Law in which the H_2 concentration variation close to the membrane is not taken into account. In this case, P_{H_2,1} is estimated as follows,

$$P_{H_2,1} = \frac{F_{in,H_2}}{F_{in}}$$

(5)

When the upstream side gas is pure hydrogen, no concentration decrease occurs and then Eq. (5) gives a reasonable estimation of $P_{H_2,1}$. On the other hand, when the upstream side gas is a mixture, the hydrogen concentration varies as in Line 2 in Fig. 4 and then, the value of $P_{H_2,1}$ is overestimated when Eq. (5) is used, as shown in Fig. 4.

In this case, we modify both the numerator and denominator of Eq.(5) by taking into
account the hydrogen permeation as shown by Line 3. In this case, \(P_{H_2} \) is estimated as follows,

\[
P_{H_2} = \frac{F_{in,H_2} - F}{F_{in} - F}P_1
\] (6)

In this experiment, however, the mixture which is supplied to the retentate side of the membrane, is produced by steam reforming. Then, we use the actual reformed gas composition to estimate the permeation rate of the membrane and to validate the proposed modified Sieverts’ equation. In our experimental study, \(F_{in,H_2}\) and \(F_{in}\) are then determined as follows,

\[
F_{in,H_2} = F_{per} + F_{H_2,off-gas}
\] (7)

where \(F_{H_2,off-gas}\) is obtained by Eq. (8) below.

\[
F_{H_2,off-gas} = x_{H_2,off-gas} \times F_{all,off-gas}
\] (8)

Then, inlet total gas flow rate \(F_{in}\) is determined from the Eq. (9), as shown below.

\[
F_{in} = F_{per} + F_{all,off-gas} + F_{unreacted}
\] (9)

By substituting \(P_{H_2} \) in Eq.(4) with Eqs.(5) and (6), the following equations are obtained.

Ordinary Sieverts’ Equation:

\[
F = \frac{qA}{d} \left( \sqrt{\frac{F_{in,H_2}}{F_{in} - F}} - \sqrt{\frac{P_{H_2}}{F_{in} - F}} \right)
\] (10)

Modified Sieverts’ Equation:

\[
F = \frac{qA}{d} \left( \sqrt{\frac{F_{in,H_2} - F}{F_{in} - F}} - \sqrt{\frac{P_{H_2}}{F_{in} - F}} \right)
\] (11)

Eq.(11) is rewritten as follows,

\[
0 = F^3 + F^2 \left( 2 \frac{qA}{d} \sqrt{\frac{P_2}{F_{in}}} \right) + F \left( \frac{q^2A^2}{d^2} \frac{F_{in}}{F_{in} - F} - \frac{q^2A^2}{d^2} P_1 - 2 \frac{qA}{d} F_{in} \sqrt{\frac{P_2}{F_{in}}} \right) + \left( - \frac{q^2A^2}{d^2} F_{in}P_2 + \frac{q^2A^2}{d^2} F_{in,H_2} P_1 \right)
\] (12)

Eq.(12) is solved analytically using the Newton-Raphson Method.

3. Results and Discussion

The performance of the compact methanol steam reformer and of the \(H_2\) purification were investigated experimentally. In addition, the estimation method of the hydrogen permeation rate through the purification membrane is discussed, in comparison with experimental data.

3.1 Performance of Compact Methanol Steam Reformer

In this section, the experimental results of the performance of the compact methanol
steam reformer under various reference catalyst zone temperatures, pressures at the retentate side, steam to methanol ratios (S/C ratio), and reactant flow rates are presented.

3.1.1 Temperature Dependence

Fig. 5  Effect of reference catalyst zone temperature on mole fraction of reformed gas and methanol conversion rate (P₁: 0.4MPa, α: 1, nᵣ: 2.8×10⁻⁴ mol/s)

Figure 5 shows the effect of reference catalyst zone temperature on the mole fraction of reformed gas and the methanol conversion rate. The figure shows that the mole fraction of reformed hydrogen is constant in the experimental temperature range, at almost 0.75, which is the theoretical mole fraction of H₂ estimated from Eq. (1). Meanwhile, the CO₂ decreases while CO increases with an increase in reference temperature. This is mainly caused by the formation of more CO and less CO₂ at higher reference temperature due to the suppression of the exothermic water-gas shift reaction, which is shown in Eq.(3). The figure shows that the methanol conversion rate reaches maximum at around 0.75, indicating that not all of the methanol is converted to hydrogen. In addition, the conversion rate decreases significantly when the reference catalyst zone temperature is decreased from 620K to 590K. This is mainly due to a decrease in the catalyst activity, when the reference catalyst zone temperature becomes lower than 620K.

3.1.2 Pressure Dependence

Fig. 6  Effect of pressure at retentate side on mole fraction of reformed gas and methanol conversion rate (Tₜₐₜₑₐ(ref): 637K, α: 1, nᵣ: 2.8×10⁻⁴ mol/s)

Figure 6 shows the mole fraction of reformed gas and the methanol conversion rate under various operating pressures. The figure shows that the mole fractions of reformed H₂, CO₂ and CO are 0.75, 0.20 and 0.05, respectively. The reformed H₂, CO₂ and CO remained
constant, indicating that the methanol decomposition and water-gas shift reaction are little influenced by the pressure. The methanol conversion rate is almost constant at about 0.75 once the pressure reaches 0.3MPa. Initially, when the pressure decreases to 0.2MPa, the conversion rate slightly decreases. Since the contact time between the reactants and catalyst decreases with a decrease in pressure, the amount of hydrogen produced also decreases.

3.1.3 Steam/Methanol(S/C) Ratio Dependence

Figure 7 shows the effect of the S/C ratio on the mole fraction of reformed gas and the methanol conversion rate. The figure shows that the reformed hydrogen is almost constant at 0.75 though it decreases slightly when S/C ratio<1. When S/C ratio<1, there is insufficient steam to react with methanol, and as a result, the hydrogen mole fraction slightly decreases. The mole fraction of CO₂ increases while CO decreases with an increase in the S/C ratio. This is because more CO from methanol decomposition is converted to CO₂ by the water-gas shift reaction when the S/C ratio is increased. The figure shows that the conversion rate is almost constant for various S/C ratios though it shows a slight fluctuation.

3.1.4 Dependence on Reactant Flow Rate

Figure 8 shows the effect of reactant flow rate on the mole fraction of reformed gas and the methanol conversion rate. The figure shows that the mole fraction of H₂, CO₂ and CO tends to be constant at 0.75, 0.21 and 0.04, respectively. It is interesting to note that the
methanol conversion rate dramatically decreases with an increase in the reactant flow rate. This is mainly caused by the decrease in the residence time of the reactants when the flow rate is increased (7). The decrease in the residence time causes fewer reactant molecules to contact the catalyst in a sufficient time for reforming. Consequently, fewer reactants were converted to hydrogen through the reforming process.

As a conclusion for the §§ 3.1.1 to 3.1.4, the results show that when reference catalyst zone temperature is equal or higher than 620K, and pressure is equal or higher than 0.3MPa, the maximum methanol conversion rate is obtained when the reactant flow rate is low. The methanol conversion rate is insensitive to the S/C ratio within this experimental range. However, even when the reference temperature is increased or S/C ratio is decreased, the undesired CO also increases, which is mainly caused by the suppression of the exothermic water-gas shift reaction. Besides, as reported by previous study (24), at certain point of high temperature, the performance of catalyst CuO/ZnO/Al₂O₃ starts to deteriorate, which may cause the decrease in methanol conversion rate. In addition, even higher conversion rate is obtained at lower reactant flow rate, less hydrogen is produced.

3.2 Performance of Purification Membrane

In this section, the results of the hydrogen permeation rate under various operating parameters including the reference purification membrane temperature, pressure at the retentate side, S/C ratio and reactant flow rate are described.

3.2.1 Dependence on Purification Membrane Temperature

Figure 9 shows the hydrogen permeation rate under various reference membrane temperatures. The figure shows that initially, the hydrogen permeation rate increases significantly with an increase in the reference membrane temperature. This is caused by the increase in the hydrogen permeance coefficient shown in Fig.3 and significant increase in methanol conversion rate shown in Fig.5, when the reference temperature is increased. Figure 9 shows that the increase rate of the permeation rate gradually decreases when the reference temperature becomes higher than 580K, which is caused by the almost constant and slight decrease in the methanol conversion rate at this temperature range.

The CO concentration contained in the permeated gas under various operating reference membrane temperatures is mentioned. This indicates that high purity hydrogen with a very low CO concentration can be obtained for all temperature ranges, which is able to be used for PEFC application (< 10 ppm) (12).

![Fig. 9 Effect of reference membrane temperature on hydrogen permeation rate (P₁: 0.4 MPa, α: 1, n: 2.8×10⁻⁴ mol/s)](image-url)
Table 2  CO concentration at different reference membrane temperatures

<table>
<thead>
<tr>
<th>Reference Membrane Temperature, $T_{\text{mem(ref)}}$ [K]</th>
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<th>551</th>
<th>583</th>
<th>601</th>
<th>617</th>
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</thead>
<tbody>
<tr>
<td>CO concentration [ppm]</td>
<td>0.01</td>
<td>0.00</td>
<td>0.15</td>
<td>0.15</td>
<td>0.26</td>
</tr>
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</table>

3.2.2 Dependence on Pressure

Fig. 10  Effect of pressure at retentate side on hydrogen permeation rate ($T_{\text{mem(ref)}}$: 583K, $\alpha$: 1, $\tilde{n}$: $2.8 \times 10^{-4}$ mol/s)

Table 3  CO concentration at different pressures

<table>
<thead>
<tr>
<th>Pressure, $P_1$ [MPa]</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO concentration [ppm]</td>
<td>0.09</td>
<td>0.16</td>
<td>0.15</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Figure 10 shows the effect of pressure at the retentate side on the hydrogen permeation rate. The hydrogen permeation rate increases with an increase in the pressure, which is caused by the larger difference between hydrogen partial pressure at the retentate side and the permeated side. The figure shows that the increase rate of the hydrogen permeation rate gradually decreases. Details of this trend are discussed in § 3.3.1.

Table 3 shows the high purity hydrogen with low CO concentration, which is less than 0.3 ppm, is obtained under various pressures.

3.2.3 Dependence on Steam/Methanol(S/C) Ratio

Fig. 11  Effect of S/C ratio on hydrogen permeation rate ($T_{\text{mem(ref)}}$: 583K, $P_1$: 0.4 MPa, $\tilde{n}$: $2.8 \times 10^{-4}$ mol/s)

Figure 11 shows the effect of the S/C ratio on the hydrogen permeation rate. The figure shows that the hydrogen permeation rate reaches maximum at the S/C ratio around unity.
and decreases on both sides. When the S/C ratio is decreased from 1 to 0.8, the hydrogen permeation rate decreases. This is mainly due to the decrease in the hydrogen mole fraction in the reformed gas when the S/C ratio is decreased. The decrease in the hydrogen mole fraction decreases the permeation rate because the hydrogen partial pressure decreases. On the other hand, when the S/C ratio becomes higher than 1, the permeation rate tends to decrease gradually. When the S/C ratio is increased from unity, more excessive steam at the retentate side exists, which causes the decrease in the hydrogen mole fraction. As a result, the permeation rate decreases with an increase in the S/C ratio because the hydrogen partial pressure at the retentate side decreases. As shown in Table 4, all values of CO concentration are very small and fulfill the PEFC requirement (<10ppm) (12).

<table>
<thead>
<tr>
<th>S/C ratio, $\alpha$</th>
<th>0.8</th>
<th>1</th>
<th>1.2</th>
<th>1.4</th>
<th>1.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO concentration [ppm]</td>
<td>0.15</td>
<td>0.18</td>
<td>0.33</td>
<td>0.14</td>
<td>0.20</td>
</tr>
</tbody>
</table>

### 3.2.4 Dependence on Reactant Flow Rate

Figure 12 shows the effect of the reactant flow rate on the hydrogen permeation rate. The permeation rate initially increases with an increase in the reactant flow rate, and reaches a maximum when the reactant flow rate is around $2.8 \times 10^{-4}$ mol/s. When the reactant flow rate is increased from 1.7 to $2.8 \times 10^{-4}$ mol/s, the flow velocity towards the membrane surface increases. The higher flow velocity produces a higher hydrogen concentration at the membrane surface, which causes an increase in the hydrogen permeation rate. However, once the reactant flow rate exceeds $2.8 \times 10^{-4}$ mol/s, the effect of the decrease in the methanol conversion rate mentioned in § 3.1.4 on the decrease in H$_2$ partial pressure is considered to overcome the effect of the increase in the flow velocity towards the membrane. Consequently, less hydrogen is permeated due to the decrease in hydrogen partial pressure at the retentate side.

Table 5 shows that CO concentration in the permeated gas is very small, and thus is suitable for the PEFC application.

#### Table 5  CO concentration at different reactant flow rates

<table>
<thead>
<tr>
<th>Reactant Flow Rate, $\dot{n}$ [$\times 10^{-4}$ mol/s]</th>
<th>1.7</th>
<th>2.2</th>
<th>2.8</th>
<th>3.3</th>
<th>3.9</th>
<th>4.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO concentration [ppm]</td>
<td>0.00</td>
<td>0.08</td>
<td>0.05</td>
<td>0.08</td>
<td>0.06</td>
<td>0.05</td>
</tr>
</tbody>
</table>

### 3.3 Estimation of Hydrogen Permeation Rate

The hydrogen permeation rate under various pressures at the retentate side is estimated
3.3.1 Dependence on Pressure

Figure 13 shows the results of estimation for the hydrogen permeation rate under various (a) pressures at the retentate side and (b) difference of the square root of hydrogen partial pressures, along with the experimental data. Here, \( P_{H_2,1}^{\text{ref}} \) is the reference primary partial pressure of hydrogen, which is the value at the inlet of primary side. The estimation was made based on the ordinary and modified Sieverts' equations, as mentioned in Eqs.(10) and (11). The value for hydrogen permeance coefficient \( q \) is estimated from Fig. 3, as \( 2.0 \times 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-0.5} \) and \( 1.4 \times 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-0.5} \).

The figure shows that when the pressure at the retentate side \( (P_1) \) is increased, the corresponding difference of the square root of hydrogen partial pressures \( (\sqrt{P_{H_2,1}^{\text{ref}}} - \sqrt{P_{H_2,2}}) \) also increases due to the almost constant inlet hydrogen concentration and the constant atmospheric pressure of \( \text{H}_2 \). As a result, the estimated hydrogen permeation rate increases, as well as experimental result. Figure 13(b) shows that the permeation rate estimated by the ordinary Sieverts’ equation increases linearly with an increase in difference of the square root of hydrogen partial pressures, whereas the experimental result shows that the increase rate of the permeation rate gradually decreases. The figure also shows that the estimation by the modified Sieverts’ equation provides a similar trend to the experimental result. This is because the modified Sieverts’ equation takes into account the permeation of \( \text{H}_2 \) which results in the \( \text{H}_2 \) concentration decrease near the membrane. Furthermore, the modified Sieverts’ equation that considers the decrease in \( \text{H}_2 \) concentration is able to
provide a reasonable permeation rate, which is closer to the experimental value in comparison to the estimation by ordinary Sieverts’ equation.

Figure 13 shows that the gap still exists between the estimation results by the modified Sieverts’ equation and the experimental result, which corresponds to the studies by Gepert et al. (2), Israni and Harold(19). Gepert, et al. (2) explained that the gap exists because of the blockage of CO on the active membrane surface area for H2 dissociation during the permeation process, which decreases the hydrogen permeation. In addition, Israni and Harold(19) mentioned that the gap exists also because of the competitive adsorption of other non-H2 species, which are CO2, excessive methanol and steam(19).

Similar results are obtained for various reference temperatures, S/C ratios and reactant flow rates.

3.4 Membrane Surface Variation During Permeation

As discussed in the previous section, the hydrogen permeation rate for the hydrogen mixture obtained by the experiment is always lower than the estimated results. For further discussion, we observed the surface topography of the purification membrane by a Scanning Electron Microscope (SEM).

![Fig. 14](image-url)  The SEM images of (a) unused membrane and (b) used membrane

Figure 14 shows SEM images of an unused membrane and a used membrane. Figure 14(a) shows that the unused membrane has a smooth surface while Fig. 14(b) shows that the used membrane has a rough surface and uneven distribution of the black and white area, which probably causes a non-uniform permeation to occur at the surface.

The changes in the physical characteristics of the membrane surface after the permeation as shown by the figure are supposed to be due to the non-H2 species adsorption on the surface, especially CO, which decreases the hydrogen permeation.

4. Conclusion

The performance of a compact methanol steam reformer using catalyst CuO/ZnO/Al2O3 with a Pd/Ag membrane for hydrogen purification was studied experimentally. The mole fraction of reformed hydrogen under various reference catalyst zone temperatures, pressures at the retentate side, S/C ratios and reactant flow rates is almost constant at 0.75, which corresponds to the mole fraction of H2 estimated by the overall steam reforming reaction formula.

The higher hydrogen permeation rate is attained when we use the higher reference membrane temperature and higher pressure. For the S/C ratio, we obtain the maximum permeation rate when the ratio is around 1 because the hydrogen partial pressure at the retentate side becomes highest when no excessive reactant at the retentate side exists. For the reactant flow rate, the permeation rate is maximum at a certain value where the hydrogen concentration at the membrane surface becomes highest due to the maximum
effect of high flow velocity towards the membrane. Experimental results are still lower than the estimation by the modified Sieverts’ equation because of the change in the membrane surface condition as shown by the SEM image, that is supposed to be due to the non-H\textsubscript{2} species adsorption effect during permeation.

The estimation by the modified Sieverts’ equation gives a more reasonable result compared to the ordinary Sieverts’ equation, not only qualitatively but also quantitatively. This shows that the decrease in H\textsubscript{2} concentration at the membrane surface is necessary to determine the hydrogen permeation rate of the hydrogen mixture.

In addition, the compact reformer with a purification membrane produces hydrogen with a very low CO concentration, less than 10ppm which is suitable for the PEFC application.

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