

MEMS-Based Fuel Reformer with Suspended Membrane Structure

Kuei-Sung Chang^{*}, Non-member, Shuji Tanaka^{*}, Member
Masayoshi Esashi^{**}, Member

We report a MEMS-based fuel reformer for supplying hydrogen to micro-fuel cells for portable applications. A combustor and a reforming chamber are fabricated at either side of a suspended membrane structure. This design is used to improve the overall thermal efficiency, which is a critical issue to realize a micro-fuel reformer. The suspended membrane structure design provided good thermal isolation. The micro-heaters consumed 0.97W to maintain the reaction zone of the MEMS-based fuel reformer at 200 °C, but further power saving is necessary by improving design and fabrication. The conversion rate of methanol to hydrogen was about 19% at 180 °C by using evaporated copper as a reforming catalyst. The catalytic combustion of hydrogen started without any assistance of micro-heaters. By feeding the fuel mixture of an equivalence ratio of 0.35, the temperature of the suspended membrane structure was maintained stable at 100 °C with a combustion efficiency of 30%. In future works, we will test a micro-fuel reformer by using a micro-combustor to supply heat.

Keywords : Micro-fuel reformer, Steam reforming, Thermal management, Fuel cell, Suspended membrane reactor

1. Introduction

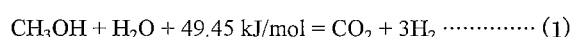
Recently, increasing desire for the longer operation time of portable information devices makes fuel cells (FCs) attractive for portable energy sources. Among FCs, a polymer electrolyte membrane fuel cell (PEMFC) emerges with its high energy density at low working temperature. However, the provision of hydrogen to a PEMFC remains a key issue to realize a micro-PEMFC.

There are many options for providing hydrogen, such as reforming hydrocarbons⁽¹⁾, storing hydrogen⁽²⁾ in metal hydride, high-pressure containers and carbon nano-structures (nanotubes, nanofibers, etc.), and producing hydrogen from alkaline solution of sodium borohydride (NaBH₄). However, physically storing hydrogen is currently not practical for portable uses because of low hydrogen content and high-pressure concerns. Metal hydride has the same problem of the low hydrogen content. Though NaBH₄ shows good performance on producing hydrogen, a method to handle the alkaline solution safely and a recycling system of used NaBH₄ are needed to be developed.

Currently, one of the best choices will be reforming light hydrocarbons portably⁽³⁾⁻⁽⁵⁾, because this allows us to utilize varieties of fuels such as harmless ethanol and self-pressurized propane/butane. And, using a micro-fuel reformer based on micro electromechanical system (MEMS), fuel reforming for portable applications will be possible.

2. Concept

For a preliminary study, we chose methanol (MeOH) steam reforming as a model reaction to focus on the systematic design of our device. Once the device meets our predetermined goals, catalyst and operating conditions will be tuned for other fuels. The total reaction of MeOH steam reforming is given in Equation 1.



The total reaction is endothermic. Supplying heat to a reforming chamber makes the reaction go forward to produce hydrogen. Figure 1 shows the schematic diagram of a MeOH steam reforming system. We are currently focusing on the part enclosed by a dashed

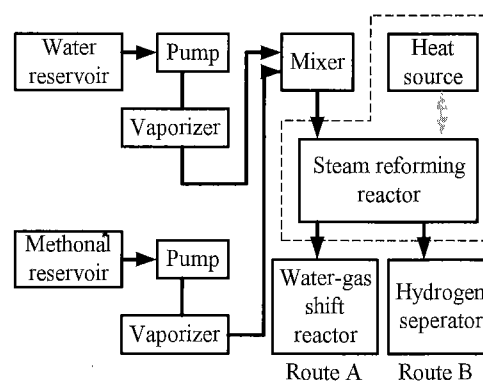


Fig. 1. Schematic diagram of methanol steam reforming.

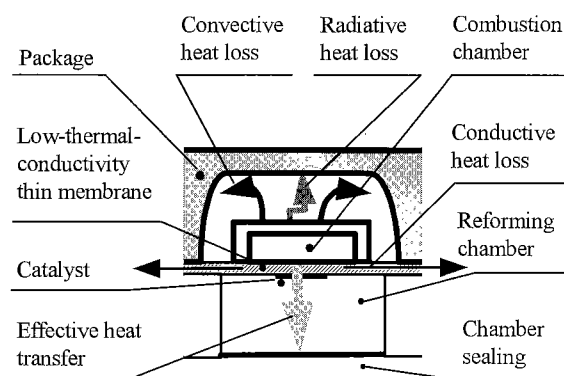


Fig. 2. Conceptual structure of a micro-fuel reformer.

^{*} Department of Mechatronics and Precision Engineering, Tohoku University.

^{**} New Industry Creation Hatchery Center (NICHe), Tohoku University 01 Aza Aoba, Aramaki, Aoba-ku, Sendai, 980-8579, JAPAN

line in Fig. 1. At this part, the properties of catalysts and the thermal management are the core roles that dominate the performance of a micro-fuel reformer. The thermal management is currently weighted because the development of good catalysts with fair MEMS-process compatibility needs a long time.

We proposed a suspended membrane structure to realize a micro-fuel reformer. Figure 2 illustrates the conceptual structure of a micro-fuel reformer. A heat source and a reforming chamber are placed at either side of a suspended membrane structure. By selectively patterning catalysts at the central area of the membrane, this structure enables good thermal isolation of the reaction zone. In addition, the thin membrane ensures good conductive heat transfer from the heat source to the reaction zone. Convective and radiative heat loss can be limited by packaging the heat source side. The micro-combustor is used as a heat source for catalytic combustion. The out-gas of FCs or a part of fuel to be reformed can be used as the combustion fuel.

3. Structure and Fabrication

In our previous study, a silicon-on-insulator (SOI) wafer chip was used to realize our conceptual design⁽⁶⁾. Figure 3 shows the cutaway cross-sectional structure of the SOI design. A silicon plate on a silicon dioxide layer enables uniform temperature distribution, preventing hot spots from happening. By selectively etching silicon at both sides of the SOI wafer chip, the membrane structure is released. Platinum micro-heaters are formed at the thin silicon plate on the suspended membrane structure. The silicon bridges which carry electrical connectors to the micro-heaters on the membrane structure should be made long and narrow for good thermal isolation. However, highly stressed thermal silicon dioxide of the SOI wafer limits the width of the free silicon dioxide membrane, which reduces the effectiveness of thermal isolation. Therefore, the power consumption was high at this design. A calculation based on the energy conservation of the membrane structure revealed that power consumption was mainly from the heat loss at the silicon bridges⁽⁶⁾.

To overcome those problems in the previous study, a low-stressed thin membrane design was applied. In Fig. 4, the cutaway cross-sectional structure of the low-stressed thin membrane design is illustrated. There are two advantages in this approach: First, the silicon plate to enable uniform temperature distribution is made underneath the low-stressed membrane, so there is no silicon bridge for carrying electrical connectors to micro-heaters. Second, the low-stressed membrane exhibits better mechanical strength than the thermal silicon dioxide layer of the SOI design.

Figure 5 shows the fabrication processes of the low-stressed thin membrane design. (a) A silicon dioxide layer was grown by thermal oxidation. (b) A 4 μm -thick low thermal-conductivity thin film is then deposited as a membrane structure. Currently, low-stressed TEOS (tetraethoxysilane, $\text{Si}(\text{OC}_2\text{H}_5)_4$) oxide plasma enhanced CVD⁽⁷⁾ is used to make the thin membrane. (c)-(f) Micro-heaters/sensors and their electrical connectors are formed on the membrane structure by electron beam evaporation with 2 lift-off processes. The micro-heaters are used to evaluate the effectiveness of thermal isolation and can be used for the ignition of combustion. However, during the evaluation of catalytic combustion, these micro-heaters can work as thin-film temperature

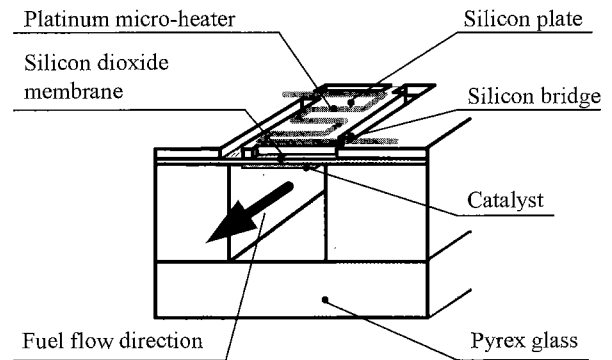


Fig. 3. Cutaway cross-sectional view of the SOI design.

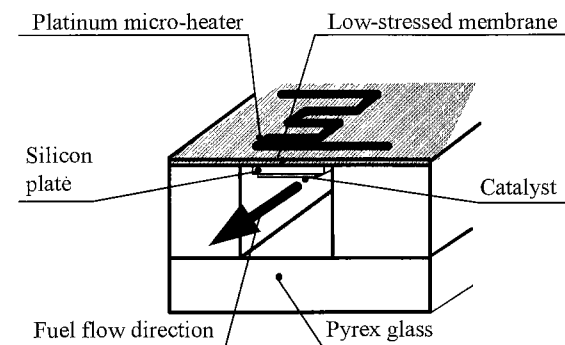


Fig. 4. Cutaway cross-sectional view of the low-stressed membrane design.

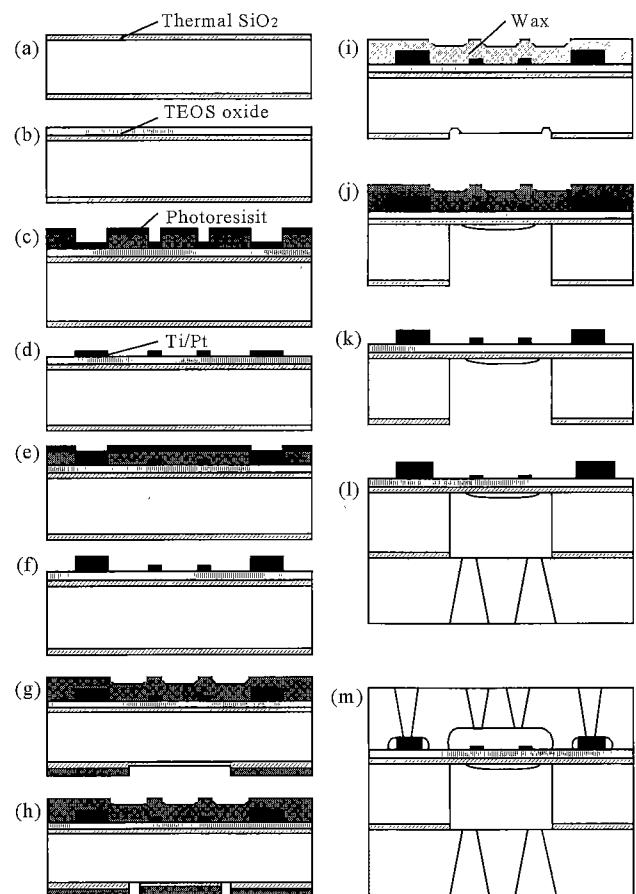


Fig. 5. Fabrication processes of the low-stressed membrane design.

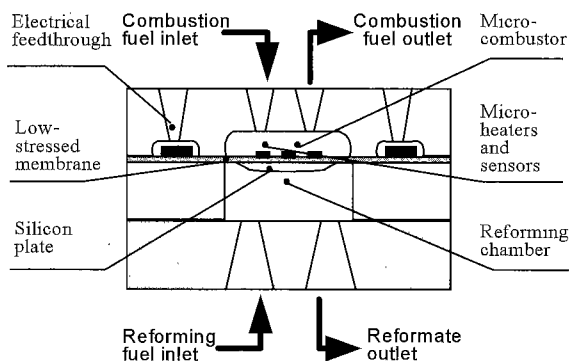


Fig. 6. Cross-sectional view of the low-stressed membrane design with a micro-combustor.

sensors. (g)-(h) To make the thin silicon plate underneath the membrane structure, a 2-step silicon dioxide mask is used. The silicon dioxide layer at the bottom side of the silicon chip is first patterned and etched thin, and then the silicon dioxide layer is removed at the edges of the to-be-formed silicon plate. (i) Using wax (Protect Wax, Nikka Seiko) to protect the upper side of the silicon chip, we etched the edges of the to-be-formed silicon plate side with 30 μm depth by KOH etchant. (j)-(k) The thin membrane is then released by deep reactive ion etching (DRIE) of silicon using a time-multiplexed inductively coupled plasma etcher (Surface Technology System). The etched-out space of silicon becomes a reforming chamber. As a result, a silicon plate is formed in the reforming chamber after DRIE. (l) Finally, the bottom side of the silicon chip is anodically bonded with a Pyrex glass. (m) And a Pyrex glass patterned with flow ways by wet etching is bonded to the top side of the silicon chip by alumina-based adhesive (CeramabondTM 503, Aremco Products) to form the micro-combustor. Figure 6 shows the structure of the completed device.

As the reforming catalyst, evaporated copper is first used, although it exhibits low catalytic performance and poor adhesion inside the reforming chamber. For preparing the combustion catalyst, sol-gel-derived alumina (Al_2O_3) powder is pre-calcined and fed into the micro-combustor. The alumina powder is loaded with platinum by feeding the platinum precursor into the micro-combustor and reducing in hydrogen atmosphere.

4. Experimental

We evaluated the performances of the micro-fuel reformer and the micro-combustor separately. When the micro-fuel reformer is tested, the microheaters are simply used as a heat source.

We set up a testing system to evaluate the conversion rate of methanol to hydrogen as shown in Fig. 7. Water and methanol mixture is fed into the micro-fuel reformer using a syringe pump. After the pre-evaporated fuel undergoes steam reforming at the reforming chamber, the product is sampled and analyzed by gas chromatography (Shimadzu GC-14B with Shincarbon-T packed column). The fuel reformer is set in a stainless steel fixture with a 1/8" inlet and a 1/8" outlet. A Viton sheet is used for sealing the connections between the fixture and the micro-fuel reformer. The temperature of the micro-heaters is feedback-controlled using the relationship between the resistance and temperature of the

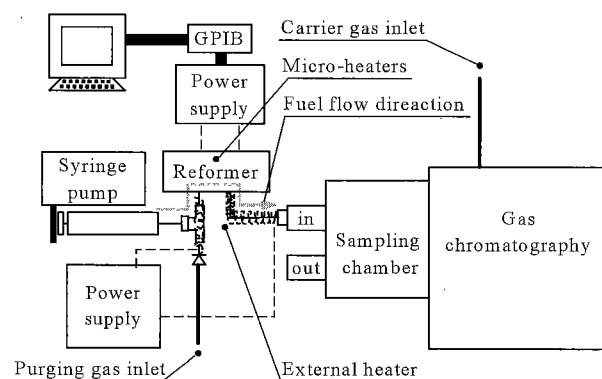


Fig. 7. Schematic diagram of the methanol-steam-reforming system.

micro-heaters.

To test the micro-combustor, hydrogen is first used as a fuel. Mass-flow controllers are used to control the flow rates of compressed air and hydrogen. After pre-mixing in a stainless steel tube, mixed fuel is fed into the micro-combustor. The temperature inside the combustor chamber is read from the electrical resistance variation of the thin-film temperature sensors.

5. Result and Discussion

Table 1 shows the first testing conditions of MeOH steam reforming. The reforming catalyst was first reduced at 250 °C for 2 hours. After that, argon (100 sccm) was introduced to purge the testing system until no hydrogen remained. Then, the reforming of methanol was started by feeding 5 $\mu\text{l}/\text{min}$ of the fuel mixture into the micro-fuel reformer, where the reforming reaction zone was maintained at 180 °C by the micro-heaters.

In the GC result shown in Fig. 8, we confirmed a hydrogen peak produced by steam reforming of methanol at the SOI design (Fig. 3). However, carbon monoxide and carbon dioxide were not clearly detected, because the conversion rate of MeOH was low. By calibrating the area of hydrogen peak in Fig. 8, we knew the hydrogen concentration was about 24% and the conversion rate of methanol was only about 19%. The reforming process efficiency can be defined as equivalent thermal power of hydrogen generated from the micro-fuel reformer divided by the sum of thermal power and electric power added into the micro-fuel reformer. At the SOI design, the reforming process efficiency was about 6% at 180 °C. This result was attributed to the small active surface-area of the evaporated copper catalyst, the peeling of copper catalyst during reforming reaction and the heat loss at the silicon bridges⁽⁶⁾.

We are now studying MEMS-process compatible ways to apply good catalyst to the micro-fuel reformer. There are options to make large surface-area catalyst support with good adhesion to silicon. For example, we can make porous TiO_2 by sputtering and alkaline treatment of titanium.

In Fig. 9, the SOI design (Fig. 3) and the low-stressed membrane design (Fig. 4) were compared in terms of power consumption. To maintain the reforming reaction zone of a 300 $\mu\text{m} \times 7 \text{ mm}$ area at 200 °C, the calculated power consumption of the SOI design is about 2W⁽⁶⁾. In contrast, the calculated power consumption of the low-stressed membrane design without silicon left is about 0.32W at 200 °C. The power consumption of the fabricated device was

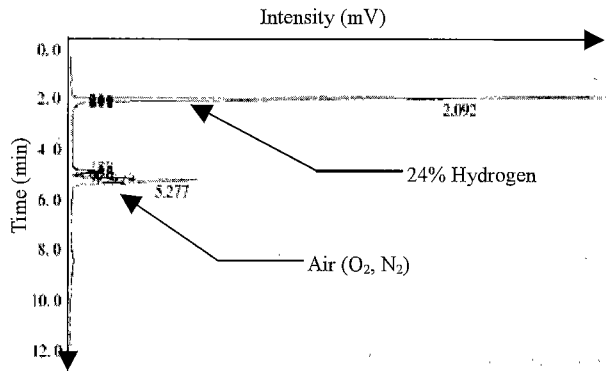


Fig. 8. Result of GC analysis.

Table 1. Methanol steam reforming conditions.

Reduction of catalyst	Atmosphere:	10 vol.% H ₂ in Ar
	Temperature:	250 °C
	Time:	2 hours
Purging	Pure Ar at 100 sccm	
Reforming	Fuel:	MeOH + H ₂ O with a mole ratio of 1
	Feeding rate:	5 µl/min
	Temperature:	180 °C

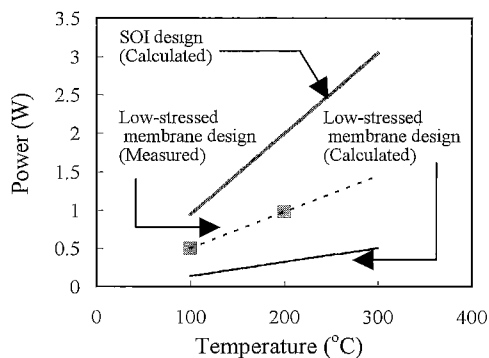


Fig. 9. Power consumption of different designs.

about 0.97W at 200 °C. This power consumption is lower than that of the SOI design but higher than expected value. It is attributed to that the silicon plate left inside the reforming chamber of the low-stressed membrane design (Fig. 4) was partly connected to the silicon side-walls.

We also tested the micro-combustor. Figure 10 shows the result of the combustion test. At first, only hydrogen (10.1 sccm) was introduced into the micro-combustor for the reduction of combustion catalyst. After reduction, the temperature was cooled down to 42 °C by keeping hydrogen flow. Next, air (69.3 sccm) was introduced into the micro-combustor to obtain an equivalence ratio of 0.35. In one minute, the temperature rose to around 85 °C without using the micro-heaters. After 24 min, the temperature reached 100 °C and lasted for 1 hour without further increasing. And then, we increased both the flow rates of hydrogen (12.8 sccm) and air (82.7 sccm) by keeping the equivalence ratio about 0.35. The temperature rose over 220 °C in 5 min. After that, the temperature sensors showed an odd value over 1200 °C in three minutes, so we stopped

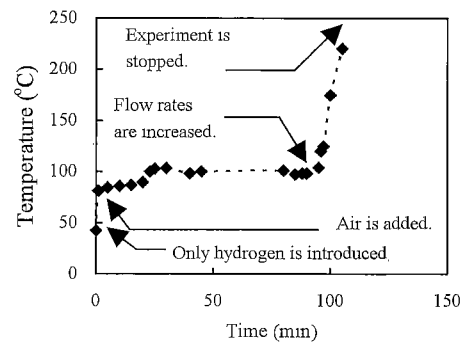


Fig. 10. Result of catalytic combustion.

the experiment. Subsequently, the device was cooled to room temperature. The electrical resistance of the sensors was back to a value equivalent to room temperature, revealing that there was no malfunction of the sensors. We restarted the experiment, but the catalytic combustion could not be confirmed again in that device. This might be attributed to that rapid combustion reaction happened due to the risen temperature, and then the temperature continued rising and finally changed the conditions of the micro-combustor. For example, the reduction of active surface area for catalytic combustion reaction could be occurred due to the aggregation of Pt nano-particles. The membrane structure was maintained at 100 °C by burning 10.1 sccm hydrogen with 1.65W equivalent thermal power. The equivalent electric power of the micro-heater to maintain the membrane structure at the same temperature (100 °C) is found to be 0.5W from Fig. 9. Therefore, the combustion efficiency of the micro-combustor was about 30%.

6. Conclusion

We are studying a MEMS-based fuel reformer for supplying hydrogen to micro-fuel cells for portable applications. The fuel reformer employs a suspended membrane structure, where a heat source is at one side of the membrane, and a reforming catalyst is at the other side. This structure enables good thermal isolation of the reaction zone and good conductive heat transfer from the heat source to the reforming catalyst to save power for reforming.

The current micro-fuel reformer consumed 0.97W to maintain its reaction zone at 200 °C, but further power saving is necessary by improving design and fabrication. Using a gas chromatography (GC) system, we confirmed the capability of hydrogen production by methanol steam reforming. The conversion rate of methanol to hydrogen was 19% at 180 °C by using evaporated copper as a reforming catalyst. To improve the conversion rate, large surface-area catalyst support with good adhesion to silicon is necessary. Some ways to apply good catalysts to a micro-fuel reformer are under development.

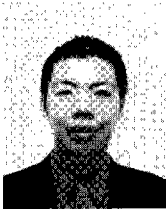
Catalytic combustion started in the micro-combustor without any assistance of micro-heaters. By feeding hydrogen and air, the temperature of the suspended membrane structure was maintained stable at 100 °C. The combustion efficiency was about 30%. In future works, we will test a micro-fuel reformer by using a micro-combustor to supply heat.

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Kuei-Sung Chang (Non-member) was born in Kaohsiung, Taiwan in 1976. He received the B.E. degree in chemical engineering from National Taiwan University of Science and Technology, Taipei, Taiwan in 1998. He is currently pursuing his doctoral degree.



Shuji Tanaka



(Member) was born in Hiroshima in 1971. He received the B.E., M.E. and Ph.D. degrees all in mechanical engineering from The University of Tokyo in 1994, 1996 and 1999, respectively. From 1996 to 1999, he was a Research Fellow of the Japan Society for the Promotion of Science. From 1999 to 2001, he was a Research Associate in the Department of Mechatronics and Precision Engineering, Tohoku University, and is currently an Associate Professor. He was awarded MNC '98 Award for Outstanding Paper in 1999. His research interests include power microelectromechanical systems and micro-power sources.

Masayoshi Esashi (Member) was born in Miyagi in 1949. He



received the B. E. and Dr.E. degrees in electronic engineering from Tohoku University, Sendai, Japan, in 1971 and 1976, respectively. He was a Research Associate in the Department of Electronic Engineering, Tohoku University, from 1976 to 1981, and was an Associate Professor from 1981 to 1990. From 1990 to 1998, he was a Professor in the Department of Mechatronics and Precision Engineering, Tohoku University. He is currently a Professor in the New Industry Creation Hatchery Center, Tohoku University, where he was a Director of the Venture Business Laboratory, and is now an Associate Direct of the Semiconductor Research Institute. He has been studying microsensors and integrated microsystems fabricated by micromachining. His current research topics include microtechnology for saving energy and natural sources.