Experimental and Numerical Investigation of Micro Catalytic Reactor for Autothermal Reforming Using Methanol and Hydrogen Peroxide with Built-in Chrome Silicide Thermocouple

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Abstract. This paper reports new concept of hydrogen generation method using hydrogen peroxide. In this research, development, performance evaluation and numerical simulation of the micro hydrogen generator by autothermal reforming process are carried out. To prove the micro reaction mechanism, chrome silicide thermocouple is built in the micro catalytic reactor by in-situ system.

1. Introduction
With the recent development of micro machining technology, micro devices with various concepts such as micro robot, micro unmanned vehicle and portable electric devices are being developed. The trend of these micro devices is that they are smaller in size, lighter in weight and require longer operating times. For decades in the MEMS (micro-electro-mechanical systems) community, the development of a high energy density power source has been and remains a great technological challenge with a viable solution yet to be found. There are several energy conversion ways. Miniaturization of conventional heat engines such as reciprocating devices and gas turbines has been investigated but the outcomes have not been conclusive due to the difficulty of operating on micro scale. One of other option for operating micro device is conversion of thermal energy to electric energy such as thermoelectric generator and thermophotovoltaic generator. Thermoelectric generator and thermophotovoltaic generator have a beneficial of a very simple structure and system for operation, and many studies have been made, but the efficiency of those methods are very low. [1] The fuel cell has steadily drawn more attention as a feasible alternative, with the advantages of having no moving parts and high thermal efficiency and relatively low heat loss, a property which is not significantly affected by miniaturization. Two types of fuel cell concepts have been suggested as micro scale power sources. The DMFC (Direct Methanol Fuel Cell) uses liquid methanol as a fuel, making it particularly suitable as a micro scale power source, but its inherent low output power density and fuel crossover problems are difficult issues to overcome. The PEMFC (Proton Exchange Membrane Fuel Cell) has a relatively high output power density but requires gaseous hydrogen as the fuel, whose storage is difficult in a micro device. A possible solution to the problem is to reform liquid fuel and generate gaseous hydrogen.

Reforming is the most commonly used process for producing large amounts of gaseous hydrogen. In general, reforming reactions are endothermic reactions that require an external heat source, and in large
plants, combustion based heaters can be used efficiently and effectively. However, in a micro-scale reforming reactor, the additional heat source and heat exchangers make the reformer complex to build and operate. An alternative scheme is to integrate an additional heat source into the existing power engine for portable power applications. [2] Internal combustion processes can yield high power, but when applied on a portable scale, problems such as vibration, noise, and low heat efficiency arise. Batteries, on the other hand, have a low energy density and short operation time, but the fuel cell does not have the problem of vibration, it operates silently, and yields a high energy density. Another major constraint in the successful development of a micro fuel cell power system is the difficulty and hazards associated with the storage and handling of hydrogen. On-board hydrogen production is the key for the development of a portable fuel cell power system. Some of the existing methods for hydrogen storage are to use compressed hydrogen tanks, liquid hydrogen tanks, or metal hydrides. Among the various methods, fuel reforming, in which gaseous hydrogen is extracted from a liquid fuel, is a particularly effective process because the fuel is stored and used in the same liquid phase with high energy density. Methanol is a good option as a reforming fuel source because of its low boiling point, it is easy to obtain, and its high hydrogen-to-carbon ratio is an advantage.

Autothermal reforming involves a combination of steam reforming and partial oxidation. [3] Steam reforming is an endothermic reaction, while partial oxidation is exothermic. The total heat balance in autothermal reforming can be controlled through the balance of the exothermic and endothermic reactions, and thus, autothermal reforming requires no additional external heat source. Furthermore, autothermal reforming can be accomplished in simple, small reactors with relatively high efficiencies. Oxygen facilitates a fast reforming reaction yielding a higher hydrogen content in the reformate gas than that from partial oxidation. However, the autothermal reforming process requires an additional air supply to provide oxygen, such that the concentration of hydrogen in the reformate gas is lower than that in the steam reforming reaction.

In this study, hydrogen peroxide decomposition is employed for the autothermal reforming of methanol. The decomposition of hydrogen peroxide is a highly exothermic reaction, and the resulting heat can be used to vaporize methanol effectively. [4] It also generates oxygen and steam, thus making it a suitable candidate for autothermal reforming with methanol. Furthermore, the substitution of air fed by an additional pump yields a hydrogen concentration as high as that in the case of steam reforming. Development, performance evaluation and numerical simulation of the micro hydrogen generator by autothermal reforming process are carried out. To prove the micro reaction mechanism, chrome silicide thermocouple is built in the micro catalytic reactor by in-situ system. This paper is studied the temperature and pressure effects as parameters for hydrogen generation.

2. Methodology
As described in the Introduction, hydrogen peroxide decomposition is to be employed for the autothermal reforming of methanol. Three sequential reactions take place in the reactor:

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\begin{align*}
    2 \text{H}_2 \text{O}_2 (g) & \rightarrow \text{H}_2 \text{O}_2 (g) + \frac{1}{2} \text{O}_2 (g) & \Delta H_{298K}^\circ = -98.1 \text{ kJ/mol} \\
    \text{CH}_3\text{OH} (g) + \frac{1}{2} \text{O}_2 (g) & \rightarrow 2\text{H}_2 (g) + \text{CO}_2 (g) & \Delta H_{298K}^\circ = -192.3 \text{ kJ/mol} \\
    \text{CH}_3\text{OH} (g) + \text{H}_2 \text{O}_2 (g) & \rightarrow 3\text{H}_2 (g) + \text{CO}_2 (g) & \Delta H_{298K}^\circ = 49.5 \text{ kJ/mol}
\end{align*}
\]

Decomposition of hydrogen peroxide, Eq. (1), takes place in the front part of the reactor, generating oxygen and steam. Methanol is partially oxidized in Eq. (2) to generate sufficient heat for the steam reforming of methanol shown in Eq. (3). The overall reaction can be expressed as follows:
Ideally, 1 mol of methanol with 0.5 mol of hydrogen peroxide generates 2.5 mol of hydrogen and 1 mol of carbon dioxide (Eq. (4)). However, the catalytic process in the reactor is complex, and the characteristics of the methanol autothermal reforming reaction in a micro reactor utilizing the decomposition of hydrogen peroxide will be investigated in this study.

3. Design micro catalytic reformer with in-situ system

3.1. Design of reformer

Micro reformers fabricated using MEMS technology are usually flat in shape because of the high bonding surfaces. In this research, the reformer was made from six glass wafers. Photosensitive glass (MEG2) wafer was selected as the structural material for its properties such as hardness to contain the product gas and resistance to acid, e.g., hydrogen peroxide. Moreover, photosensitive glass has good thermal insulation and gas sealing can be achieved easily. The dimensions of each wafer were 30 mm × 30 mm with a thickness of 1 mm and a reaction zone of 10 mm × 10 mm × 4 mm. Cu/ZnO was selected as the catalyst for both hydrogen peroxide decomposition and methanol autothermal reforming. The catalyst support was prepared from a γ-type bimodal alumina pellet from Alfa Aesar with a size of 1/16 inch, a surface area of 255 m²/g, a total pore volume of 1.14 cm³/g, and a median pore size of 70 µm and 5000 Å. γ-type bimodal alumina is a highly porous material, and is stable at the high temperatures within the reactor. The catalyst was prepared using the wetness impregnation method, with 0.6 M Cu(NO₃)₂ and 0.3 M Zn(NO₃)₂ solutions used as precursors. Impregnation was followed by drying (120 °C, 12 hours), calcination (350 °C, 6 hours), and H₂/N₂ reduction (280 °C, 6 hours). After the reduction process, copper oxide, which is made by the impregnation method, is reduced to copper.

3.2. Fabrication of reformer

The fabrication process was as follows. The fabrication process of an individual glass wafer consisted of 7 steps: (1) exposure to UV light under a chrome mask at the intensity 2 J/cm²; (2) heat treatment at 585 °C for 1 hour to crystallize the portion of the glass that was exposed to UV light; (3) dissolution of the crystallized portion of the glass in a 10% hydrofluoric acid solution to produce a membrane for the glass for bonding followed by a bonding process by pressing the wafers together at 1000 N/m² in a furnace maintained at a temperature of 500 °C; (5) removal of the membrane after the bonding process in 10% hydrofluoric acid solution; (6) insertion of alumina catalyst support in the reformer layer (Ni foam was chosen for mixing since methanol and hydrogen peroxide were injected in liquid phase. As the reaction occurs over 200 °C, a conventional injection method is needed.  Here, a 1/16 inch stainless steel tube was connected to the micro glass reformer. 1/16 inch stainless steel tubes were fitted to the front and end ferrules. Finally, the fitted stainless steel tubes were locked to the reactor; (7) construction of the complete device by thermal bonding of the etched glass layers. The gap between the stainless steel tubes and glass was filled with PDMS (polydimethylsiloxane), which is a transparent, non-toxic, non-flammable, and heat resistant material that is widely used as a sealant for MEMS devices.

3.3. Design and fabrication of in-situ system

An implantable hybrid temperature sensor for a micro scale space in a power MEMS device is proposed using chrome silicide which has a very high electromotive force, and nickel as a base metal. The fabrication procedure is performed as follows. [5] The CrSi2 was sputtered to a thickness of 5000 Å on the alumina substrate with 1 kW power in an 8 mmTorr vacuum condition. Before the lift-off process that patterns the film, the substrate should be annealed in 30 min at 400 °C, and then for 30 min at 450° C. In the second step, the nickel film is deposited on the substrate using the same procedure as that used for the CrSi2 deposition, and the contact hole for the junction was built. In order to insulate the whole
metal areas excluding the electrode contact with the outer measurements, an oxide layer of 1 μm SiO2 was fabricated in the final process. The thicknesses of the junctions were 1μm. The RTDs have a thickness of 5000 Å, a length of 58 mm, and a width of 40 μm.

![Figure 1. Fabricated micro catalytic reformer with in-situ system](image)

4. Results

4.1. Experimental results

To measure and figure out the reaction temperature, chrome silicide (CrSi2) thermocouple module which we were fabricated micro catalytic reformer with in-situ system were used in experiment setup. Methanol and hydrogen peroxide were injected precisely by syringe pump.

In the autothermal reformer using hydrogen peroxide, the temperature decrease between the inlet and outlet was 10 – 20 ºC. This smaller temperature decrease is due to the uniform distribution of the hydrogen peroxide decomposition. Methanol conversion was observed to be 4 ~ 5% lower than in conventional autothermal reforming as a result of the low decomposition rate of hydrogen peroxide by the catalyst. We determined that hydrogen peroxide concentration was directly related to methanol conversion rate, peak reactor temperature and carbon monoxide concentration. For example, when we increased the hydrogen peroxide concentration, methanol conversion rate, peak reactor temperature, and carbon monoxide concentration also increased. At lower hydrogen peroxide concentrations, the decomposed water volume increased, creating a water gas shift (WGS) reaction. This WGS reaction prevented high carbon monoxide concentrations from forming in the product gas because of the resulting reaction between water and carbon monoxide. In thermodynamic point at the low temperature the WGS reaction is dominant, but in the real case the reaction rate is too slow for the low temperature.

![Figure 2. Methanol conversion and Hydrogen production rate](image1)

![Figure 3. Temperature profile of micro catalytic reformer measured by in-situ system](image2)
By parametric study, at the condition of 200 ºC and the rate of methanol to 40% of hydrogen peroxide are 4 to 1, the Carbon monoxide contents are reduced by less than 1000ppm. Using the present concept we could reduce the concentration of carbon monoxide in the product gas of the reformer by more than 80%.

4.2. Simulation results
Numerical simulation was accomplished by fluent. The chemical reaction was simulated using user defined function method. The temperature distribution of reactor was calculated and the design parameters of micro reactor were confirmed by simulation results.

![Temperature distribution (K)](image)

**Figure 4.** Temperature results of numerical simulation of micro reactor

5. Conclusion
The micro catalytic reformer with in-situ system was fabricated using photosensitive glass using thermal bonding with new connecting concepts for sustaining high reaction temperature. And the chrome silicide thermocouple for measuring reaction in micro system was fabricated. Using the present concept we could reduce the concentration of carbon monoxide in the product gas of the reformer by more than 80% due to low temperature gradient because of decomposition of hydrogen peroxide. At that carbon monoxide contents, micro reactor with autothermal reforming using hydrogen peroxide can be possible to load micro power sources without any devices.

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