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Development of multi-layered microreactor with methanol reformer for small PEMFC

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Abstract

A glass multi-layered microreactor with a methanol reformer that could provide power to portable electronic devices was developed to supply hydrogen to a small proton exchange membrane fuel cell (PEMFC). The microreactor consisted of four units: a methanol reformer with a catalytic combustor, a CO remover and two vaporizers. The dimensions of the microreactor were estimated by thermal simulation in order to achieve the required reaction temperature of each unit.

In this study, the glass multi-layered microreactor was produced using anodic bonding. The number of glass pieces of which the microreactor was composed was 13. The experimental temperature of each unit, as well as the heat loss, for a methanol reformer of temperatures at 280 °C was measured and compared with the results from thermal simulation.

Keywords: Microreactor; Fuel cell; Methanol steam reforming; Thermal insulation; Thermal simulation; Anodic bonding

1. Introduction

In many fields, fuel cells have been proposed as a possible solution to issues involving energy production and the environment. A small proton exchange membrane fuel cell system is suitable for portable electronic devices. There are two types of small proton exchange membrane fuel cell (PEMFC) systems: direct methanol and fuel reforming. Direct methanol systems can be operated at room temperature, but have a relatively low power density due to methanol crossover and to the low reaction rate of methanol oxidation over the anode electrocatalyst. On the other hand, fuel reforming systems are able to supply high power density but are difficult to miniaturize due to the complicated structure of the reformer. However, microfabrication technology can be used to miniaturize the reformer.

In our previous studies, we examined the components of the multi-layered microreactor including the microreactor used in methanol reforming, the CO remover and the vaporizer [1,2]. It has also been reported that using a vacuum package for thermal isolation allows the microreactor to be kept at a constant temperature with low heat loss [3]. To further improve system efficiency, it was necessary to optimize the microreactors' dimensions and the integration of each microreactor.

The multi-layered microreactor was produced by stacking 13 glass pieces using anodic bonding. Anodic bonding is a popular technique that is used to make micro-sensors since at low temperatures it can bond, without the use of adhesives, silicon, or virtually any other metal with good adhesion strength, to sodium-containing glass. A low bonding temperature does not produce any negative effects on the catalyst. However, anodically bonding more than four pieces of glasses has been difficult because alkali-metal ions spread out over the cathode surface.

The purpose of this study is to produce a multi-layered microreactor, whose design was based on the result of thermal simulation, and to improve the thermal efficiency of the system.

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2. Experimental and result

2.1. Design of the microreactor based on thermal simulation

Fig. 1 shows a simplified cross-sectional diagram of the multi-layered microreactor, while Fig. 2 shows a photograph of the multi-layered microreactor. The microreactor is composed of four units, each with a different temperature. Its functions are separated into two reaction systems. One reaction system is the hydrogen production system in which the methanol aqueous solution is fed and then vaporized at vaporizer 1; it is reformed to H_2 with CO_2 and a trace of CO at the methanol reformer; and finally the CO is preferentially oxidized at the CO remover. The other reaction system, the catalytic combustion system, is used to supply heat to the hydrogen production system. In this system, the methanol is vaporized at vaporizer 2 and then burned at the catalytic combustor. Fig. 3 shows a schematic of these two reaction systems.

Each unit described above requires a different reaction temperature. The methanol reformer with catalytic combustor requires temperatures of 280 °C, while the CO remover requires temperature of 180 °C. Each unit must be able to maintain the desired reaction temperature. Based on computational fluid dynamics, a thermal simulation involving the chemical reactions and thermal heat transfers, including radiation was performed to determine the temperature distribution of each reaction, and hence to optimize the structural design of the microreactor. To reduce heat loss by convection and radiation, thermal insulation from ambient air is necessary to improve system efficiency. Vacuum insulating technology is suitable for minimizing the heat loss while maintaining a compact package design. Thus, a vacuum insulating structure was used to decrease overall size and minimize heat loss. As well, thermal insulation from ambient air and a high-infrared reflectivity coating that suppresses radiation from the glass reactors, which have high infrared emissivity, also improve system efficiency. These four units were designed to be stacked and placed in a small glass vacuum package coated inside with a thin Au film, which has a high IR reflectivity of 98% that prevents heat loss by radiation.

2.2. The production of a multi-layered microreactor

The dimensions of the microreactor, shown in Fig. 2, are 22 mm wide by 21 mm long by 10.7 mm thick. A Au thin film heater was placed on top of each unit for initial heating; these film heaters also worked as temperature gauges.

Li-containing glass, which allows a lower temperature and voltage anodic bonding, was selected as the component for the microreactor. The multi-layered microreactor was constructed by stacking 13 pieces of glasses, which have serpentine microchannels for catalytic reaction and holes for gas

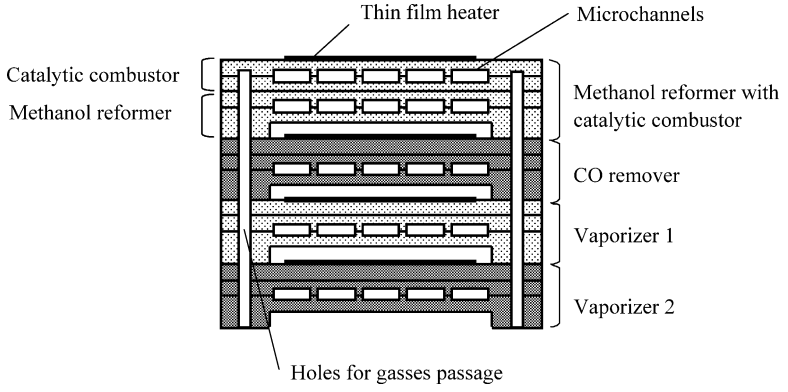

Fig. 1. Cross-sectional diagram of the multi-layered microreactor.

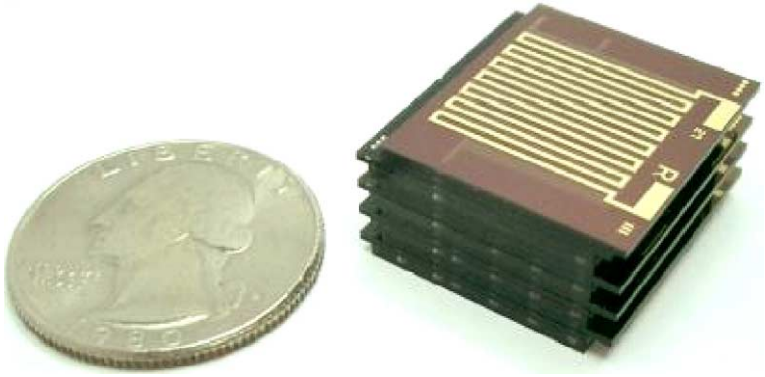

Fig. 2. Photograph of the multi-layered microreactor.

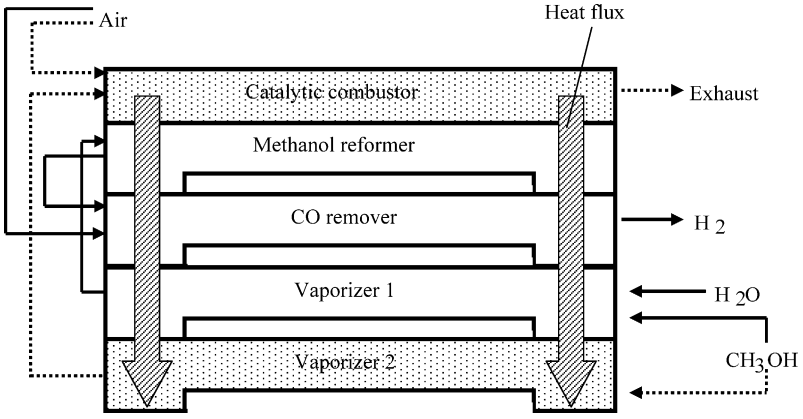

Fig. 3. Schematic of methanol reforming system.

passage. The gap between each unit limits heat transfer paths to neighboring units and allows a temperature difference to be maintained for each unit. Fig. 4 shows a process flow diagram for the production of the microreactor.

On one side of all the glass substrates, a high-resistance oxide buffer layer of a thin Ta–Si–O system film (500 nm thickness) and a thin Ta film (200 nm thickness) were formed, in this order, using sputtering. On the other side of some of the substrates, Ta (50 nm thickness) film, W (50 nm thickness) film and Au (300 nm thickness) film were deposited, in this order, using sputtering to create a thin film heater. Each film was formed as designed using photolithography. Microchannels and holes were shaped by sandblasting the glass substrates, which were covered by a dry-film photoresist processed by photolithography, using #400 SiC. All the substrates were diced after the chemical removal of the dry-film photoresist. The necessary catalysts were deposited on each of the microchannels on some glass chips. Finally, the 13 glass chips were anodically bonded. The final product has a complicated three-dimensional channel.

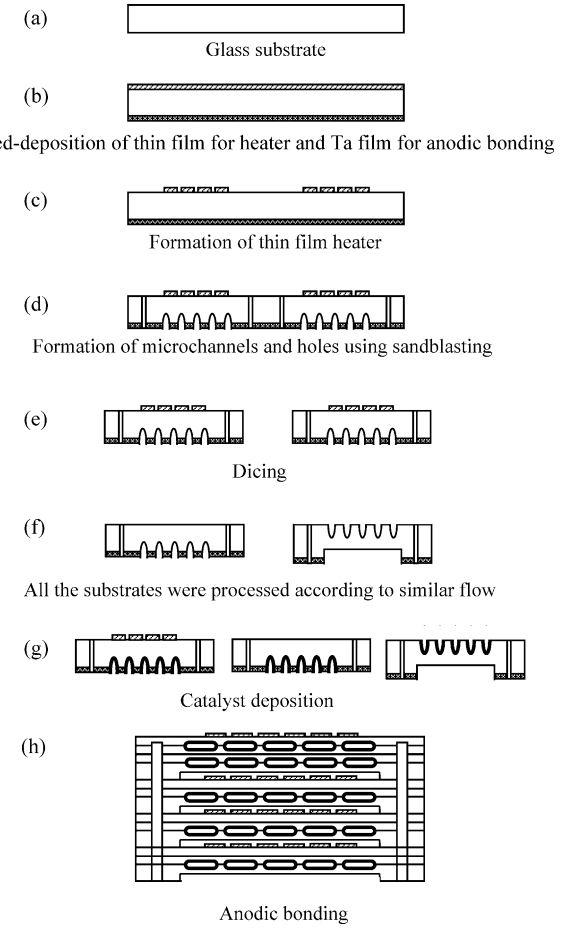

Fig. 4. Process flow diagram for producing the microreactor.

2.3. Multi-layered anodic bonding

2.3.1. Glass-to-glass anodic bonding

It has been established that anodic bonding processes introduce thermal strain due to the different thermal expansion coefficient between glass and silicon (or other metal). However, the difference in the thermal expansion coefficient between glass and thin metal films is negligible because of the thinness of the films. Glass-to-glass anodic bonding using a thin metal film, such as Ta, deposited by sputtering is proposed. Glass substrates were bonded at about 400 °C with an applied voltage ranging from 300 V to 1 kV such that Ta of one glass is positive with respect to the other glass. A glass–Si–glass sandwich structure is easily produced by anodic bonding. Replacing the Si wafer with a glass substrate onto which Ta film was deposited on both sides permitted the three-glass structure to be produced using anodic bonding. Applying a reverse voltage to the anodically bonded material causes some damage to the primary bonded interface [4]. Therefore, a glass with a metal deposited on one surface is required for the anodic bonding of more than four pieces of glass. Of note, the electric field should be applied so that the alkali-metal ions drift in one direction. The mobile sodium ions still cause damage to thin films. Fig. 5a and b shows a damaged Ta film deposited on the anodically bonded Pyrex glass surface, and an SEM image of an anodically bonded Pyrex glass surface on the cathode electrode side,

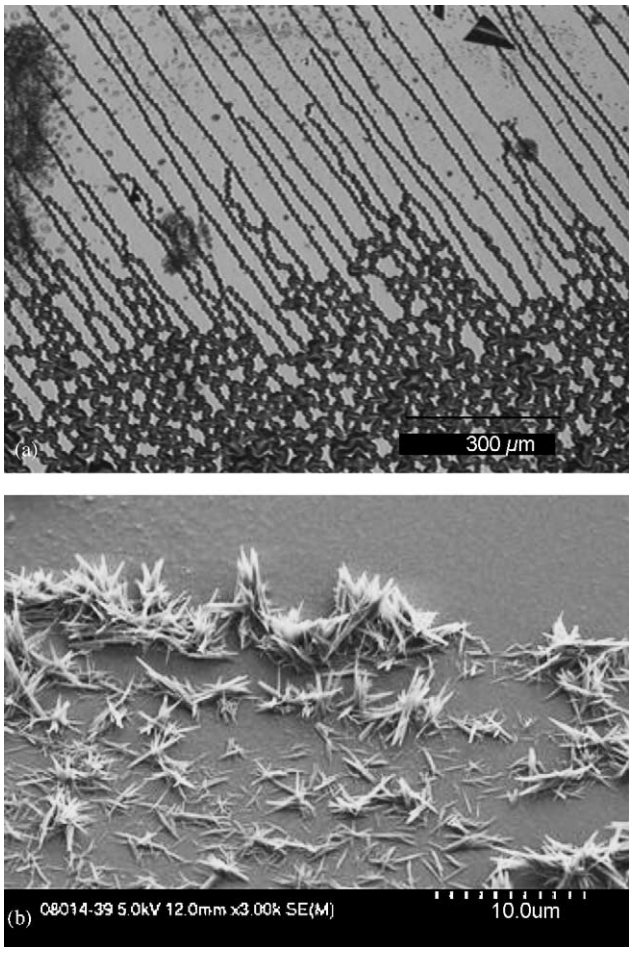

Fig. 5. The damaged Ta film deposited on the anodically bonded Pyrex glass surface (a) and photomicrograph of the anodically bonded cathode surface of Pyrex with a patterned Au heater (b).

respectively. The needle-like material observed in Fig. 5b is sodium spread on the glass surface. This phenomenon is not only limited to glass containing sodium, but also occurs with glass containing lithium. Placing a dummy glass between the cathode electrode and the Pyrex glass can reduce the amount of sodium found on the surface when there is no metal film on the bonded glass cathode surface. These alkali-metal ions have a negative effect on the thin metal film. The alkali-metal ions migrating to the cathode electrode in the large electrostatic field are blocked by a metal film with few interstices. The sodium ions then concentrate on the interface between the metal film and the glass. As a result, the concentrated sodium ions damage the metal film. A solution to this problem was found by using a buffer layer. The buffer layer with many interstices through which alkali-metal ions can pass and the ability to conduct electricity without affecting the anodic bond were required.

2.3.2. Ta–Si–O system buffer layer

A Ta–Si–O system oxide amorphous buffer layer was developed in order to suppress the damage resulting from alkali-metal ions. Ta–Si–O films were deposited using an RF magnetron sputtering device with a hot isostatic pressing (HIP) sintered target composed of Ta and SiO_2. The density of Ta–Si is between that of Ta and that of Si. However, the density of Ta–Si–O, whose oxygen concentration is close to 70%, is much smaller than that of Si_2O and Ta_2O_5 [5]. These results suggest that thin Ta–Si–O system films may have many interstices through which alkali-metal ions can pass. A $(Ta_{0.7}Si_{0.3})_{0.32}O_{0.68}$ film which has high resistivity of about 50 kΩ cm and has many interstices was used for buffer layer.

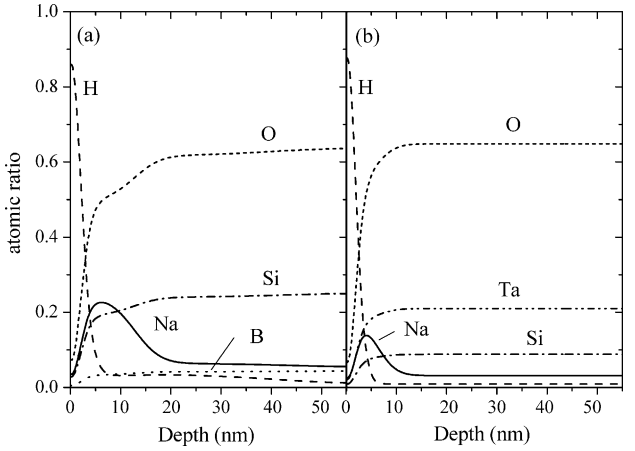

Fig. 6. RBS/HFS analysis of the anodically bonded Pyrex glass surface with a Ta–Si–O film (150 nm thickness) (b) compared to Pyrex glass without a Ta–Si–O film (a).

Since the analysis of lithium is difficult due to its low atomic number, sodium-containing Pyrex glass was used for the following analysis. Rutherford backscattering (RBS) and hydrogen forward scattering (HFS), used to analyze the cathode-side surface of the Pyrex that was anodically bonded to Si, confirmed that the buffer layers were effective in suppressing alkali-metal ion damage. Further confirmation was provided by observing the Au pattern deposited on this surface with optical microscopy. Fig. 6 shows the RBS/HFS analysis of a Pyrex glass surface with a Ta–Si–O film (150 nm thickness) compared to a Pyrex glass surface without a Ta–Si–O film. The reduction in sodium concentration is observed close to the surface. Increasing the thickness of the Ta–Si–O film decreases the sodium concentration. Fig. 7 shows the photomicrograph of a Pyrex glass surface with a Ta–Si–O film (500 nm thickness) compared with a Pyrex glass surface without a Ta–Si–O film. As expected, damage due to alkali-metal ions decreased with the Ta–Si–O film.

2.4. Development of the thin film heater

The multi-layered microreactor should be placed in a vacuum package for thermal insulation to improve system efficiency. Each unit of the microreactor requires a temperature gauge and heater. Reducing the number of lead wires decreases the heat leakage to ambient air and leads to the simplification of its structure. In this respect, thin films, which

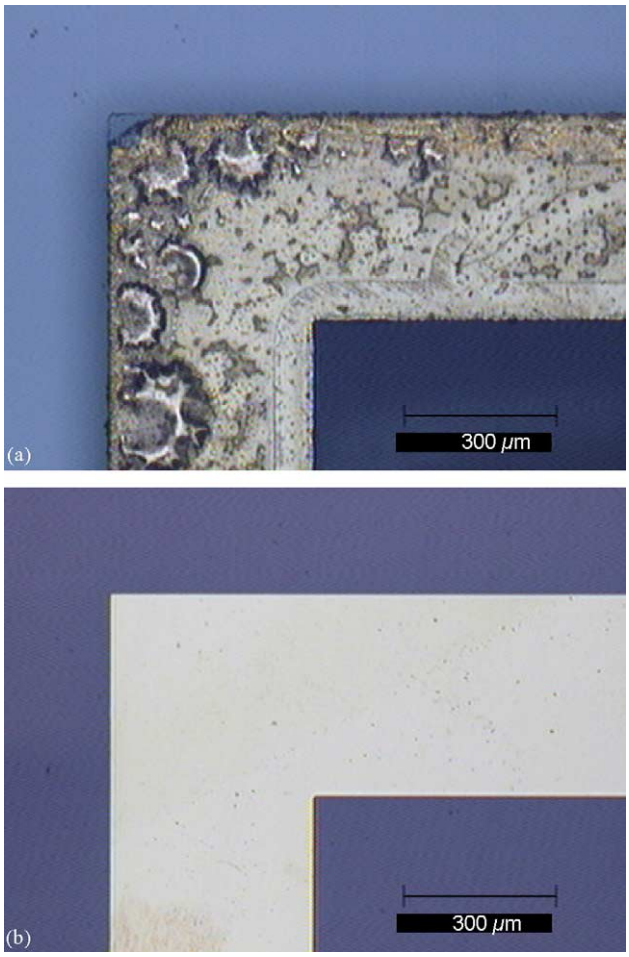

Fig. 7. Photomicrograph of the anodically bonded Pyrex glass surface with a Ta–Si–O film (500 nm thickness) (b) under a patterned Au heater compared to Pyrex glass without a Ta–Si–O film (a).

function both as a temperature gauge and a heater, must be developed. Au film was selected because of its chemical stability and ease of deposition and processing. The Au film should be deposited on the substrate using an adhesion layer, such as Ti or Cr film, since Au does not oxidize readily. The resistance of Au/Ti greatly increase at and above about 200 °C and the change was irreversible. This change in the resistance probably resulted from mutual diffusion between Au and Ti. Similar phenomenon were also observed for the Au/Cr film and the Au/Ta film. Thus, an Au/Ti heater is useless as a temperature gauge. Therefore, a W film was formed under Au film to prevent diffusion, while the Ta film with good adhesion to glass substrate was formed beneath the W film. The resistance of the Au/W/Ta thin film heater changes linearly over the range of temperatures shown in Fig. 8. R_0 is the resistance of the thin film heater when the temperature is 0 °C. The resistance of the film heater at 300 °C is 1.8 times that at room temperature. This large change in the resistance makes it suitable for use as a temperature gauge.

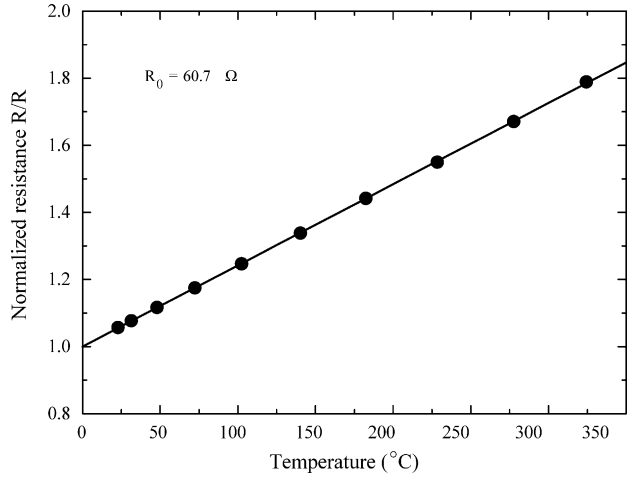

Fig. 8. The relationship between the normalized resistance of Au/W/Ta film and temperature.

2.5. Temperature distribution of the microreactor

Thermal simulations were used to estimate the temperature of each microreactor unit within the glass vacuum package (25.8 mm × 24.8 mm × 14 mm) coated inside with a thin Au film. The optimization of the microreactor dimensions in the vacuum package enabled each unit to have the necessary temperature for the reactions, as well as a sufficiently low heat loss (1.8 W) [6]. The simulated temperatures of each unit and heat loss were compared with the experimental values. The actual temperature of each unit placed in the vacuum package was measured as follows. A vacuum package made of SUS304 (51 mm × 45 mm × 35 mm) instead of glass was used for thermal insulation. Electroplating was used to form a thin Au film on the inner surface of the package. The package was evacuated and kept at approximately 10^{-2} Pa using a rotary pump and an oil diffusion pump. Electricity consumption, used to maintain the temperature of the reformer

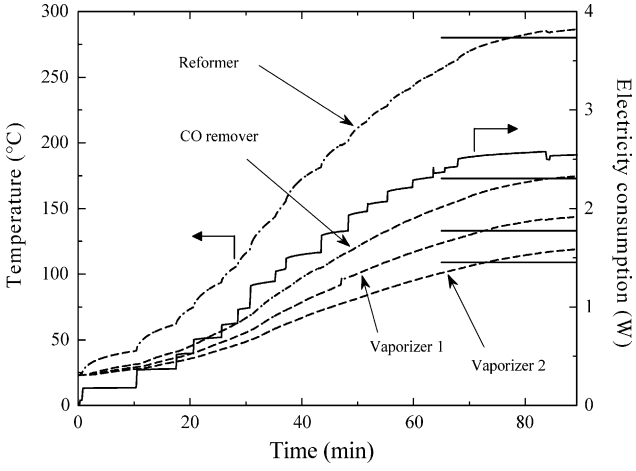

Fig. 9. Temperature of each unit and electricity consumption in comparison with thermal calculations of temperature distribution for the microreactor placed in the vacuum package.

at 280 °C by applying a current to the Au heater on the reformer, to balance to heat loss, was measured. At the same time, the temperature of each unit was also measured. Fig. 9 shows the experimental temperature of each unit and the electricity consumption when a current was applied to the Au heater on the reformer. The four straight lines described in Fig. 9 show the simulated temperature of each unit. The actual temperatures of each unit corresponded closely to the simulated values. However, an experimental result for heat loss (2.6 W) was slightly larger than the simulated result. It is probable that the discrepancy resulted from a difference in the value assigned to the thermal conductivity of the package.

3. Conclusion

In this study, a multi-layered microreactor with methanol reformer was developed. The design of the microreactor was optimized using thermal calculations and simulation. The observed temperature distribution when the microreactor was placed inside the vacuum package for thermal insulation was similar to the expected distribution.

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