

Short communication

Hydrogen production with integrated microchannel fuel processor for portable fuel cell systems

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Abstract

An integrated microchannel methanol processor was developed by assembling unit reactors, which were fabricated by stacking and bonding microchannel patterned stainless steel plates, including fuel vaporizer, heat exchanger, catalytic combustor and steam reformer. Commercially available Cu/ZnO/Al₂O₃ catalyst was coated inside the microchannel of the unit reactor for steam reforming. Pt/Al₂O₃ pellets prepared by ‘incipient wetness’ were filled in the cavity reactor for catalytic combustion. Those unit reactors were integrated to develop the fuel processor and operated at different reaction conditions to optimize the reactor performance, including methanol steam reformer and methanol catalytic combustor. The optimized fuel processor has the dimensions of 60 mm × 40 mm × 30 mm, and produced 450sccm reformed gas containing 73.3% H₂, 24.5% CO₂ and 2.2% CO at 230–260 °C which can produce power output of 59 Wt.

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1. Introduction

Small polymer electrolyte membrane fuel cells (PEMFCs) can be an attractive power sources for portable electronic devices. In order to apply fuel cell systems to portable devices, it is essential to develop a small and lightweight hydrogen supplier. Several systems including metal hydrides, chemical hydrides and hydrocarbon fuel reformers have been investigated as small hydrogen suppliers. Among them fuel processors have received great attention because of their high energy density and instant recharge of liquid fuel. However, fuel processors involve complex reactions for hydrogen production from hydrocarbons resulting in high reactor volume for the chemical reactions. Hence, the concept of the

microchannel reactor was employed to miniaturize the complicated chemical plant, mainly due to its advantages such as high surface to volume ratio, which is several orders of magnitude higher compared to traditional chemical reactors, and low linear dimensions, which enhance heat transfer and mass transfer in the reactor [1]. There are several hydrocarbon fuels as potential hydrogen sources for PEMFC systems. Among them methanol is an attractive fuel for the fuel processor because of its low reforming temperatures, low steam to carbon ratio, good miscibility with water and low content of sulfur compounds [2].

Recently, several investigations have been reported on the microchannel fuel processor using methanol as fuel for portable PEMFC applications. Pacific Northwest National Laboratory (PNNL) demonstrated 40W equivalent microchannel fuel processor consisting of a vaporizer, steam reformer and recuperative heat exchanger [3].

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Recently, they also reported sub-watt methanol processors revealing high thermal efficiencies up to 33% and low carbon monoxide below 100 ppm [4]. Motorola labs disclosed an integrated fuel cell system with ceramic methanol processor comprising fuel vaporizer, heat exchanger, reformer and catalytic combustor. The system was operated for 1 week generating 0.7 W electrical power [5]. Reuse et al. fabricated an integrated fuel processor with methanol steam reformer and methanol combustor employing two independent passages using microstructured stainless steel plates. In the microchannel reactor, kinetic models for steam reforming and complete combustion were also developed [6]. These previous studies revealed that the performance of micro fuel processors strongly depends on the reactor fabrication processes including microchannel design, material choice, catalyst coating method and reactor integration. Hence, they employed a variety of reactor construction processes and evaluated the integrated reactor performance to develop more a compact and more efficient hydrogen generator.

In this study, we developed an integrated methanol processor consisting of fuel vaporizer, heat exchanger, catalytic combustor and reformer based on our own reactor design, fabrication process and integration. Microchannels were patterned on the stainless steel plates and fabricated to make unit reactors. Catalyst was deposited inside the microchannel of the reformer unit. Granular combustor catalyst was packed inside cavity reactor. The catalytic combustor provided heat for the endothermic reforming reaction and the vaporization of liquid fuel. Vaporizer, heat exchanger, catalytic combustor and reformer units were integrated to make a unitized hydrogen supplying system. The performance of integrated

reactor was evaluated and the maximum throughput of the fuel processor was also determined.

2. Experimental

2.1. Fabrication of microchannel reactor

A stainless steel plate was used to fabricate unit microchannel reactors and integrated fuel processor. Microchannels were patterned on the stainless steel plates with 500 μm thickness using a wet chemical etching. Two different types of patterned plates with mirror image were prepared as shown in Fig. 1. The plates can be used as a co-current or counter-current heat exchanger in which the reforming and combustion reactions can be performed separately. A manifold plate has two holes for flow path and two triangular manifolds for uniform distribution of flow through each microchannel. Designing of microchannel shape was performed based on the simulation data of the channel. The plate has 34 straight microchannels which are 300 μm wide, 200 μm deep and 34 μm long as shown in Fig. 1. All stainless steel plates were stacked together and bonded by brazing to make unit reactors such as fuel vaporizer, heat exchanger and reformer as shown in Fig. 2.

The unit reactor for methanol steam reforming should be coated by reforming catalyst. For the catalyst coating to stainless steel plates, all plates were precoated by Al_2O_3 , before bonding the microchannel plates, to enhance the adherence of the catalyst layer on the microchannel walls. Then a commercial $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst (ICI Syntex 33–5) was coated inside microchannel reformer by slurry coating method. The

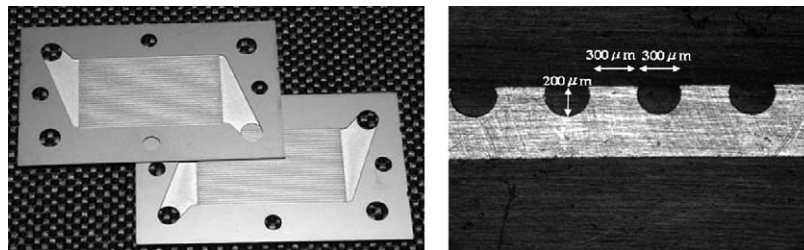


Fig. 1. Microchannel plates (left) and cross-sectional shape of the microchannel (right).

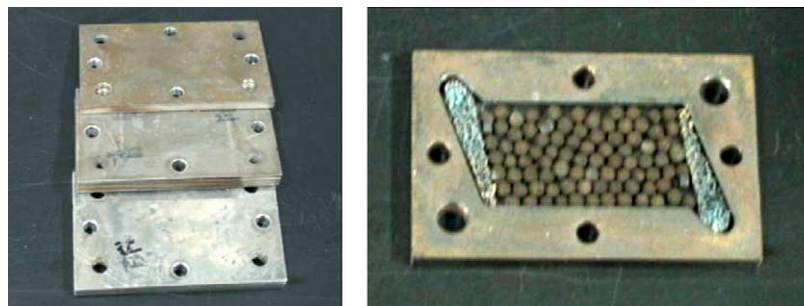


Fig. 2. Unit reactors fabricated by stacking and bonding of several microchannel plates (left) and catalytic combustor filled with Pt/Al₂O₃ pellets (right).

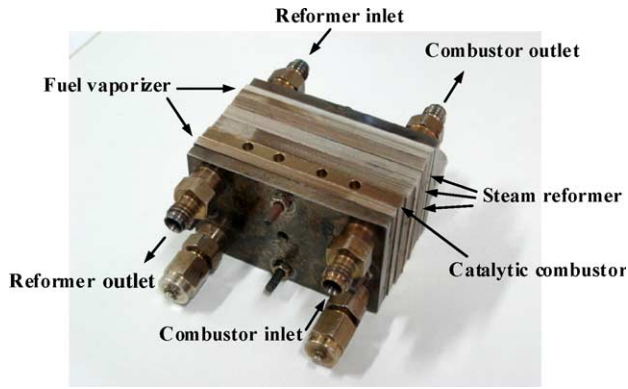


Fig. 3. Integrated methanol fuel processor composed of fuel vaporizer, heat exchanger, reformer and catalytic combustor.

catalyst slurry was prepared by mixing the catalyst, 20 wt.% alumina sol (NYACOL[®] AL20DW colloidal alumina, PQ Corporation), distilled water and 2-propanol. About 20 mg of the catalyst was coated on each microchannel plate. The coated catalyst was strongly adhered to the channel plate and hardly peeled off, which were tested in an ultrasonic cleaner (ultrasonic frequency 40–50 kHz, 30 min). A catalytic combustor was prepared by filling Pt/Al₂O₃ pellet into the cavity reactor as shown in Fig. 2. The Pt/Al₂O₃ combustion catalyst was synthesized by coating 5 wt.% Pt on the granular Al₂O₃ by incipient wetness method.

The fabricated unit reactors were stacked together to make an integrated fuel processor with independent two passages of reformer and combustor as shown in Fig. 3. The stacked reactors were tightened by end-plates to prevent the leak and mixing of gases between reformer and combustor. Two thermocouples were inserted to the end-plates of the reactor to detect the reaction temperature.

2.2. Experimental set-up

The experimental apparatus consists of feed sections for steam reforming and catalytic combustion, reaction section in the integrated reactor, and the analysis section with a gas chromatograph system.

The feed of methanol and water mixture into the reactor for steam reforming was performed by a syringe pump and methanol and air into the reactor for combustion was supplied by syringe pump and mass flow controller.

Before the reaction the catalyst coated inside channel of the integrated reactor was fully reduced by flowing H₂/N₂ stream into the reactor at 230 °C for 2 h by electrical heating. The reactor was packed by insulation for thermal isolation. The steam reforming reaction was conducted in the temperature range of 200–260 °C in the basis of reformer side end-plate and the temperature was controlled by varying methanol feeding into the combustor.

The product stream was separated using a cold trap maintained at 5 °C and the flow rate of dry reformed gas was

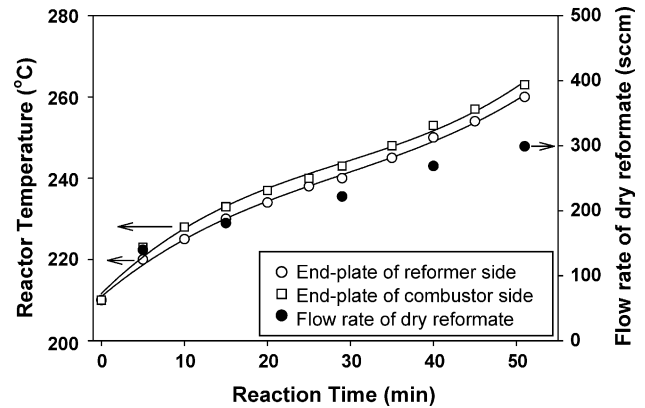
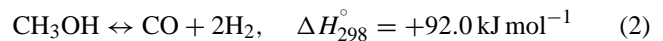
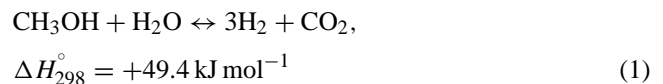


Fig. 4. Performance of the integrated fuel processor including steam reformer and catalytic combustor with respect to reaction time. Reformer feed: 0.3 sccm (S/C = 1.1), combustor feed: 0.2 sccm (O₂/C = 1.1), GHSV: 38,400 h⁻¹ (94 ms).

measured by a soap-bubble meter. The composition of dry reformed gas was analyzed by a gas chromatograph (Agilent 6890N). More details on the experimental installation can be found in the previous study [7].

3. Results and discussion

It is well known that the methanol steam reforming reaction for hydrogen production over the Cu/ZnO/Al₂O₃ catalyst involves the following reactions.



Eq. (1) is the algebraic summation of Eqs. (2) and (3). Eq. (2) represents methanol decomposition. Eq. (3) represents a water–gas shift reaction. The major products of this process are H₂ and CO₂. The minor quantities of CO are also produced. For the application of PEMFCs, the composition of produces gas requires high concentration of H₂ and low concentration of CO. To improve the H₂ and CO₂ selectivity, it is beneficial to increase the steam to carbon ratio (S/C ratio). However, the increase of S/C ratio requires more heating for vaporizing the additional water in the feed. Hence, it is necessary to compromise between the selectivity and system efficiency. In this study we employed 1.1 of S/C ratio based on the previous study [7].

Fig. 4 shows the performance of the integrated microchannel reactor. The reactor was started up by electrical heating up to 210 °C then methanol catalytic combustor was operated to supply the heat for the methanol reforming and fuel vaporization. When 0.2 cc min⁻¹ methanol was fed into the

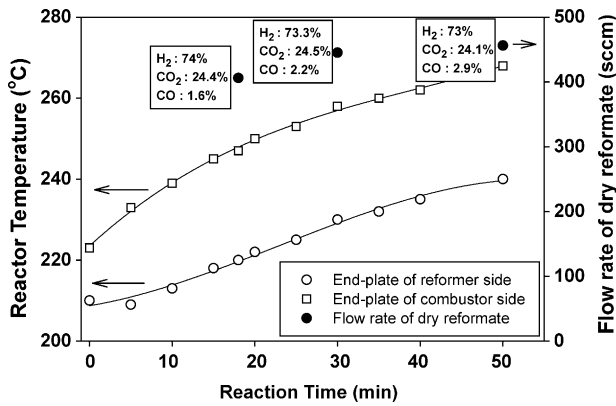


Fig. 5. Performance of the integrated fuel processor including steam reformer and catalytic combustor with respect to reaction time. Reformer feed: 0.3 sccm (S/C = 1.1), combustor feed: 0.2 sccm ($O_2/C = 1.1$), GHSV: $12,800 \text{ h}^{-1}$ (282 ms).

combustor with excess air the temperature of integrated reactor system steady increased with reaction time as shown in Fig. 4. Hence, we started up the reformer simultaneously with the combustor and investigated the hydrogen production performance of the reactor system with respect to reaction temperature from 220 to 260 °C as shown in Fig. 4. The temperature difference between two end-plates of the reactor was less than 3 °C. Flow rate of reformed gas including H_2 , CO_2 and CO increased from 140 sccm to 300 sccm with increasing reaction temperatures from 220 to 260 °C, which corresponds to the increase of methanol conversion from 31 to 66%.

When the catalytic reactor volume increased by three times resulting in the increase of space time from 94 to 282 ms, the flow rate of reformat improved significantly from 140 to 406 sccm at 220 °C of end-plate temperature of reformer side as shown in Fig. 5. More than 99% of methanol was converted at 240 °C of reformer side temperature. However, the reactor showed very high temperature difference between two end-plates of the reactor mainly due to the increase of reactor volume and relatively low heat transfer between unit reactors. The product gas composition of the reactor revealed 73–74% H_2 , 24–25% CO_2 and 1–3% CO at all reaction temperatures. CO concentration increased from 1.6 to 2.9% with increasing reaction temperatures from 220 to 260 °C. This is mainly due to the enhanced methanol decomposition (Eq. (2)) and suppressed water–gas shift reaction (Eq. (3)) at high reaction temperatures. Hence, it is necessary to develop active reforming catalyst at low reaction temperature to minimize CO concentration at reformed gas. But, additional CO clean-up unit should be integrated to the fuel processor to reduce the CO concentration of the reformed gas below 10 ppm which is applicable to PEMFC systems.

Fig. 6 shows the effects of reactor residence time and reaction temperature on the performance of integrated fuel processor. The results clearly reveal that the steam reforming of methanol strongly depends on the reaction conditions, and the hydrogen production improved with increasing reactor

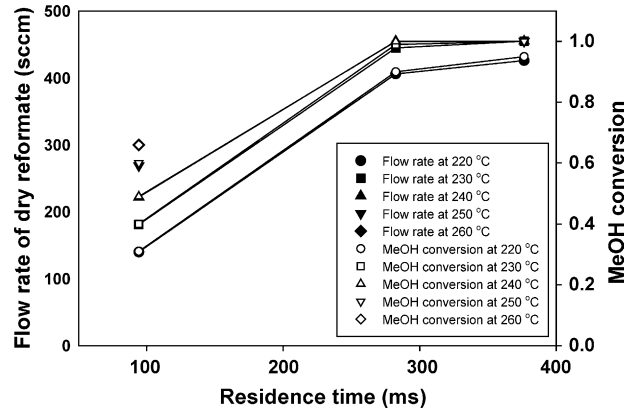


Fig. 6. Performance of the integrated fuel processor including steam reformer and catalytic combustor with respect to reactor residence time and reaction temperature. Reformer feed: 0.3 sccm (S/C = 1.1), combustor feed: 0.2 sccm ($O_2/C = 1.1$).

Table 1

Optimum operating conditions and performance of the integrated reactor	
Reactor temperature (°C)	230–260
Pressure	Atmospheric pressure
S/C (steam to carbon ratio)	1.1
Feed flow rate of reformer ($\text{cm}^3 \text{ h}^{-1}$)	18
Feed flow rate of combustor ($\text{cm}^3 \text{ h}^{-1}$)	12
Methanol conversion of reformer	>99%
Gas composition, dry basis	73.3% H_2 24.5% CO_2 2.2% CO
H_2 production rate	0.88 mol h^{-1} =330 sccm =59 Wt
Estimated electric power (We)	28
Assumptions	
Fuel cell efficiency	60%
H_2 utilization	80%
Integrated reactor volume	72 cm^3 (60 mm × 40 mm × 30 mm)

volume and reaction temperature. The results also indicate that 282 ms of residence time is enough for the production of 450 sccm reformed gas below 240 °C. Based on the above results the optimum operating conditions and the performance of the integrated reactor were summarized in Table 1.

4. Conclusion

An integrated microchannel methanol processor consisting of fuel vaporizer, heat exchanger, catalytic combustor and steam reformer was developed. Unit reactor was fabricated by stacking and bonding several microchannel plates. Commercially available Cu/ZnO/Al₂O₃ catalyst was coated

inside microchannel of the unit reactor for steam reforming. Pt/Al₂O₃ pellets prepared by incipient wetness method were filled in the cavity reactor for catalytic combustion. Other unit reactors were used as heat exchanger and fuel vaporizer. Those unit reactors were assembled and two reactions occurred independently in the integrated reactor for hydrogen production by methanol steam reforming and for heat generation by catalytic combustion. The integrated reactor has the dimensions of 60 mm × 40 mm × 30 mm, and produced 450 sccm reformed gas including 73.3% H₂, 24.5% CO₂ and 2.2% CO at 230–260 °C which can produce power output of 59 Wt.

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