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Novel micro fuel processor for PEMFCs with heat generation by catalytic combustion

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Abstract

Microchannel reactor offers opportunities for the development of compact fuel processor for PEMFCs. The design and experimental work concerning a microdevice for the methane steam reforming with hydrogen catalytic combustion is presented herein. We designed novel flow channel on reformer sheets and microholes on combustor sheet to inhibit the hot spot, which takes place in front of the reactor. Experimental results show that the Pt–Sn/Al_2O_3 coated microchannel combustor was active enough to initiate hydrogen combustion at room temperature and able to increase reactor temperature up to 800 °C by hydrogen combustion uniformly. The performance of the microchannel reformer was investigated at various operating conditions. The developed micro fuel processor generates enough hydrogen for power output of 26 W as fuel cell.

Keywords: Microchannel reactor; Fuel processor; PEMFCs; Hydrogen combustion; Methane steam reforming

1. Introduction

Fuel cells are an alternative for clean energy generation [1]. Especially, polymer electrolyte membrane (PEM) fuel cell have received a great attention as attractive power sources for mobile and small stationary power units because of low operation temperature, high energy density, low weight, compactness, potential for low cost and volume, long stack life, fast start-ups and suitability to discontinuous operation [2].

A typical fuel processor of steam reforming for PEMFCs is composed of five unit operation such as fuel vaporizers/preheaters, fuel reformers, carbon monoxide clean-up processes, heat exchanger and combustor as shown in Fig. 1.

The application of this conventional steam reformer for hydrocarbon takes up to 30–40% of the volume of the fuel cell system [3]. This large size requires heavy investments and long start-up times. In order to apply PEMFCs to portable devices commercially, a fuel processor should be of high energy density and compact size inevitably.

Microchannel reactor (MCR) is a good solution for compactness of fuel processing. MCR has many advantages, such as enhanced heat and mass transfer, the flow uniformity, high specific-surface area, safe control in explosive regime and easier scale-up without geometry change [4][5]. Microchannel fuel processors containing catalytic combustion or electric heater integration have been recently developed [3,6–10]. They used methane and methanol for combustion so that needed the evaporator and/or pre-heater. The anode-off gases containing hydrogen can be introduced into combustor as a fuel. Since hydrogen combustion on Pt catalysts can take place under room temperature [11], there is no need of any evaporator or pre-heater.

However, hydrogen catalytic combustion in MCR has some challenges for application. Since hydrogen is extremely light in comparison with air and flows/diffuses upward across the catalyst body [12], the temperature profile of catalytic bed tends to be considerably non-uniform. Janicke et al. [13] reported that there was hot spot in front of the reactor when H_2/O_2 mixture was introduced in microchannel reactor/heat exchanger. This hot spot and its movement depending on the gases flow rate [14] should be carefully controlled in order to apply hydrogen catalytic combustion for hydrocarbon steam reforming.

We tested methane steam reforming with hydrogen catalytic combustion in novel designed microchannel reactor.

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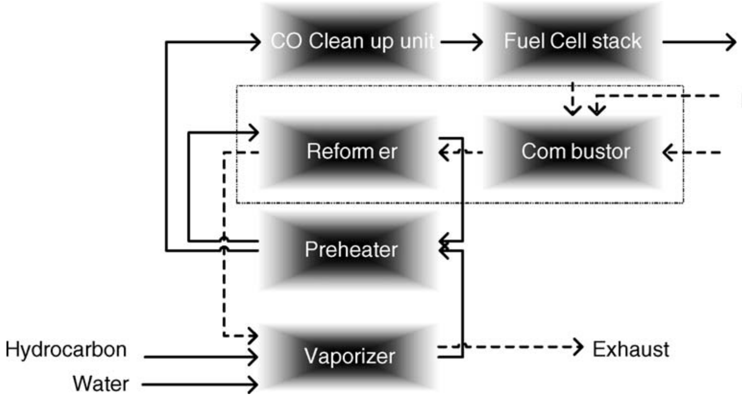

Fig. 1. Schematic diagram of fuel processor-fuel cell system of steam reforming, consisting of five-unit operation and a fuel cell. The divided box is the reformer with external combustor.

The combustor was designed to introduce fuel and air separately. Pt–Sn/Al_2O_3 and Rh–Mg/Al_2O_3 was impregnated by wash-coating in combustor and reformer of MCR, respectively because Rh–Mg catalyst has good activity for methane steam reforming [15] and Pt–Sn catalyst does for hydrogen combustion [16]. Especially, in order to heat up reaction temperature of reformer over 700 °C uniformly for methane steam reforming, hydrogen and air was separately introduced to the microchannel combustor. The reactor was heated up to 800 °C uniformly and methane steam reforming could be carried out in the reformer with hydrogen combustion in the combustor. And it was confirmed that combustion and methane steam reforming could be handled in one compact reactor.

2. Experimental

2.1. Design of microchannel reactor (MCR)

The designed MCR consists of cover plate, base plate and 25 sets (50 plates) microchannel sheets. Inconel plate was used to fabricate the microchannel sheets and stainless steel for cover and base plates. Microchannels were patterned on a plate using a wet chemical etching method. The cover plate has three conduits and base plate has two conduits, which act as flow inlet and outlet. Each microchannel sheets have two conduits and two flow distribution chambers for enhancing the uniform distribution. Especially, we designed an inventive gas flow channel and microholes to introduce fuel for combustion separately. Each sheet having 22 channels has the following dimensions of the flow path, 500 μm in diameter, 250 μm in depth and 17 mm in length. Combustor sheets and reformer sheets were stacked alternately and then bonded by brazing method. The dimensions of the combustor (25 plates) and reformer (25 plates) unit excluding fittings were about 40 mm × 40 mm × 30 mm. Fig. 2 shows the assembled unit of microchannel fuel processor and a combustor sheet. In detail, Fig. 3 is the schematic representation of the novel designed microchannel sheets and flow paths. Pt–Sn/Al_2O_3 catalyst for hydrogen combustion and Rh–Mg/Al_2O_3 catalyst for methane steam reforming were prepared by a first alumina wash-coating followed by the subsequent impregnation of Pt–Sn and Rh–Mg solution in combustor and reformer, respectively. The microchannel reactor was first pre-treated in air at 800 °C for 2 h before alumina coating. The deposited catalyst thin films were characterized by scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDX).

2.2. Hydrogen catalytic combustion and methane steam reforming

Hydrogen combustion (1) and methane steam reforming (2) take place in each microchannel sheets, respectively, as described below

$$H_2 + 0.5O_2 \rightarrow H_2O \quad (\Delta H^\circ_{298} = -242\,\mathrm{kJ\,mol^{-1}}) \tag{1}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (\Delta H^\circ_{298} = 206.2\,\mathrm{kJ\,mol^{-1}}) \tag{2}$$

A Stoichiometric mixture of hydrogen and air are separately introduced as shown in Fig. 2 and Fig. 3 for combustion. And then hydrogen and air are mixed in the MCR manifold. Methane, sometimes N_2, and steam are supplied into the microchannel reformer for methane steam reforming or reactor cooling. Temperature was controlled by the mixture flow rate of hydrogen and air. Methane steam reforming tests were carried out with steam to carbon ratio of 3.0. Fig. 4 is the schematic diagram of experimental set-up. Gas was supplied by mass flow controller (MFC, Brooks 5850 series) and steam as water was done by micro liquid pump (NS, MINICHEMI PUMP, 1-1000 μl/min). Water was introduced when the reformer temperature was 120 °C. Liquid components were separated by cold trap in the produced stream. The flow rate of reformed gas was measured by a soap bubble flow meter. Reactants and products gases were analyzed by a gas chromatography (Agilent 6890N) equipped with HP-MOLSIV, HAYESEP D columns and thermal conductivity detectors (TCD). Temperature was monitored by data acquisition/switch unit (Agilent 34790A) equipped with K type thermocouple into fuel inlet, combustor outlet and reformer outlet conduits. The microchannel fuel processor was insulated by ceramic wool before test.

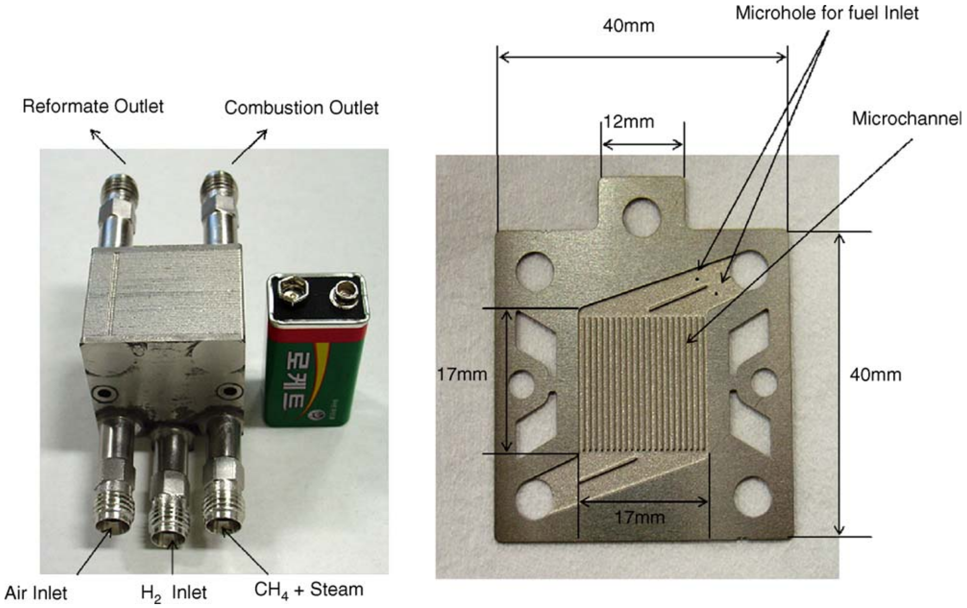

Fig. 2. Photograph of assembled catalytic combustor/reformer and a microchannel sheet for hydrogen combustion and uniform pre-heating of the reformer. Two microholes were designed for combustive fuel separately feeding.

3. Results and discussion

3.1. H_2 combustion and reforming in MCR

Though hydrogen/oxygen reaction is very fast and has broad explosion limits for H_2 (4–94% in O_2 on volume percent basis), yet the challenges of this explosive reaction can be solved by using a microchannel reactor. Since dimensions of microchannels (500 μm × 250 μm) are smaller than the quenching distance for H_2/O_2 mixtures, which is commonly known about 1000 μm [17], MCR can suppress flame propagation. Furthermore, Veser [5] reported that the explosion limit depended on the reaction condition such as temperature and pressure and the reactor having 100 μm in diameter was inherently safe at ambient pressure. Additionally, the explosion limit diameter of H_2/O_2 mixture was between 1000 and 100 μm at 850 °C in temperature and ambient pressure. We detected the temperature at fuel inlet, reformer outlet and combustor outlet to confirm that our reactor was able to control hydrogen combustion and heat up the reactor up to 800 °C uniformly. Initial flow rate of the hydrogen and air was 3.8 and 9.9×10^{-2} mol min^{-1}, respectively (section (A)). At that time N_2 of 4.9×10^{-3} mol min^{-1} and steam of 1.5×10^{-2} mol min^{-1} was introduced into the reformer. Water was introduced when the temperature of reformer was 120 °C. When the combustor outlet temperature reached 800 °C, hydrogen and air flow

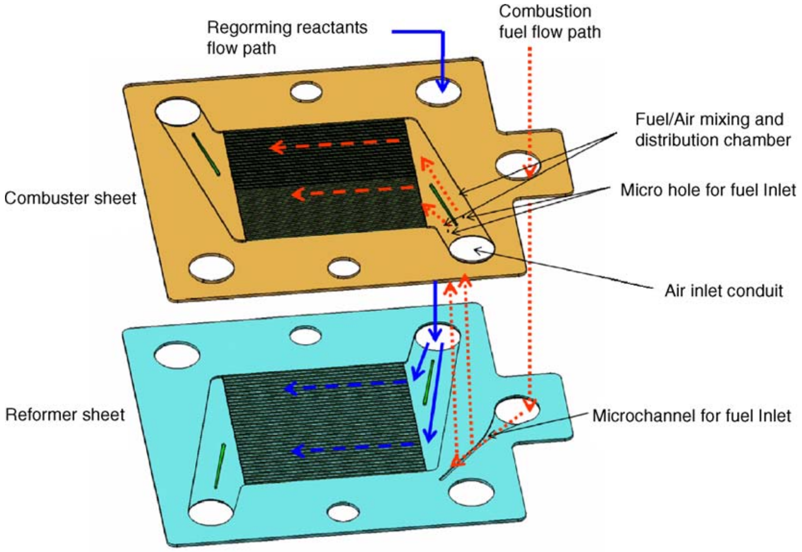

Fig. 3. The schematic representation of the novel designed microchannel sheets and flow paths. Red dotted line: fuel for combustion flow path; red dashed line: fuel/air mixture and combustion off gas flow path; blue solid line: reforming reactants flow path and blue dashed line: reformate flow path.

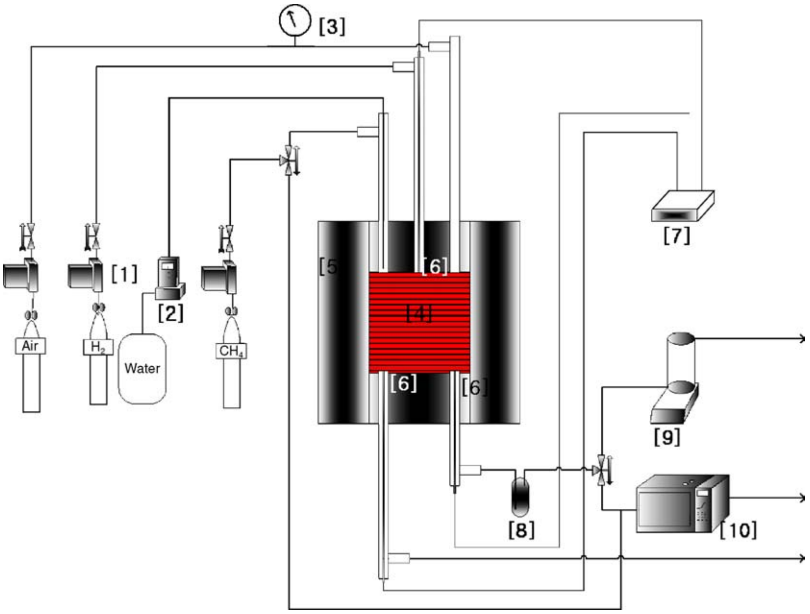

Fig. 4. Schematic diagram of experimental set-up. (1) Mass flow controller(MFC); (2) micro liquid pump; (3) pressure gauge; (4) microchannel fuel processor; (5) ceramic wool for reactor insulation; (6) K type thermo couple; (7) data acquisition/switch unit; (8) cold trap; (9) bubble flow meter and (10) gas chromatography (GC).

rate was increased to 4.2 and 1.1×10^{-2} mol min^{-1}, respectively (section (B)). And then methane of 4.9×10^{-3} mol min^{-1} was introduced for methane steam reforming instead N_2 when reformer outlet temperature was 750 °C (section (C)). In the section (A) as shown in Fig. 5, hydrogen combustion was initiated at room temperature. And the temperature could be controlled by increasing hydrogen/air flow rate in section (B). However, the start-up time of reactor was so long that it took about 2.5 h to reach the reformer outlet temperature of 700 °C. In order to apply this microchannel reactor to fuel processors or other dynamic processes, many efforts, such as increasing catalyst-loading weight on the microchannel and introduction of igniter, need to decrease the start-up time. After methane steam reforming began in section (C), reactor temperatures were decreased. It indicates that the heat produced from combustion was consumed by methane steam reforming which is an endothermic reaction. And the final operating temperature of reformer can be controlled at 700 °C constantly by the hydrogen combustion. Moreover, there were not any explosion sounds like that Janicke et al. [13] reported. The temperature difference between fuel inlet and combustor outlet was within 110 °C. The reason why there was temperature difference was that the reactants for reforming and/or the coolants introduced by co-current flow cooled down the inlet side. However, temperature of reformer outlet was similar to fuel inlet. It indicated that the heat transfer of the reactor was very good.

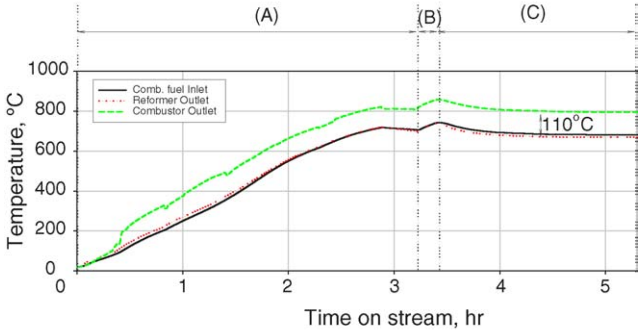

Fig. 5. Reactor temperature plotted as a function of time on stream: (A) H_2 of 3.8×10^{-2} mol min^{-1} and air of 9.5×10^{-2} mol min^{-1} into combustor, N_2 of 4.9×10^{-3} mol min^{-1} and water of 1.5×10^{-2} mol min^{-1} as liquid into reformer; (B) H_2 of 4.2×10^{-2} mol min^{-1} and air of 1.1×10^{-1} mol min^{-1} air into combustor and (C) H_2 of 2.2×10^{-2} mol min^{-1} and air of 1.1×10^{-2} mol min^{-1} into combustor, CH_4 of 4.9×10^{-3} mol min^{-1} and water of 1.5×10^{-2} mol min^{-1} into reformer.

3.2. *Effects of hydrogen flow rate on combustion*

In other to carry out methane steam reforming, we varied the hydrogen flow rate into MCR to examine the capacity of combustion section. The introduced hydrogen flow rate was from 2.1 to 3.9×10^{-2} mol min^{-1} and it made the temperature of reactor increased. Fig. 6 shows the results that the incremental rate of reformer outlet temperature was decreasing with an increase of hydrogen flow rate. It indicates that there is upper limit of reactor capacity for hydrogen combustion because the increased reactants flow rate cooled down the temperature of the reactor. To expand the combustor's capacity, heat exchanger for heat recovery from combustion outlet and reforming outlet would be proposed. The heat exchanger will preheat the reactants such as air, fuel, water and methane.

3.3. *Product gas compositions and CH_4 conversion with reforming temperature*

Major gas product of methane steam reforming is hydrogen and CO, and minority of CO_2 as produced via water–gas shift

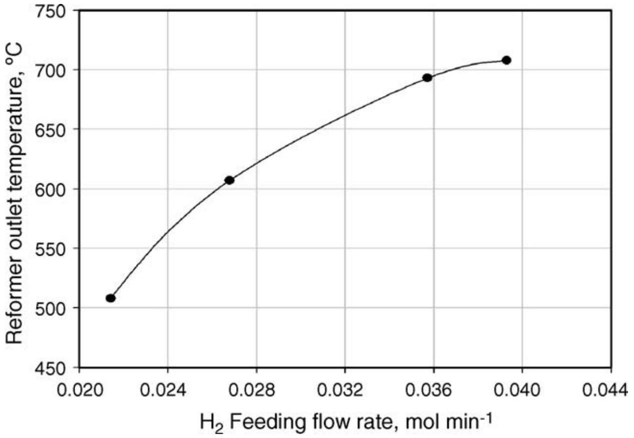

Fig. 6. The reformer outlet temperature changes via hydrogen flow rate. CH_4 feed flow rate = 2.5×10^{-3} mol min^{-1}; steam to carbon ratio = 3.0.

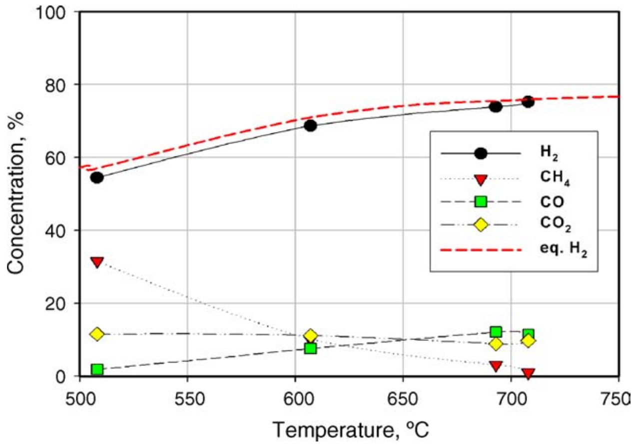

Fig. 7. The effect of reformer outlet temperature on composition of dry reformate. CH_4 feed flow rate = 2.5×10^{-3} mol min^{-1}; steam to carbon ratio = 3.0.

reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (\Delta H^\circ_{298} = -41.1\,\text{kJ}\,\text{mol}^{-1}) \qquad (3)$$

The excess molar ratio of steam, S/C ratio 3.0, was for the purpose of by-product carbon formation inhibition. For the same condition for the previous methane steam reforming, the composition of product gas with different reforming temperature is in Fig. 7. We controlled the MCR temperature by varying the hydrogen/air flow rate as shown in Table 1. As the reformer outlet temperature increased from 508 to 708 °C, the concentration of H_2 increased from 54 to 75 volumetric % as shown in Fig. 7. The concentrations of CO also increased with temperature increasing. Since the concentration of CO should be less than 20 ppm for application to the fuel cell, additional CO-clean-up processes such as WGS, PrOx and/or methanation are required to reduce CO concentration.

Table 1
The condition of combustion for methane steam reforming

Case	Combustion section (10^{-2} mol min^{-1})		Temperature (°C)	
	Air	H_2	Comb. outlet	Reformer outlet
1	5.4	2.1	615	508
2	6.7	2.7	721	607
3	8.9	3.6	800	693
4	9.8	3.9	821	708

CH_4 feed flow rate = 2.5×10^{-3} mol min^{-1}; steam to carbon ratio = 3.0.

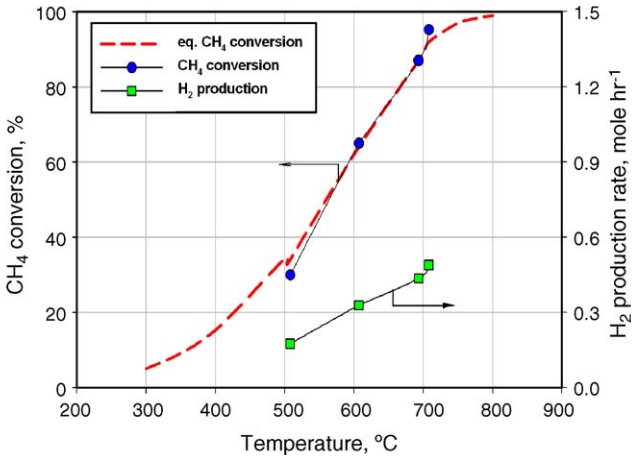

Fig. 8. A CH_4 conversion and H_2 production rate according to reformer outlet temperature. CH_4 feed flow rate = 2.5×10^{-3} mol min^{-1}; steam to carbon ratio = 3.0.

The CH_4 conversion and H_2 production rate for a constant feed flow rate indicate the performance of fuel processor. Fig. 8 shows CH_4 conversion and H_2 production rate according to reformer outlet temperature. Combustion condition is in Table 1. The CH_4 conversion and H_2 production rate were increased with increasing reformer outlet temperature. When reformer outlet temperature was 708 °C, the CH_4 conversion and H_2 production rate was 95% and 8.3×10^{-3} mol min^{-1}, respectively. Furthermore, the methane conversion was very similar to the equilibrium conversion rate. It indicated that the reformer having microchannels showed very fast molecular diffusion. The electrical power with a typical fuel cell can be anticipated by 60% efficiency of fuel cell and 80% utilization of H_2. According to this assumption, the anticipated power outlet of MCR reformer is about 16 W as fuel cell power.

3.4. The effect of feed flow rate on a methane conversion and production rate of H_2

The effect of feed flow rate on the methane conversion was investigated for the maximum throughput of the developed fuel processor. Methane feed flow rate was increased from 2.5 to

Table 2
The conditions of combustion and methane steam reforming

Case	Combustion section		Reforming section	
	Air (10^{-2} mol min^{-1})	H_2 (10^{-2} mol min^{-1})	CH_4 (10^{-2} mol min^{-1})	Steam (10^{-2} mol min^{-1})
1	9.8	3.9	0.25	0.75
2	10.7	4.2	0.36	1.1
3	11.2	4.4	0.49	1.5

Table 3
The energy balance and performance of developed fuel processor

Case	Reaction no.	Flow rate (10^{-2} mol min^{-1})	Conversion (%)	Portion (%)	Total ΔH°_{298} (kJ h^{-1})
1	1	3.9	100	100	−566
	2	0.25	95	54	16
	4	0.25		46	11
	H_2 regen.	0.82			118
	Efficiency		25.6%		
2	1	4.2	100	100	−610
	2	0.36	86	57	22
	4	0.36		43	13
	H_2 regen.	1.1			157
	Efficiency		31.5%		
3	1	4.4	100	100	−639
	2	0.49	78	58	27
	4	0.49		42	16
	H_2 regen.	1.4			198
	Efficiency		37.7%		

4.9×10^{-3} mol min^{-1}. The steam to carbon ratio was kept at 3.0 to reduce the by-product carbon formation. The temperature of reformer outlet was kept around 700 °C. Hydrogen/air flow rate was increased with increasing methane and water flow rate to maintain the reformer outlet temperature as shown in Table 2.

As shown in Fig. 9, methane conversion was decreased with increasing methane feed flow rate in contrast with H_2. The heat necessary for steam-reforming reaction, which is endothermic, could be supplied sufficiently by hydrogen combustion with increasing methane feed flow rate. There is a trade-off relationship between methane conversion and H_2 production rate to achieve the high throughput and efficiency. When methane flow rate was 4.9×10^{-3} mol min^{-1}, reformer outlet temperature was 698 °C to achieve 80% conversion of methane. In this operation condition, the hydrogen production rate was 1.4×10^{-2} mol min^{-1}. It indicates that anticipated power output of this fuel processor is 26 W.

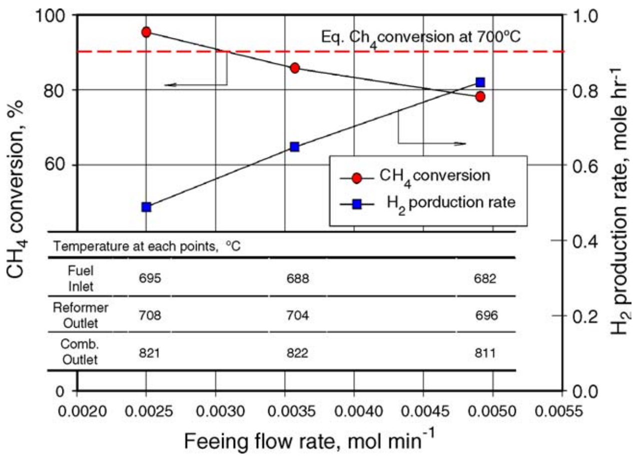

Fig. 9. CH_4 conversion and H_2 production rate, and the temperature profile for reforming in variation with feed flow rate. Steam to carbon ratio = 3.0, dashed line is equilibrium methane conversion rate at 700 °C.

On the other hand, reaction (2) and (3) can be summarized into

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad (\Delta H^\circ_{298} = 165.1\,\mathrm{kJ\,mol^{-1}}) \tag{4}$$

And the energy balance and performance were presented in Table 3. As shown in Table 3, the energy efficiency was increased with an increase in methane feed flow rate. However, the efficiencies, in all cases, were below 40%. The reason why the efficiencies somehow low was that there was not heat recovery from combustion and reforming off gases. Temperatures of combustion off gas and reforming off gas, in case 3, were 811 and 696 °C, respectively. If there had been heat recovery system, the energy efficiency would have increased.

Furthermore, the object of this study was development of combustor of hydrogen from anode-off gases. Hydrogen combustion in conventional reactor is very difficult because of backfire. In this study, we showed the possibility of the combustion of anode-off gases.

4. Conclusions

A microchannel reformer integrated microchannel combustor was designed and manufactured for catalytic hydrogen combustion. Pt–Sn/Al_2O_3 wash-coated microchannel combustor was active enough to initiate hydrogen combustion at room temperature. This reactor was able to increase reactor temperature up to 800 °C by hydrogen combustion. At that time the temperature difference between combustor and reformer was 110 °C. However, the start-up time of reactor was so long that it took about 2.5 h to reach the heat exchanger outlet temperature of 700 °C. In other to apply this microchannel reactor to fuel processors or other dynamic processes, care has to be taken to decrease the start-up time. If this kind of reactor applies to the fuel processor, start-up equipments such as igniter will be a good solution.

The performance of the microchannel reformer was investigated at various operating conditions. As the result, this reformer generates hydrogen for power output of 26 W as fuel cell. It indicates that this reactor requires 2.4 l/kW.

The energy efficiency was somehow low as below 40%. It was that there was no heat recovery system. Further investigations are required for the heat exchanger for reactants preheating, CO-cleanup processes and thermal integration of the total system.

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