

Micromachined methanol steam reforming system as a hydrogen supplier for portable proton exchange membrane fuel cells

Dae-Eun Park^{a,*}, Taegyu Kim^b, Sejin Kwon^b, Choong-Ki Kim^a, Euisik Yoon^c

^a Department of Electrical Engineering and Computer Science, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea

^b Department of Mechanical Engineering, KAIST, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea

^c Department of Electrical and Computer Engineering, University of Minnesota, 200 Union Street S.E., Minneapolis, MN 5545, United States

Received 1 March 2006; received in revised form 3 July 2006; accepted 4 July 2006

Available online 21 August 2006

Abstract

In this paper, a novel hydrogen-supplying device for fuel cells has been designed, fabricated, and demonstrated. The proposed hydrogen supplier is a micromachined one-chip fuel processing system including vaporizer, catalytic combustor and methanol steam reformer. This fuel processing system utilizes the thermal energy generated from the catalytic hydrogen combustion to heat up the entire system. For the catalytic combustion, we have introduced carbon nanotubes as a supporting structure of Pt catalyst for the first time. We have also developed a new coating method of reforming catalyst (Cu/ZnO/Al₂O₃) and observed that adequate amount of hydrogen can be generated for PEM fuel cells. We have successfully reported the feasibility of the proposed fuel processing system.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Micro fuel reformer; Micro fuel cells; Carbon nanotubes; Catalytic combustor; Methanol steam reformer; Micro fuel processing system

1. Introduction

1.1. Basic operation of fuel cell

Recently, mobile information devices, such as notebook PC, PDA, cellular phone, portable multimedia player (PMP) and digital camera, are spreading out quickly. As their functions are getting complex, and advanced, their electric energy consumption is also increasing exponentially. There is a strong demand for a new portable electrical energy source since the power requirement of these mobile information devices exceeds what the conventional batteries can provide. Fuel cell is a promising candidate for the portable power source because the most of fuels, such as methanol, and hydrogen, have much higher energy density than batteries (shown in Table 1 [1,2]).

As shown in Table 2 [3], the type of fuel cells has been classified into proton exchange membrane (PEM) fuel cell, alkaline fuel cell, phosphoric acid fuel cell, molten carbonate fuel cell, and solid oxide fuel cell according to the electrolyte material.

Direct methanol fuel cell (DMFC) is very similar to PEMFC except that it directly uses methanol instead of hydrogen as a fuel.

PEMFCs and DMFCs are competing against each other in the micro fuel cell area for portable applications due to their low operating temperature. Early researches on the micro fuel cells focus on DMFC research due to its simple structure (no fuel reformer) and easy refueling of methanol. But the crossover of methanol into polymer electrolyte gradually degrades the performance of fuel cell, and this is the biggest bottleneck of commercializing the micro DMFC. Therefore proton exchange membrane fuel cells (PEMFCs) have received a great attention as an attractive power source for portable electronic devices. However, there is a very fundamental issue which has to be resolved in PEMFCs before they are widely adopted and safely deployed. Since the PEMFCs require pure hydrogen, which is explosive, as a fuel, several researchers have been attempting to supply pure hydrogen to PEMFCs safely. Candidates for the hydrogen supplying units are high pressurized gas container, metal hydrides, chemical hydrides, and fuel reformer. Among these trials, the fuel reforming methods are good methods to extract pure hydrogen from other fuel sources which are safely handled.

* Corresponding author. Tel.: +82 42 879 9915; fax: +82 42 879 9920.
E-mail address: calvin@iml.kaist.ac.kr (D.-E. Park).

Table 1
Current practical battery technology [1] and hydrocarbon energy densities

Technology	Energy density (kW _e h/l)	Energy density (kW _e h/kg)	Comments
Primary cells			
Alkaline	0.330	0.124	–
Zn–air	1.050	0.340	–
Li/SOCl ₂	0.700	0.320	–
Secondary cells			
Lead acid	0.070	0.035	–
Ni–Cd	0.055	0.035	–
Ni–metal hydride	0.175	0.050	–
Li-ion	0.200	0.120	–
Li-polymer	0.350	0.200	Anticipated
Hydrocarbons			
Methanol	4.384	5.6	Thermal energy
Butane	7.290	12.60	Thermal energy
iso-Octane	8.680	12.34	Thermal energy

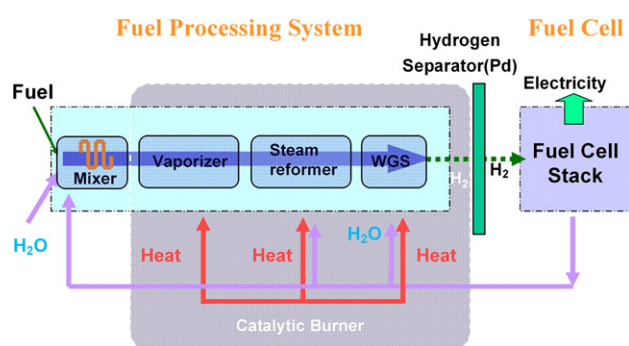


Fig. 1. Schematic of the entire fuel cell system for PEMFC.

Methanol steam reforming is one of the approaches on the rise due to its high energy density and relatively low reforming temperature (200–300 °C). In addition to this, the methanol steam reforming produces a relatively small amount of carbon monoxide at low temperature. Carbon monoxide is known to be very poisonous to Pt catalyst used in PEMFCs.

Fig. 1 shows the schematic of entire fuel cell system for PEMFC. A series of pre-processings should be performed in

the fuel reformer module. The fuel reformer module can be classified into four units: (1) fuel vaporizer/preheater, (2) fuel steam reformer, (3) hydrogen purification unit (membrane separator), and (4) micro combustor/heat exchanger. First, fuel is introduced, mixed with water and is heated by the vaporizer. In the next stage, the heated and steamed fuel is reformed by reforming catalyst to generate hydrogen in a steam reformer chamber. Typically, this hydrogen-rich gas includes undesirable by-products such as carbon dioxide, carbon mono-oxide, and methane. The fuel cell module can readily endure carbon dioxide, nitrogen, and methane, but it can be severely poisoned by extremely small amount of carbon mono-oxide. Therefore, CO gas should be reduced to below 10 ppm through a membrane separator (such as a thin layer of palladium–silver alloy) for hydrogen purification. However the Pd–Ag membrane separator does also require the operation temperature at higher than 200 °C.

In this work, we have integrated all the components of the fuel reformer module except for hydrogen purification unit. One of the approaches in our work is that we generated the heat from the embedded micro combustor in order to maintain the operation temperature required for both fuel reforming and hydrogen purification at higher than 200 °C. To miniaturize micro fuel reforming systems, the reliable catalyst coating in a microchannel has also been a challenging issue [4]. In this work, we have developed a new catalyst coating method into microchannels for methanol steam reforming. We have also developed the PDMS catalytic combustor using carbon nanotubes as a supporting material of Pt catalyst to make the efficient heat generator.

2. Reforming system design

Fig. 2 shows the proposed micromachined fuel processing system composed of a vaporizer, a steam reformer and a catalytic combustor. The catalytic combustor generates the heat by using a small portion of hydrogen produced in the reformer as a fuel and air as an oxidant. The heat generated from the catalytic combustion can effectively heat up the two intertwined micro channels (300 μm-deep, 150 μm-wide, and 50 μm-thick) at higher than 200 °C. One channel is used for the vaporizer to

Table 2
Summarized properties of each fuel cell [3]

	AFC	PAFC	MCFC	SOFC	PEMFC	DMFC
Electrolyte	KOH	H ₃ PO ₄	Li/K alkali carbonates mixture	YSZ	Ion exchange membrane	Ion exchange membrane
Temperature (°C)	150–200	150–200	~650	500–1000	50–100	50–100
Fuel	H ₂	H ₂	H ₂ , CO	H ₂ , CO	H ₂	MeOH
Oxidant	O ₂	O ₂ , air	O ₂ , air	O ₂ , air	O ₂ , air	O ₂ , air
Mobile ion	OH [–]	H ⁺	CO ₃ ^{2–}	O ₂ [–]	H ⁺	H ⁺
Efficiency (%)	70	40–45	50–60	50–60	<40	<40
Characteristics	High efficiency	CO tolerance	High efficiency	High efficiency	Low temperature	Low temperature
Problems	High cost	Big size, PA leakage	Material erosion	Material erosion	High cost, CO poisoning	High cost Low efficiency MeOH crossover
Application	Space vehicles (Appolo)	200 kW CHP	~MW CHP	2 kW–2 MW CHP	Vehicles, portable device	Portable device

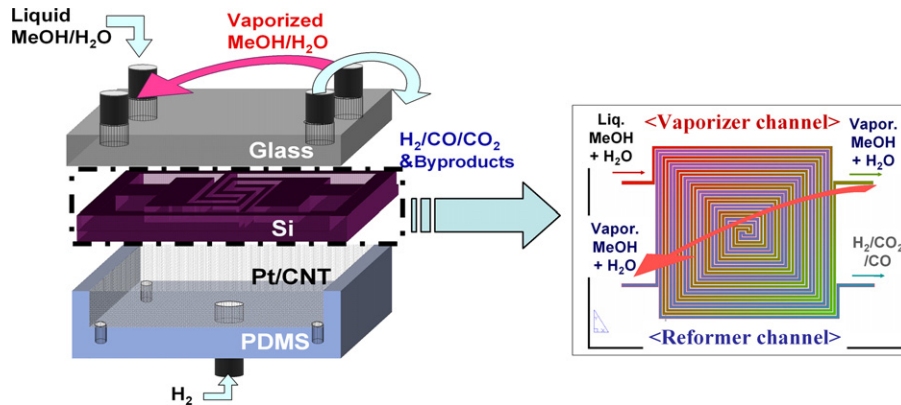


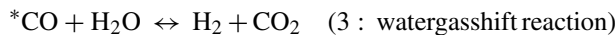
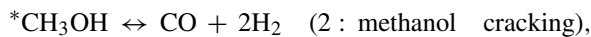
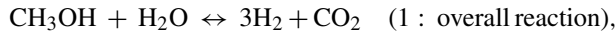
Fig. 2. Schematic view of the proposed methanol steam reforming system.

vaporize the liquid methanol and water mixture, and the other is for the reaction channel to reform the steamed methanol.

In this scheme, we can enhance the resident time of reactants with catalyst, which is a critical parameter to assure high reforming rate [5], by increasing the channel length (~28 cm).

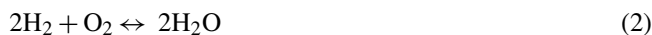
Methanol steam reforming and hydrogen catalytic combustion have several catalytic reactions as given in Eqs. (1) and (2). These catalytic reactions are strongly dominated by their catalysts and supports. Therefore, it is important to select a good catalyst material and its support.

- Reaction equation of methanol steam reforming



(1)

- Reaction equation of hydrogen catalytic combustion



First, we selected the commercially available Cu/ZnO/Al₂O₃ as reforming catalyst due to its high performance and low cost. But it is difficult to introduce and integrate this catalyst into microchannels due to its bulky size and low adhesion on silicon substrate. In order to address this issue, we proposed a new coat-

ing method of Cu/ZnO/Al₂O₃ catalyst which will be describe in detail in the next section.

For the PDMS catalytic combustor, we have chosen platinum as a catalyst due to its high activity in hydrogen combustion. However, selecting a supporting material for Pt catalyst is not trivial. In general, catalyst supports should have the following characteristics:

- (1) inertness to undesired reactions,
- (2) large surface area to enhance the reaction area,
- (3) reliable mechanical properties including attrition resistance, hardness, and compressive strength,
- (4) chemical stability under reaction and regeneration conditions.

From these aspects, Al₂O₃ is widely used as a support of various catalysts. But it has some restrictions for MEMS application due to its high calcination temperature (typically over 500 °C). Carbon nanotubes (CNT) can be a promising candidate for MEMS applications from these aspects [6]. This is because high temperature treatment is not required for CNTs without the reduction process of Pt catalyst (200–250 °C).

In order to verify the possibility of the carbon nanotubes as a supporting material for Pt in catalytic combustion, we have tested CNTs in a quartz-test-bed (inner size of combustion chamber: 10 mm × 1 mm × 1 mm) as shown in Fig. 3. In this preliminary experiment, the temperature is monitored on the

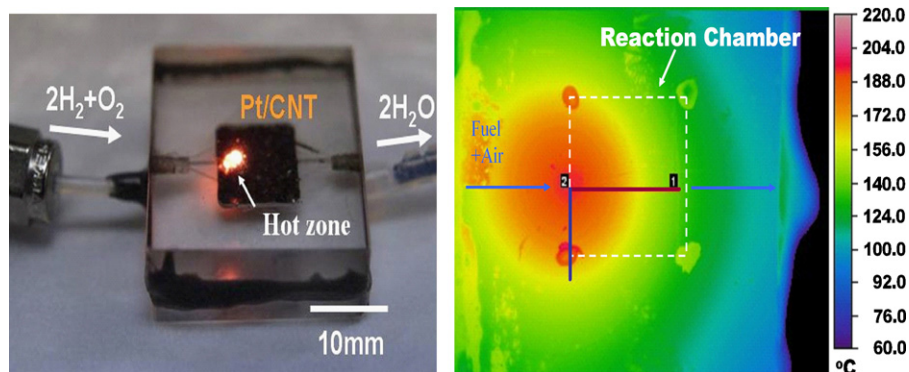


Fig. 3. Quartz test bed for the feasibility test of carbon nanotubes as a catalyst support: (a) test setup and (b) IR image at the surface of quartz test (H₂ flow: 50 sccm).

outer surface of the quartz test bed (the thickness of the upper plate is 5 mm) by using IR temperature camera (NEC San-ei, TH9100). We could measure the combustion temperature higher than 200 °C.

Based on this result, we have decided to use CNTs as a support of Pt catalyst in the proposed system. The preparation sequences of combustion catalyst will be shown in the following section. However, this procedure can be achieved at relatively low temperature (<230 °C), while Al₂O₃, which is widely used as a support, requires high temperature calcination (>500 °C). This allows us to use PDMS for making a combustor chamber.

3. Catalyst preparation

3.1. CNT preparation as a support for Pt catalyst

As mentioned before, carbon nanotubes could help enlarging the surface area of catalyst while providing mechanical stability. In this work, multi-walled carbon nanotubes (MWNT) are selected as a support of catalyst. (The CNT that we used is CVD MWNT 95, Iijin Nanotech Co. Ltd.).

We found it is difficult to treat and handle these MWNTs, because they are likely to be tangled with one another and their adhesion to the substrate (e.g. silicon) is not good. Therefore, it is necessary to guarantee the optimized dispersion process and promote the adhesion. We mixed MWNT powders with a CNT vehicle (which is composed of additive inorganic materials, organic binder materials and nitro cellulose) to enhance the adhesion. After the preparation of MWNTs, Pt was introduced by using a solution of H₂PtCl₆·xH₂O (Aldrich, 99.9 + %) in de-ionized water at room temperature. We dispersed MWNTs in ethanol solution with sonification for 1 h to reduce the tangling of MWNTs. This ethanol solution with MWNTs is poured into the PDMS mold, and dried at 70 °C for 12 h. Then, Pt ions supplied from H₂PtCl₆·xH₂O solution are reduced at 230 °C in the hydrogen flow. Table 3 summarizes the procedure to make 10 wt.% Pt catalyst.

3.2. Cu/ZnO/Al₂O₃ Catalyst coating inside a microchannel

CuO/ZnO/Al₂O₃ is a widely used catalyst for methanol synthesis [7]. The Cu-based catalysts such as Cu/ZnO/Al₂O₃, which

Table 3
Preparation steps of Pt catalyst using carbon nanotubes as supports for hydrogen catalytic combustion

Material specifications	CVD multi-walled nanotubes (Iijin nanotechnology) Length: 10–50 μm, diameter: 10–20 nm
Procedure	
Mixing	1 g MWNT, 20 ml ethanol, 0.5 ml vehicle (CNT paste)
Incorporation of Pt (10 wt.% Pt)	0.25 g H ₂ [PtCl ₆]·6H ₂ O + 1 ml H ₂ O
Dispersion	Sonification (>1 h)
Molding	Pour the solution into PDMS mold
Drying	70 °C, >12 h
Reduction	H ₂ , 10 sccm, 200–250 °C, >3 h

Table 4
Preparation steps of Cu/ZnO/Al₂O₃ catalyst for methanol reformer

Material	Commercial Cu/ZnO/Al ₂ O ₃ pellets
Procedure	
Grinding	Ball-mill (particle size: <1 μm)
Mixing	Cu/ZnO/Al ₂ O ₃ powder 0.5 g + bentonite (inorganic binder) 0.25 g + ethanol 10 g
Dispersion	Sonification (>1 h)
Injection	Syringe
Drying	70 °C, >12 h

is the reduced catalyst of CuO/ZnO/Al₂O₃, could be used for methanol steam reforming. It is widely used as a commercial catalyst in a packed bed form (pellet). However, it is not desirable to use this catalyst in a packed bed form for micro channel reactors because it may have high pressure drop and possible channeling of gases in addition to poor heat transfer [8]. If the catalysts are coated on the wall of a reactor, they can provide lower pressure drop and better heat transfer in the reactor bed. The reaction is occurred on the active sites of the catalyst. Also, it is important to enlarge the surface area of the catalyst in order to maximize the exposed active sites of the catalyst.

For this reason, we developed a new catalyst coating process on the micro channel of a silicon wafer using the commercial Cu/ZnO/Al₂O₃ catalyst in the form of pellet. First, we grind the catalysts with ball-mill machine (grain size: <1 μm), and disperse the grinded catalysts into a solvent (DI water or ethanol). Bentonite is used as an inorganic binder to enhance the adhesion between the catalyst and the substrate such as silicon or glass. This grinding process enhances the degree of dispersion. Catalyst slurry is prepared by adding the grinded catalyst and binder (catalyst:binder = 2.5:1) into ethanol solvent (7 solid wt.%) and stirring vigorously for sufficient dispersion.

The prepared catalyst is injected into the pre-made channel structure by two syringes. To avoid the clogging of catalyst in a microchannel, one of syringes is sucking the air inside a microchannel and the other is injecting the catalyst solution into the microchannel. The injected catalyst has been dried for 12 h. The detailed processes are summarized in Table 4.

On the bare silicon wafer, each coating step deposits the catalyst layer of 5–8 mg/cm² and the thickness of catalyst layer is about 50 μm. Fig. 4 shows the DRIE etched silicon wafer coated with the catalyst by the proposed method. The porous structure of the coated catalyst is also shown in Fig. 4. This porous structure enlarges the surface area (contact area between reactant gas and the active sites of catalyst).

4. Fabrication

The fabrication process of the entire chip can be summarized in the following steps. It will be shown in Fig. 5.

- (1) Silicon deep RIE to form microchannels, Fig. 5(A-a)–(A-d).
- (2) Glass sandblast for inlets and outlets, Fig. 5(B-a).
- (3) Silicon-to-glass anodic bonding and dicing, Fig. 5(B-b).

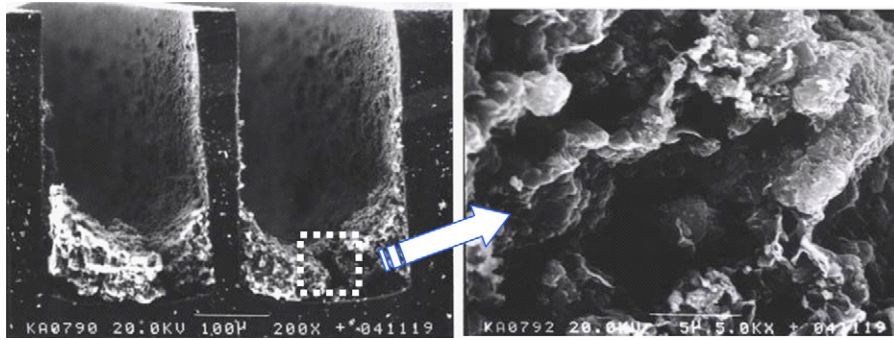


Fig. 4. SEM picture of a microchannel coated with Cu/ZnO/Al₂O₃ catalyst.

- (4) Injection of reforming catalyst, Fig. 5(B-c).
- (5) High temperature epoxy bonding of 1/16 in. SUS tube Fig. 5(B-d).
- (6) PDMS chamber formation for combustor, Fig. 5(C-a)–(C-b).
- (7) Pouring Pt/CNT onto PDMS combustor and drying, Fig. 5(C-c).
- (8) Reduction of Pt-catalyst Fig. 5(C-c).
- (9) Epoxy-bonding between PDMS and silicon wafer. Fig. 5(C-d).

Fig. 6 shows the photograph of the fabricated chip after A–B steps in Fig. 5. Fig. 7 shows the completed one-chip fuel processing system.

5. Results and discussion

To measure the inner temperature of a catalytic combustion chamber, K-type thermo-couple is inserted into the PDMS combustor. In this experiment, we have used hydrogen gas as fuel and air as oxidant. The temperature profiles measured for

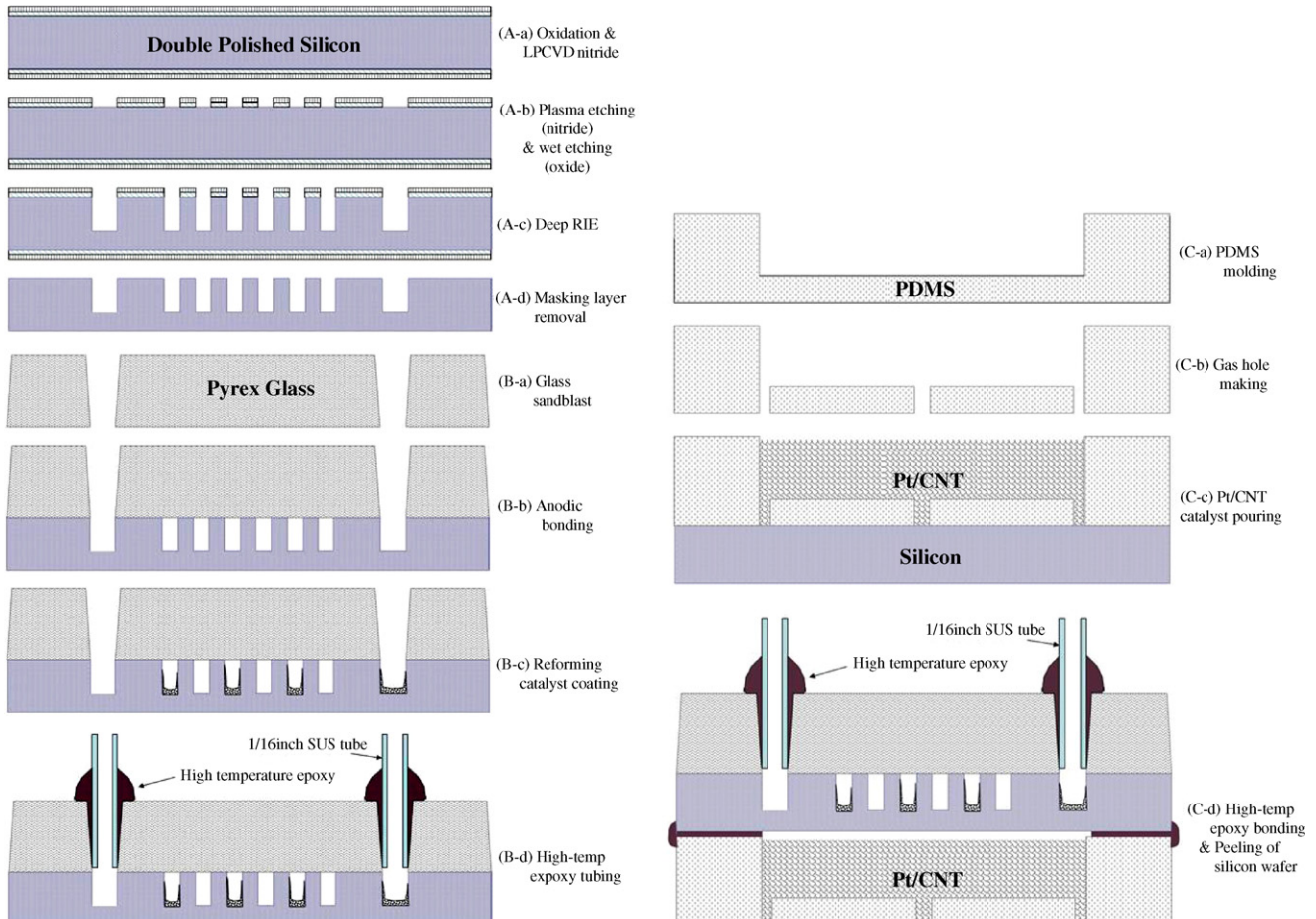


Fig. 5. Fabrication procedure.

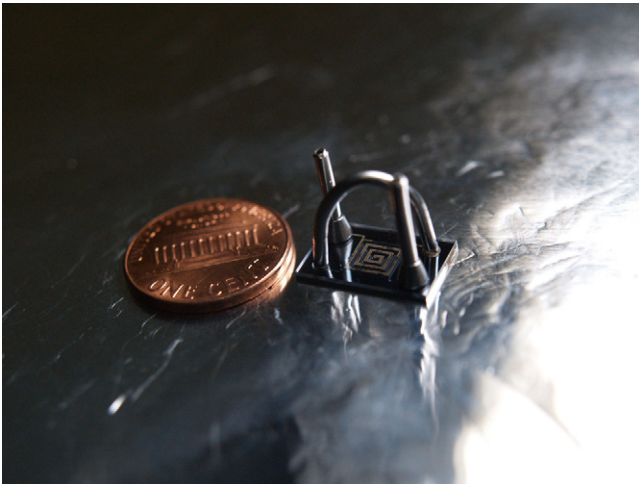


Fig. 6. Fabricated result of the methanol steam reformer module.

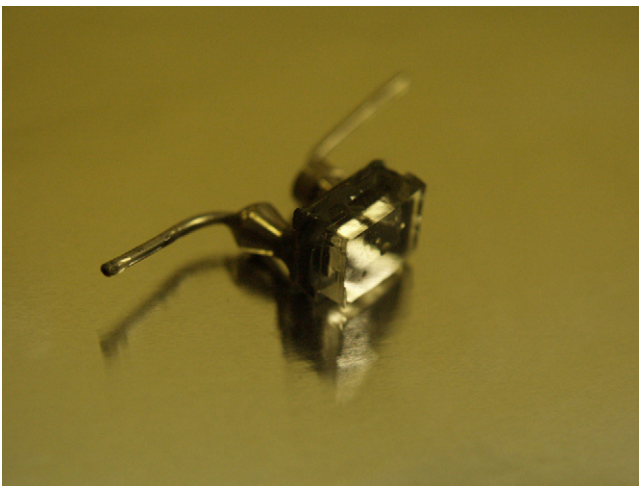


Fig. 7. Fuel processing module integrated with a catalytic burner using carbon nanotubes as a support of Pt catalyst.

various hydrogen flow rate and measuring positions are shown in Fig. 8. (equivalent ratio is fixed to 1) These results show that this combustor could generate enough heat to raise the temperature higher than the one required for methanol steam reforming reaction (200–350 °C).

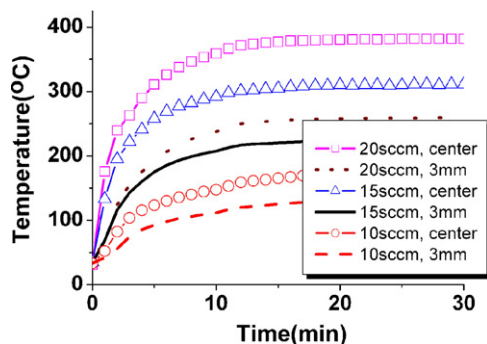


Fig. 8. Results of catalytic combustion for various H₂ flow rate and measuring position (equivalence ratio = 1).

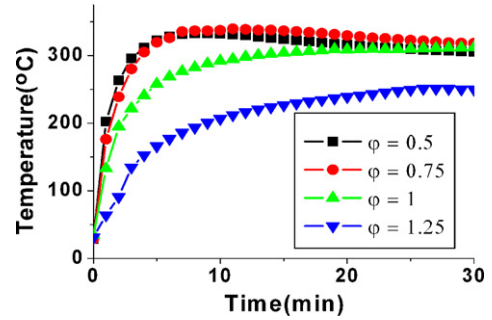


Fig. 9. Results of catalytic combustion for various equivalence ratio.

The temperature differences between the measuring positions (the center and 3 mm away from center) are almost 100 °C. This abrupt decline is caused from the fast reaction velocity of catalytic combustion. The higher flow rate of hydrogen gives the higher temperature.

Fig. 9 shows the effect of fuel equivalence ratios (equivalence ratio (ϕ) = stoichiometric ratio/air-fuel ratio). It shows that lean-burn ($\phi < 1$) combustion is more efficient in the catalytic combustion than rich-burn ($\phi > 1$) combustion.

From Figs. 8 and 9, we could get the information about the temperature distribution inside the combustion chamber. However, we have to know the temperature distribution inside the reformer channel where the chemical reaction for methanol steam reforming occurs.

Contact temperature measurement techniques such as thermo-couple are not desirable especially for micro combustor because such methods can affect the temperature of the sample or contaminate it with the material of the contact sensor.

Therefore, we have used non-contact IR temperature camera (NEC San-ei, TH9100PMV) in order to measure the temperature inside the methanol reformer on the PDMS combustor. Also, we have used the specific samples which have six holes patterned by sandblasting machine in order to measure the temperature inside the reformer channel. This specific sample and a temperature-monitoring sample are shown in Fig. 10.

One of six holes is located at the center where the gas inlet exists, and the others are located at 1.9, 3.1, 4.3, 5.5 mm and

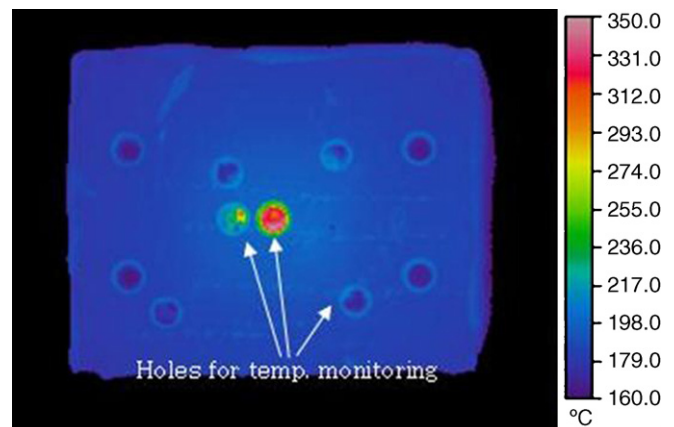


Fig. 10. A sample of temperature monitoring by using IR camera (NEC San-ei, TH9100PMV).

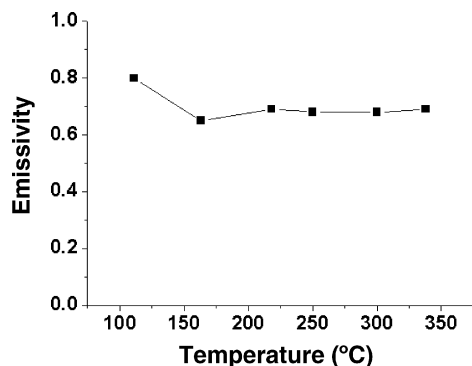


Fig. 11. Emissivity of silicon when using IR camera (NEC San-ei, TH9100PMV).

6.7 mm away from the center. Except the six holes, all the area is covered by pyrex glass in order to guarantee the condition to be similar to the original structure.

Using non-contact IR camera to measure its temperature is more difficult than attaching a thermometer or thermocouple to it (although sometimes this is the only convenient way) because it is difficult to measure the accurate radiation emissivity of material. Unfortunately, silicon is known to be notoriously difficult non-contact temperature measurement targets.

Therefore, the emissivity of silicon is measured by using thermo couple and the IR temperature camera. Although the contact measuring method could affect the temperature of sample, the effect is not considered for simplification. To measure the emissivity of silicon, the bare silicon is heated on the digital hotplate, and the thermo couple is located on the bare silicon. Then the emissivity is determined by controlling the emissivity number to keep the temperature monitored by IR camera similar to the temperature monitored by thermo couple. Fig. 11 shows the emissivity of silicon measured by IR camera for the calibration. From the result, we have selected 0.69 for the emissivity of silicon.

In this picture, the emissivity is set to 0.69. Therefore the temperature of pyrex glass except for 10 holes (6 holes for temperature monitoring + 4 holes for gas interconnection) is not accurate and its value is not meaningful (the emissivity of pyrex glass is 0.80–0.81).

Fig. 12 shows the trend of temperature as time goes by. The increasing tendency of the temperature at the center is stag-

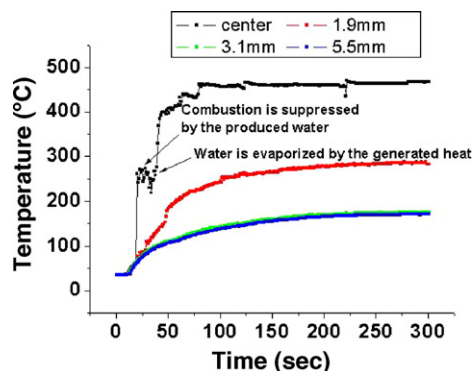


Fig. 12. Temperature trend.

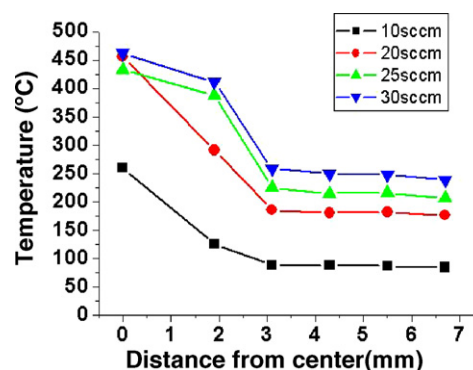


Fig. 13. Temperature distribution inside the reformer channel for various flow rates.

nated for 20 s at the 18 s after the gas was injected because the water produced during hydrogen reaction suppresses the catalytic combustion. Therefore the heat generated by hydrogen combustion is used to vaporize the water.

By using IR camera, we have measured the temperatures at various positions and hydrogen flow rates. All data of this section are taken at the condition of equivalent ratio = 1. This temperature profile is shown in Fig. 13. From the result, we can estimate that the generated heat is concentrated within 3 mm distance. Therefore, we could assume that the catalytic combustor which has several gas inlets would be more efficient than only one gas inlet for uniform heat distribution. It seems that the temperature difference between Fig. 13 and Fig. 8 is caused by the difference between the measurement methods (contact measurement and non-contact measurement).

This flow rate is comparable to the hydrogen produced from the reformer. Therefore, it is necessary to reduce the flow rate of hydrogen required for catalytic combustion. In order to do this, we need to reduce the heat loss of the combustor to the surroundings.

In our previous work [9], we had used 'Parapak Q (Supelco, Inc.)' column for the gas chromatography (HP6890N) in order to measure the methanol steam reforming results. However, the compositions of dry gases show strange values since the column could not discriminate the CO gas peak from the air peak. Therefore, we have selected 'Carboxen 1000 (Supelco, Inc.)' column for the gas chromatography analysis.

In order to simplify the measurement of methanol steam reforming, we have used the stainless frame and the fabricated reformer module. This measurement setup for methanol steam reformer module is shown in Fig. 14. The graphite film gasket can excellently reduce the leakage between the fabricated sample and the outer measurement system. Then, heat is supplied by a digital hotplate or a mini furnace.

Fig. 15 shows the composition of dry gases produced during the steam reforming process. Fig. 16 shows the methanol conversion rate. The feed rate is 1 cm³/h and S/C ratio (steam to carbon ratio = molar ratio of water and methanol) is 2. The composition ratio of the reforming results is very close to the ideal value of the conventional macrosized reformers. Fig. 17 shows the hydrogen production rate. The hydrogen production rate is calculated from the total gas production rate measured from

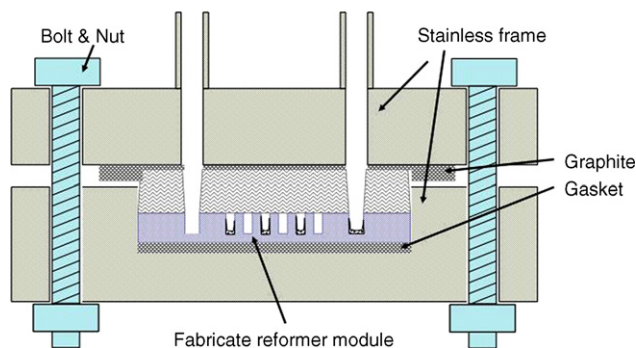


Fig. 14. Measurement setup for methanol steam reformer module.

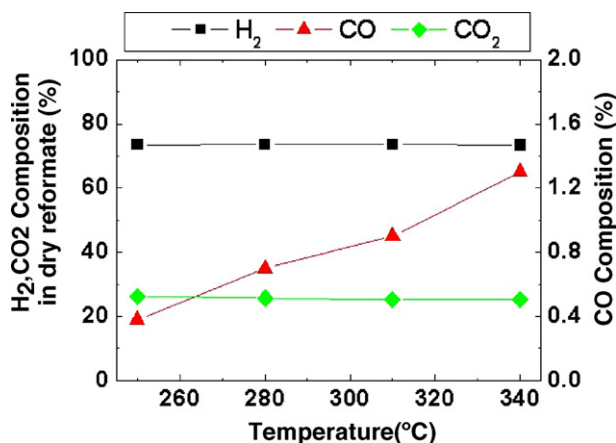


Fig. 15. Composition of reformate dry gas composition as a function of temperature (feed flow rate = 1 cm³/h, S/C = 2).

soap-bubble meter and dry reformate composition in Fig. 15. The hydrogen production rate approaches almost 2 sccm with 1 cm³/h feed flow rate. Fig. 18 shows the CO selectivity (=CO₂ produced/(CO produced + CO₂ produced)) of more than 95%. It means that CO gas molecules generated from methanol decomposition are almost converted into CO₂ gas through water gas shift reaction.

The fabricated methanol reformer module as shown in Fig. 6 is loaded with just 1–2 mg catalyst (the instrumental error: 1 mg). Although this methanol reformer module is loaded with very

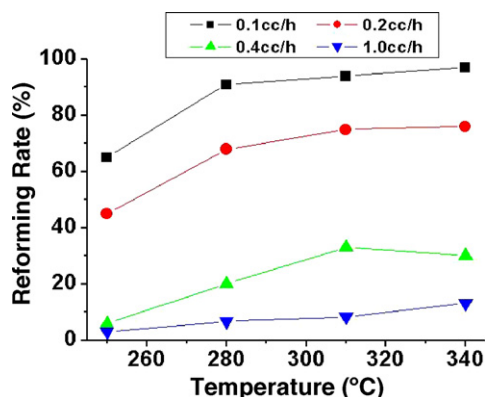


Fig. 16. Methanol conversion rate (or reforming rate) as a function of temperature (S/C = 2).

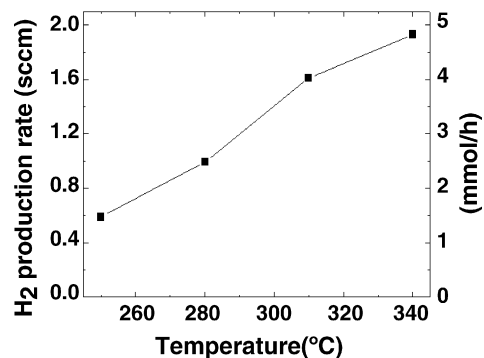


Fig. 17. Hydrogen production (reforming) rate as a function of temperature (feed flow rate = 1 cm³/h, S/C = 2).

small amount of catalyst, its performance is better than the photosensitive glass reactors (~25% conversion rate at 0.1 cm³/h feedrate, S/C = 2; amount of loaded catalyst: 37.5 mg and 5 mg) due to the enhanced residence time.

We have also measured the reforming results with the integrated system. The weight of catalyst loaded inside reformer module is about 1–2 mg (measurement error = 1 mg). With this sample, the reforming test has been executed with methanol feed flow rate of 1 cm³/h (S/C = 2, that is, methanol concentration = 33%). The hydrogen flow rate consumed as a fuel for catalytic combustion is 30 sccm, and the air flow rate for oxidant is 72 sccm. Its result is very similar to the result of 270 °C operating temperature in Figs. 16 and 17. But, the reformate dry gas composition is similar to the result with 340 °C operating temperature in Fig. 15 because the high temperature of center region increases the concentration of CO gas. The methanol conversion of 9% has been achieved from this experiment. The gas composition of dry reformate is shown in Table 5. The hydrogen production rate is ~0.91 sccm.

In this paper, we have demonstrated the feasibility of the proposed fuel reformer module. The fabricated reformer module satisfies the hydrogen production rate (>1.5 sccm) required for 0.1 W PEMFC. However, the hydrogen required for catalytic combustion is much higher than expected. And, it severely decreases the efficiency of the proposed methanol steam reforming system. In order to improve this inefficiency of the proposed methanol steam reforming system, the capacity of hydrogen

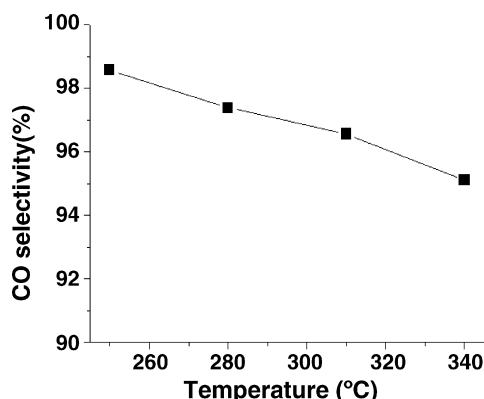


Fig. 18. CO selectivity (feed flow rate = 1 cm³/h, S/C = 2).

Table 5

Reformate dry gas composition (reformer: feed flow rate = 1 cm³/h, S/C = 2), (combustor: H₂ flow = 30 sccm, equivalence ratio = 1)

Gas	Reformate dry gas composition (%)	Production rate (sccm)
H ₂	72.5	0.91
CO ₂	26.1	0.33
CO	1.4	1.41

production should be increased by enlarging the reformer channel size and increasing the catalyst loading or the hydrogen consumption in catalytic combustor should be decreased by reducing the heat loss to the surroundings.

6. Conclusion

In this work, we have successfully integrated the fuel reformer module with a microcombustor for portable PEMFC applications. The microcombustor recycles hydrogen generated from the reformer and provides the heat required for continuous methanol reforming. For the first time, we have introduced carbon nanotubes as a supporting structure of Pt catalyst for the catalytic combustor. We have also developed a new coating method of reforming catalyst (Cu/ZnO/Al₂O₃) and observed that adequate amount of hydrogen can be generated for portable PEM fuel cells. The flow rate of produced hydrogen is adequate for 0.1 W PEMFC. But, the input flow rate of hydrogen for catalytic combustion is much higher than the output flow rate of hydrogen produced from the reformer. Therefore, we have to take steps to improve the inefficiency of the proposed methanol steam reforming system. In this paper, we have successfully reported the feasibility of the proposed fuel processing system.

References

- [1] J.D. Holladay, et al., Microfuel Processor for use in a miniature power supply, *J. of Power Sources* 108 (2002) 21–27.
- [2] D. Linden (Ed.), *Handbook of Batteries*, McGraw-Hill, New York, 1995, p. 6.5.
- [3] J. Larminie, A. Dicks, *Fuelcell System Explained*, Wiley (Chapter 1) 2000.
- [4] W.Y. Lee, R. Besser, H. Chen, L. Bednarova, Thin-film catalyst development as key part of rational heterogeneous microreactor design and fabrication, in: *Proceedings of the Power MEMS'03*, Makuhari, Japan, December 4–5, 2003, pp. 141–144.
- [5] T. Kim, D.H. Lee, C. Yoon, D.-E. Park, S. Kwon, E. Yoon, Preparation, coating and patterning of Cu-based catalysts for methanol steam reforming by micro fuel reformer, in: *Proceedings of the ASME FUELCELL'05*, Fuelcell 2005-74057, Michigan, USA, May 23–25, 2005.
- [6] M. Carmo, V.A. Paganin, J.M. Rosolen, E.R. Gonzalez, Alternative supports for the preparation of catalysts for low-temperature fuel cells: the use of carbon nanotubes, *J. Power Sources* 142 (1–2) (2005) 169–176.
- [7] L.F. Brown, et al., A comparative study of fuels for on-board hydrogen production for fuel-cell-powered automobiles, *Int. J. Hydrogen Energy* 26 (2001) 381–397.
- [8] Jaime Bravo, et al., Wall coating of a CuO/ZnO/Al₂O₃ methanol steam reforming catalyst for micro-channel reformers, *Chem. Eng. J.* 101 (2004) 113–121.
- [9] D.-E. Park, et al., Development of methanol steam reforming system integrated with catalytic combustor using carbon nanotubes as catalyst supports, in: *Proceedings of the IEEE MEMS'06*, Istanbul, Turkey, January 22–26, 2006.

Biographies

Dae-Eun Park received the BS and MS degrees in Electronics engineering from Korea Advanced Institute Science and Technology (KAIST) in 1999 and 2001, respectively, and is currently working towards the PhD degree in Department of Electrical Engineering and Computer Science at KAIST. His present research interests are in power MEMS applications including micro reciprocating engine actuated by internal combustion, micro fuelcell and micro methanol reforming system for micro fuelcell.

Taegy Kim received the BS degree in Aeronautical and Mechanical Engineering from Hankuk Aviation University in 2003, and the MS degree in Aerospace Engineering from KAIST in 2005, and is currently working towards the PhD degree in Department of Aerospace Engineering at KAIST. His present research interests are in technical research interests include micro power systems, micro fuel cell, fuel reformer, and micro thermo-chemical system.

Sejin Kwon received the BS degree from Seoul National University in 1982, the MS degree in Aerospace Engineering from KAIST in 1984, and PhD in Aerospace Engineering from University of Michigan, Ann Arbor. In 1997, he joined the Department of Aerospace Engineering at KAIST, where he is now an Associate Professor. His current research area includes micro catalytic reactor, micro fuel cell, and micro propulsion devices. He is a member of AIAA.

Choong-Ki Kim received the BS degree from Seoul National University, Seoul, Korea, in 1965 and the MS and PhD degree in electrical engineering from Columbia University, New York, in 1967 and 1970, respectively (S'69–M'70–SM'91–F'95). From 1970 to 1975, he was with the Research and Development Laboratory, Fairchild Camera and Instrument, Inc., Palo Alto, CA, where he worked on the development of linear/area CCD image sensors. In 1975, he left Fairchild to join the faculty of the Department of Electrical Engineering of Korea Advanced Institute of Science Technology, Seoul, Korea, where he is presently a Professor. His current research interest includes SOI, rapid thermal processing, CMOS Image Sensor, HgCdTe photodiode and MEMS. Dr Kim was the Chairman of the IEEE Korea Section in 1992. He is a recipient of the third Hoam prize in the field of Science and Technology in 1993. He is a life member of KIEE, KITE, KPS, and SPIE.

Euisik Yoon received the BS and MS degrees in electronics engineering from Seoul National University in 1982 and 1984, respectively, and PhD degree in electrical engineering from the University of Michigan, Ann Arbor, in 1990. From 1990 to 1994, he was with the Fairchild Research Center of National Semiconductor Corp., Santa Clara, CA, where he was engaged in researches on deep submicron CMOS integration and advanced gate dielectrics. From 1994 to 1996, he was a Member of Technical Staff at Silicon Graphics Inc., Mountain View, CA, working on the design of the MIPS microprocessor R4300i and the RCP 3-D graphic coprocessor. From 1996 to 2005 he worked in the Department of Electrical Engineering at Korea Advanced Institute of Science and Technology (KAIST), Taejeon, Korea, as an Assistant and Associate Professor. In 2005, he joined the Department of Electrical and Computer Engineering at University of Minnesota, Twin cities, where he is now an Associate Professor. His present research interests are in MEMS, integrated microsystems, and VLSI circuit design. Dr Yoon was the co-recipient of the Student Paper Award at the IEEE International Microwave Symposium in 1999 and 2000, respectively, concerning the topics on MEMS inductors and RF MEMS switch work. He served in various Technical Program Committees including Microprocesses and Nanotechnology Conference, International Sensor Conference and IEEE AP ASIC Conference. Currently, he is serving in IEEE ISSCC program committee and Transducers technical program committee.