MEMS-based micro-fuel processor for application in a cell phone

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Abstract

The operation of a micro-electro-mechanical system (MEMS)-based micro-reformer was investigated for application in a cell phone. Different aspects like the time required to attain the desired temperature of the system, the time required to get the required hydrogen flow, catalyst durability, flow uniformity of the mixture of methanol and water and volume of the total system were considered. A loading procedure for the catalyst in the micro-reformer was developed. Catalyst deactivation was observed after operating continuously for 8 h, but it regained its original activity after the reformer was shut down for at least 2 h. The deactivation of the catalyst was analyzed by catalyst characterization. The comparison of the performance between a parallel channeled and serpentine channeled micro-reformer was carried out. The performance with the serpentine channeled micro-reformer was always higher than with parallel channeled micro-reformer. The shorter residence time in the parallel-channeled micro-reformer may be one of the reasons behind its low activity.
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Keywords: MEMS; Methanol; Steam reforming; Fuel processor

1. Introduction

Micro-fuel cells offer potential advantages compared to conventional batteries in terms of energy density. They also offer continuous operation without recharging. The extra energy density has become essential for the increasing additional functionalities created in wireless electronic equipment. This type of portable electronics has become thinner and thinner in addition to having extra functionalities. Micro-fuel cells have also the potential for a very small volume and for lightweight packaging.

The fuel for micro-fuels cells can be one among pure hydrogen, pure hydrocarbons (alcohol, i.e. methanol and ethanol; formic acid) and reformed hydrogen. Pure hydrogen storage is simply impossible for the practical application in electronic equipment due to the storage problem in the small size available. There is also concern in terms of safety while carrying hydrogen in wireless electronic equipment. In a direct alcohol fuel cell system, the main studies center around methanol (direct methanol fuel cell, DMFC) though there is recent trend of studying ethanol keeping in mind its lower toxicity and higher power density. DMFC has the drawbacks of a high crossover rate and a low rate of fuel oxidation. The reformed hydrogen fuel cell (RHFC) is expected to become a more compact system compared to a DMFC system, because a RHFC has approximately one order of magnitude higher power density than a DMFC. In terms of substrate materials, different materials have been used such as stainless steel, aluminium, alumina, silicon wafer, polydimethyl siloxane (PDMS), low temperature co-fired ceramic (LTCC) and printed circuit board (PCB) for the micro-reformer and micro-fuel cells. Each direction has its own advantages and drawbacks. The advantages of using a silicon wafer as a micro-reformer is its mature MEMS technology applicability and potential reduction of the reactor's size.

RHFC can be divided into two categories based on the operating temperature of the reformer. Generally, methanol and sodium borohydride are used as the reformer feed at relatively high temperature and low temperature operation, respectively. Methanol is more attractive with respect to being a less hazardous material.

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There is growing consensus for RHFC with a methanol feed that a combination of a micro-fuel cell system and a rechargeable battery will be the most applicable, in which the fuel cell continuously recharges the battery and the battery in turn provides electricity to the portable device. It should also be noted that incorporation of a polybenzimidazole (PBI)-based high temperature tolerating proton exchange membrane facilitates the design of the micro-fuel processor.

In micro-RHFC systems, a micro-channel reactor is generally used as the micro-fuel processor. The micro-channeled reactor possesses the unique advantage of high heat transfer and mass transfer characteristics which lead to fast responses to transient loads and a low mixing time of the fluid. The other advantage is that the flows are mostly laminar, directed, and highly symmetric in the micro-channels. Very narrow residence times can be achieved through micro-channels which minimize the backmixing [1].

There is always an issue over the use of the catalyst in the micro-channels either by catalyst coating or packing in micro-channels. The catalyst coating is advantageous with respect to low pressure drop, but the high loading of the catalyst is very difficult in the coating method, especially in the case of a silicon wafer, where the anodic bonding with the Pyrex glass is required (which means the upper surface of the fin should be very clean to get effective bonding with the Pyrex glass) after the catalyst loading. Therefore there is a question of durability of the micro-reformer from the insufficient amount of the catalyst loading. On the other hand, it is possible to load the catalyst in sufficient amount by catalyst packing inside the micro-channels after anodic bonding with Pyrex glass and the catalyst loss is very low if we can place an appropriate filter at the inlet and outlet of the channels.

In the literature, the use of micro-packed bed reactors for the reforming of methanol to produce hydrogen has been reported. Pattekar and Kothare [2] presented a silicon reactor fabricated by deep reactive ion etching (DRIE). Micro-channels of depth ranging from 200 to 400 μm and width of 1000 μm were fabricated in 1000 μm thick silicon substrates using photolithography followed by DRIE. A photoresist coating of up to 10 μm thickness (Shipley 1045, single/dual coat) was used as the etch mask for DRIE. The catalyst used was commercial one (Sud Chemie, Cu/ZnO/Al$_2$O$_3$ catalyst) and was loaded by passing the water-based suspension of catalyst particles (size range: 50–70 μm) through the micro-channel device. By this process, the particles were trapped in the micro-channels due to the presence of the filter near the outlet which allowed only particles smaller than 20 μm to pass through. This resulted in a micro-packed bed of catalyst particles. The temperature sensor was a platinum resistance-temperature device (RTD) with a linear temperature versus resistance characteristic. The heater was a platinum line meandering along the micro-channels (also on the backside of the substrate). They obtained 88% methanol conversion at 1:1.5 molar ratio of methanol and water and the feed rate was 5 cm^3 h^{-1}. Most recently, Pattekar and Kothare [3] developed a radial flow micro-packed-bed reactor which possesses less pressure drop compared to conventional one due to variable (increasing) flow cross section along the reaction path.

The different workers tried the catalyst coated micro-channel reactor and a plate type reactor expecting a low pressure drop, less channeling of gas and better response in transient behavior. Details are given in Kundu et al. [1]. The methanol steam reforming reactions using micro-channeled a stainless steel plate was carried out by Zapf et al. [4], Park et al. [5], and Men et al. [6,7]. A micro-channeled aluminium plate for the steam reforming of methanol (SRM) was used by Pfeifer et al. [8,9]. This reaction using a wall coated catalyst on the aluminium material and was reported by de Wild and Verhaak [10] and Fukuhara et al. [11]. Pattekar et al. [12] made use of a silicon chip for hydrogen production by methanol steam reforming. The reactor housing was made of stainless steel, electrically heated and sealed with graphite. The micro-channel was serpentine, of 1000 μm width and 230 μm depth fabricated by photolithography and KOH etching. A Cu catalyst was sputtered to a thickness of 33 nm on to the top. Preliminary simulations revealed a non-uniform temperature distribution in the reactor housing, pointing to the importance of proper insulation especially in lower power systems. At a feed composition of 76 mol% methanol in steam, less than 7% conversion was achieved at 250 °C. Selectivity to carbon monoxide was higher than that to carbon dioxide and 7 mol% hydrogen was found in the product. Recently, Kwon et al. [13] and Kawamura et al. [14] performed the SRM reaction in a micro-channel reactor made from a silicon wafer with a catalyst coating. The other user of catalyst coated micro-channeled silicon wafer was Srinivas et al. [15] for the application of preferential CO oxidation. They coated the micro-channeled silicon wafer with an alumina sol as the undercoating followed by a wash-coating of Pt/Al$_2$O$_3$ catalyst. They also compared the catalytic performance using the catalyst coated onto the micro-channels in a packed bed reactor. The problem in micro-channel reactors lies on low durability of the catalyst. There is limited literature concerning the durability of the catalyst, where catalyst deactivation at fast rate has been reported [10,11].

Based on the above literature, it is clear that there have been limited experiments on a MEMS-based reformer. The durability test was also not performed in every case except de Wild and Verhaak [10] and Fukuhara et al. [11] though their purpose was different. In the present work, a MEMS-based micro-reformer with a micro-vaporizer was designed which can be integrated with a PEM fuel cell for application in a cell phone. Two types of channels were made for the micro-reformer and the performance was compared. The durability test for each type of micro-reformer was performed and characterized.

2. Experimental set-up

Fig. 1 shows the experimental set-up. It mainly consists of a liquid feed pump (Younglin Instrument), a compact reactor unit comprising a vaporizer chamber followed by the reactor chamber and a temperature indicator. The reactor was heated through an electrical heating system by on chip platinum lines deposited on the rear side of the silicon wafer as shown in Fig. 2h or by heating through an electrical hot plate. A micro-channeled
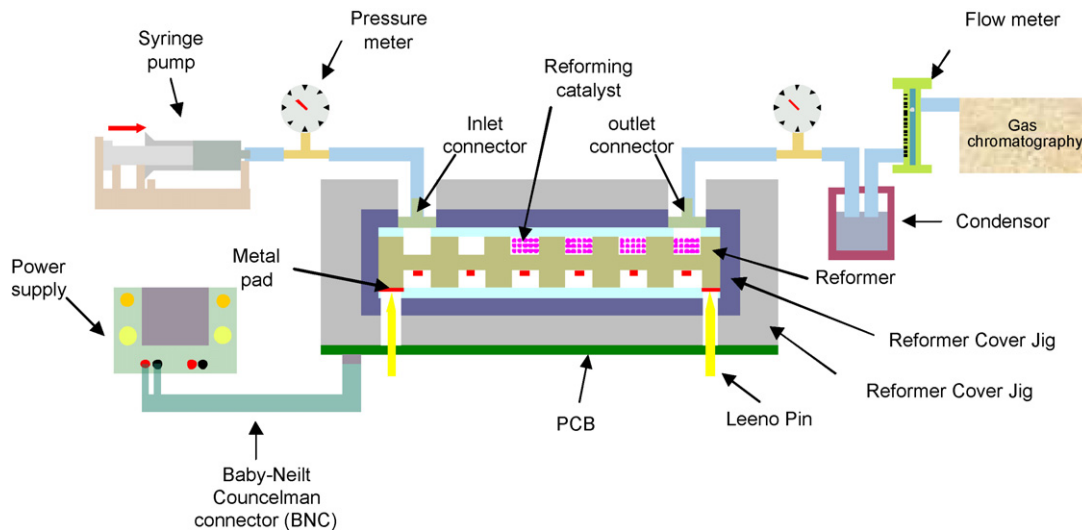
Fig. 1. Experimental set-up.

plate made from a silicon wafer was used as the reactor considering its mature technology and potential reduction in size. Standard photolithography steps followed by deep reactive ion etching were used for the etching of a silicon substrate to form the micro-channels, vaporizer and filter. After etching, the channeled side was bonded with Pyrex glass having three ports (one for catalyst introduction, one for the inlet and one for the outlet) by anodic bonding. The split type channels were made in the micro-vaporizer region in order to reduce the back-pressure at the inlet port which helped to get a more uniform flow of fluid. The dimensions of the micro-reformer were 30 mm in length and 30 mm in width and each channel was 28 mm in length. The dimension of each channel and fin are provided in Fig. 2f. The width of each channel was 1 mm and the depth of the channel was 300 μm. The width of fin (channel wall) was 100 μm. The catalyst used was the commercial one ($Cu/ZnO/Al_2O_3$; Johnson Matthey). Before packing inside the channels, the catalyst beads were crushed by mortar and pestle and the particle size of 50–100 μm was separated by sieving prior to use. The catalyst particles were packed through port "p" (Fig. 2a) by injecting the catalyst slurry made with DI water followed by displacing inside the channel far away from the entry port by gravity and pressurizing by water. The catalyst particles were trapped in the micro-channels by four filters—one at the inlet and three at the outlet of the channel area. The filter was in the form of 90 μm thick parallel walls spaced 10 μm apart oriented parallel to the direction of the fluid flow (Fig. 2c and e). The maximum amount of catalyst loaded was 140 mg. The uniform packing of the catalyst in the micro-channels was obtained and shown in Fig. 2d. The feed rate of the liquid mixture was varied from 0.01 to 0.02 ml min^{-1}. This corresponds to LHSV = 3.5−7 h^{-1} and GHSV = 6500−13 000 h^{-1}. The water and methanol ratio in the feed was 1.2:1 for getting low concentration of CO. The external tubing was made in the inlet and outlet of the micro-vaporizer and micro-reformer. The tubes were fixed with silicon wafer by epoxy [J-B Weld (UK) Ltd.] after curing for 20 min at 80 °C. Two thermocouples of type K, one in the

heating plate, one on the upper surface of the silicon wafer were fixed in order to monitor the temperature of the system. The total volume of micro-reformer was 0.9 cm^3 in which 30% of the total volume was utilized for reaction and vaporization zone.

The produced gas stream was directed through a cold trap to remove liquid components and then passed to an on-line micro-gas chromatograph for analysis of H_2, CO and CO_2 or to a bubble flow meter for measuring flow. The micro-gas chromatograph (Varian CP-4900) was equipped with a Molecular Sieve 5A and Porapak Q column and a TCD detector using Argon as the carrier gas.

3. Results

A catalyst from Johnson Matthey ($Cu/ZnO/Al_2O_3$) was used for the methanol steam reforming reaction. The temperature rise from room temperature to above 200 °C in the micro-reformer was achieved within 20 min. The catalyst loaded in the micro-reformer was activated for 1.5 h at 220 °C with the water and methanol mixture at a flow rate of 0.02 ml min^{-1}. The state of hydrogen evolution during the activation stage is shown in Fig. 3. The first generation of hydrogen was observed after 20 min. Steady state was observed after 40 min during activation (which can be called the induction time). The fact that there was a considerable induction time before high conversions were achieved, are indications that the catalyst undergoes chemical changes during exposure to the methanol–water mixture. Except for the activation stage, all other restarting phases of the micro-reformer took 5 min to produce hydrogen after reaching the desired temperature. The performance of parallel and serpentine patterned micro-reformers has been shown in Figs. 4 and 5. The performance shown here was after 1 h operation of the micro-reformer after the activation stage. The performance in a serpentine channeled micro-reformer was always higher than that in a parallel channeled micro-reformer. This may be due to the shorter residence time of the reacting vapors in the par-
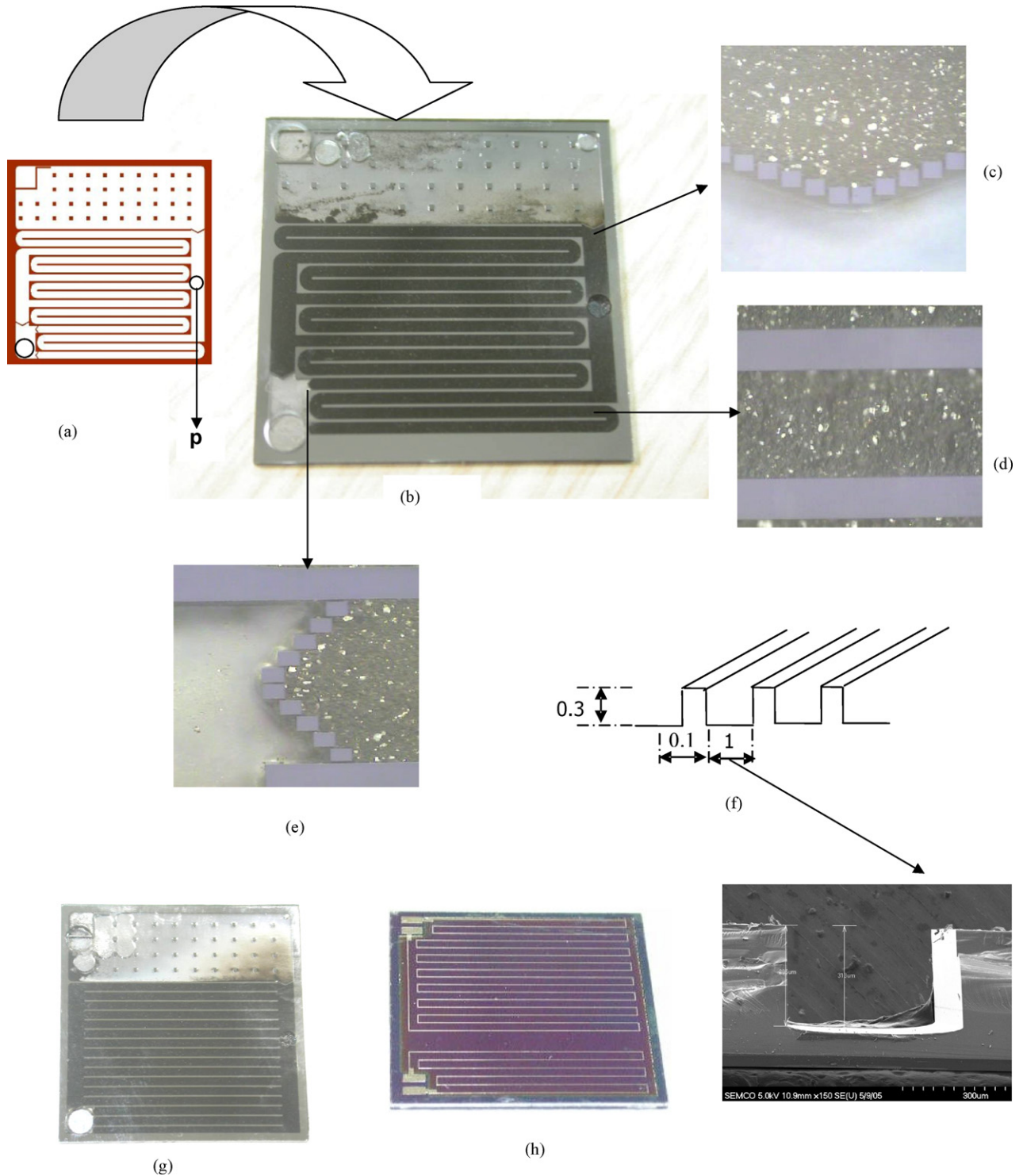
Fig. 2. (a) Schematic diagram of the micro-channeled silicon wafer; (b) photograph of serpentine patterned silicon wafer with catalyst; (c) microscopic imaging of filter at the inlet point of the reactor part; (d) microscopic image of catalyst packing inside the channels; (e) microscopic image of filter at the outlet of the reactor part; (f) specification of the channels; (g) imaging of parallel patterned silicon wafer with catalyst; (h) on-chip platinum lines for heating on the back side of the micro-reformer.

allel channeled micro-reformer. The typical value of residence time is about ∼500 ms for sufficient conversion of methanol to hydrogen [16].

Figs. 6 and 7 show the GC analysis of the produced gases from steam reforming of methanol. The average concentra-

tion of H_2 and CO_2 in the produced gas was 75% and 24% respectively, whereas the maximum concentration of CO was 1.5%. The flow rate of dry reformate gas was 25 ml min^{-1} at 20 °C and atmospheric pressure with serpentine channeled micro-reformer at the feed rate of 0.02 ml min^{-1}, whereas that
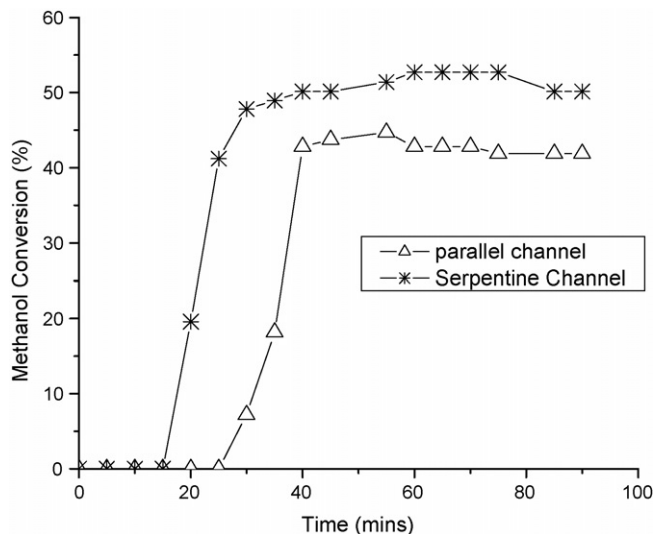
Fig. 3. The catalyst performance during activation stage (water and methanol mixture flow rate: 0.02 ml min^{-1}, temperature: 220 °C, catalyst: Cu/ZnO/Al$_2$O$_3$, catalyst amount: 140 mg).

Fig. 5. The comparison of the performance of serpentine and parallel channeled micro-reformer in terms of methanol conversion (catalyst: Cu/ZnO/Al$_2$O$_3$, catalyst amount: 140 mg, water and methanol mixture flow rate: 0.02 and 0.01 ml min^{-1}).

value for parallel channeled micro-reformer was 23 ml min^{-1} at the same condition. Average hydrogen production rate was 0.0445 mol h^{-1} assuming 80% fuel cell operating efficiency and average methanol conversion of 85% which can produce 2.4 W using serpentine channeled micro-reformer at 260 °C and feed rate of 0.02 ml min^{-1}. Therefore the produced gas from the micro-reformer can be used directly as a feed for the micro-fuel cell operated at a high temperature with a PBI membrane. The different points with the same symbol in Figs. 6 and 7 indicate the repeatability of the experiments at the same condition. The CO concentration varied from 0.8% to 1.5% at 260 °C and 0.02 ml min^{-1} flow rate because of flow rate fluctuation and calibration error in micro-GC detecting very low concentration of

CO of the reformate gas. The durability test of the serpentine channeled micro-reformer has been presented in Fig. 8. During 8 h continuous operation, about 15–20% conversion decreased in the last 3 h, but it regained the original performance after the break. For the steam reforming reaction, the appropriate ratio of Cu$_2$O and copper should be maintained in the catalyst in order to get high performance. The temporary decay of the catalyst activity after continuous 8 h operation with so low amount of catalyst may be due to an unbalancing of the ratio of amorphous Cu$_2$O and crystalline Cu under the extremely reducing conditions. Fig. 8 also shows that after 25 h, the catalyst activity remained the same; it only needs some time to regain its original form after a long continuous operation. In the case of a parallel channeled micro-reformer (Fig. 9), the catalyst deactivation occurred faster and there was no sign of regaining the
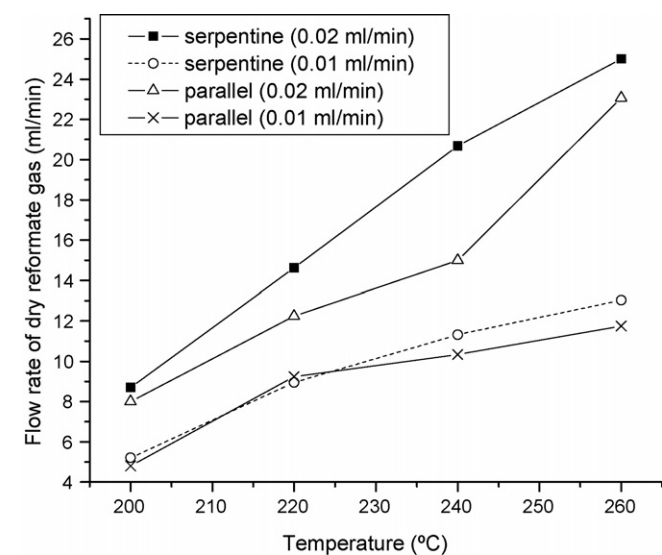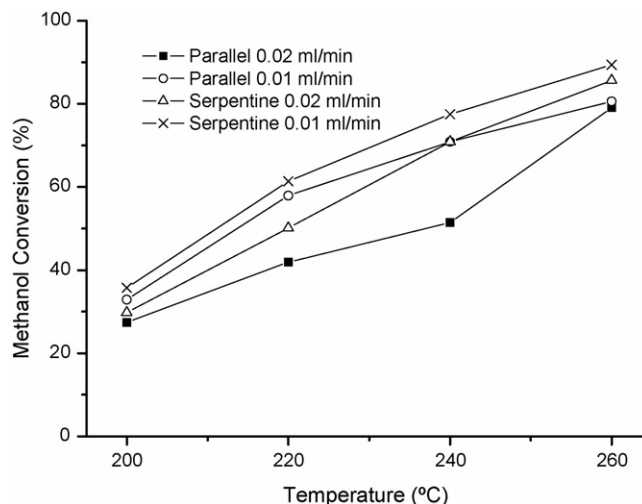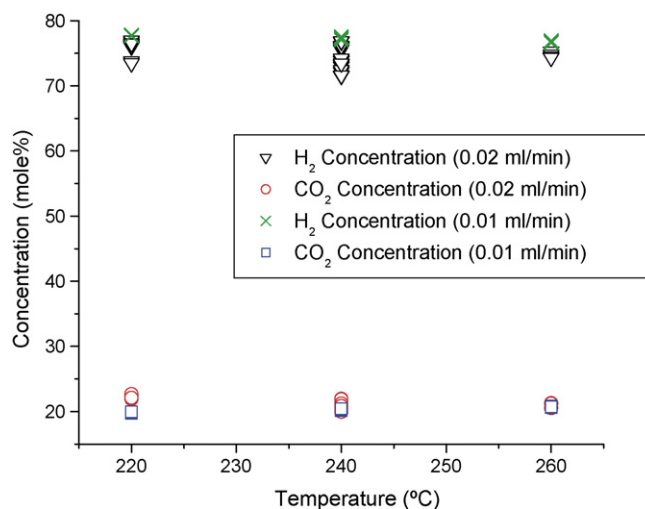

Fig. 4. The comparison of the performance of serpentine and parallel channeled micro-reformer in terms of flow rate of dry reformate gas (catalyst: Cu/ZnO/Al$_2$O$_3$, catalyst amount: 140 mg, water and methanol mixture flow rate: 0.02 and 0.01 ml min^{-1}).

Fig. 6. Concentration of CO$_2$ and H$_2$ in dry reformate gas at different temperature (serpentine channel) (catalyst: Cu/ZnO/Al$_2$O$_3$, catalyst amount: 140 mg, water and methanol mixture flow rate: 0.02 and 0.01 ml min^{-1}).
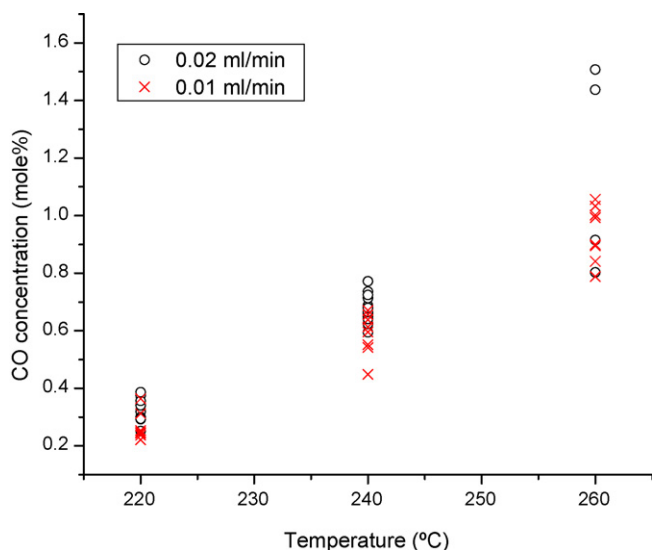
Fig. 7. CO concentration in dry reformate gas at different temperature (serpentine channel) (catalyst: Cu/ZnO/Al$_2$O$_3$, catalyst amount: 140 mg, water and methanol mixture flow rate: 0.02 and 0.01 ml min^{-1}).
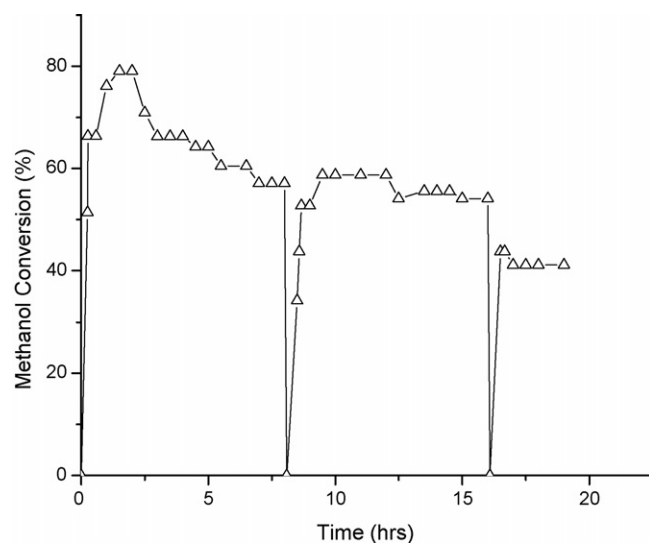

Fig. 9. Durability test at 260 °C and 0.02 ml min^{-1} with parallel channeled micro-reformer (catalyst: Cu/ZnO/Al$_2$O$_3$, catalyst amount: 140 mg).

performance after shut down for a few hours. The XRD characterization (Fig. 10) was carried out with the deactivated catalyst of the parallel channeled micro-reformer after operation for 20 h and we found that the CuO crystalite size increases from 81 to 115 Å (calculated by Scherrer equation) in the deactivated catalyst. The growth of Cu crystallites on the catalyst surface would reduce the amount of Cu with a simultaneous increase in Zn surface concentration. The fast deactivation of the catalyst in parallel channeled micro-reformer may be due to more exposure of temperature in a non-uniform behavior and maldistribution of the reactant. There is also the possibility of some Cu$_2$O converting into metallic copper under such a non-uniform reducing atmosphere by which the cat-

alyst can not be regenerated after deactivation. The parallel channels also created a lot of problems such as leakage of the inlet tubing which may be due to the higher back-pressure. The XRD pattern of the catalyst in the serpentine channeled micro-reformer after operation of 25 h, has also been shown in Fig. 10. The CuO peak is almost identical with that of a fresh catalyst.

The total time required to get hydrogen from the micro-reformer and to achieve steady state was about 30 min. Therefore it is difficult to operate a cell phone by a micro-fuel cell itself. The combination of a micro-fuel cell system and a rechargeable battery in which the fuel cell acts as a recharger to the battery of the cell phone seems to be more suitable.
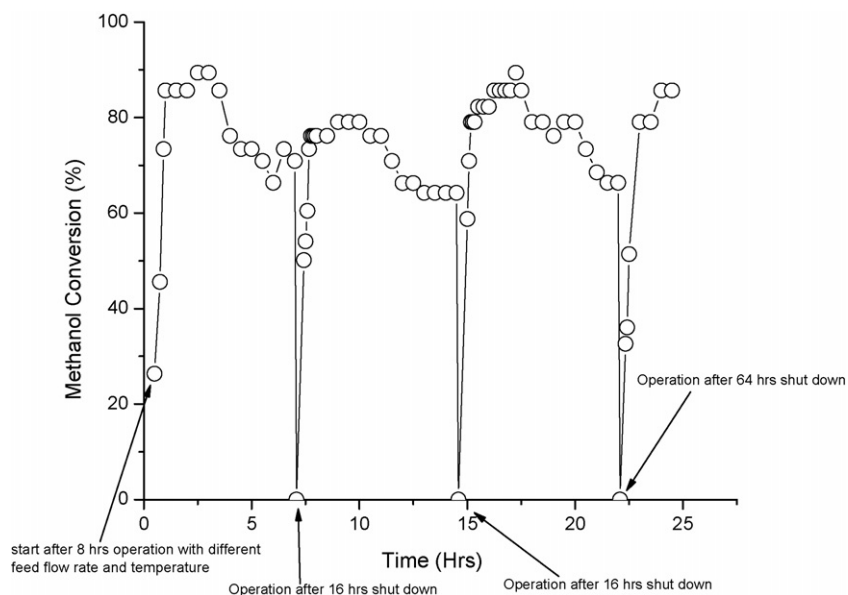

Fig. 8. Durability test at 260 °C and 0.02 ml min^{-1} with serpentine channeled micro-reformer (catalyst: Cu/ZnO/Al$_2$O$_3$, catalyst amount: 140 mg).
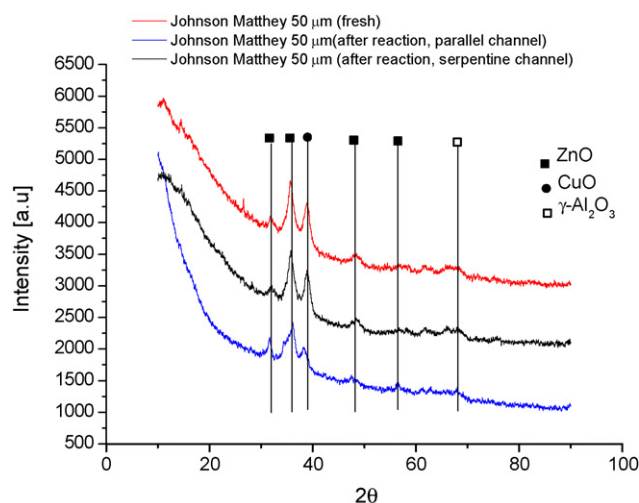
Fig. 10. XRD analysis of Johnson Matthey catalyst (before and after reaction) for parallel and serpentine channeled micro-reformer.

4. Conclusions

A silicon-based micro-vaporizer plus micro-reformer was fabricated for a reformed-hydrogen fuel cell for application in a cell phone. The total volume of the fuel processor was $0.9\,cm^3$ in which 30% was utilized for the reaction and vaporization zones. The produced gas mixture from the micro-reformer showed that the maximum CO concentration was 1.5%, which can be used directly as a feed without a purification stage for a high temperature operating micro-fuel cell. The average hydrogen production rate was $0.0445\,mol\,h^{-1}$ which can produce 2.4 W assuming an 80% fuel cell operating efficiency. The performance with a serpentine channeled micro-reformer was always superior to that of a parallel channeled micro-reformer. A durability test also confirmed that the catalyst in a serpentine channeled micro-reformer exhibited better durability than that in a parallel channeled micro-reformer. Considering the time required to reach steady state, however, it is more suitable to apply the micro-fuel cell in a hybrid system where the RHFC can recharge the battery used to supply the electricity to the portable equipment.

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