MEMS fabricated micro reformer with a wall coated catalyst and an embed heater

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\textbf{ABSTRACT:}

For commercializing micro fuel cells, the minimizing size of a reformer is a critical issue to increase the energy density of Reformed Hydrogen Fuel Cell, which is a kind of hydrogen fuel cell. In this paper, MEMS fabrication technology was used to reduce the size of reformer and steam reforming catalyst was coated on the wall of micro channel by a novel process. The X-ray diffraction (XRD) patterns show that the coated catalyst is just a Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} effective to steam reforming. The four reformers of 3cm \times 3cm were formed in one silicon wafer and the volume of a micro reformer is 0.9 cc. The methanol water mixture of 1:1.5 was supplied for performance test of steam reforming and the heat for reaction was caused by the embed Pt heater. The feed of methanol water mixture is 0.01-0.02 ml/min and a peak production rate of hydrogen is about 16 cc/min, which is sufficient for a 2W fuel cell. The mol concentration of CO is below 3%, which is acceptable to high temperature membrane fuel cell operating at 180 degrees around.

\textbf{KEYWORDS:} Micro fuel processor, MEMS, Wall coated catalyst, Micro channel reactor, Steam reforming

\textbf{Introduction}

The hydrogen fuel cells have long been considered as a promising alternative power source of the future due to their high efficiency in the conversion of fuel to usable energy.\textsuperscript{1} In the context of portable and mobile power sources, fuel cells have the potential of providing energy storage densities several times than those possible using current state-of-the-art lithium-ion batteries. However, the difficulties and hazards involved in the storage and handling of the hydrogen fuel in either compressed gas or liquid form have been a major barrier in the successful commercialization of miniature hydrogen proton exchange membrane fuel cells (PEMFC). Also, the stored energy density of hydrogen in compressed or liquid form is significantly lower in comparison to storage in the form of liquid hydrocarbons, such as methanol, which can be reformed for generation of the hydrogen gas when needed. Hydrogen storage in metal hydrides and carbon nano fiber (CNT) has been proposed but a number of limitations have been recognized, including high weight of the hydride storage unit, lower energy density, and high cost.\textsuperscript{2} Therefore, the development of a compact and efficient micro fuel 'reformer' for on-demand hydrogen delivery to portable PEMFC has been the subject of considerable research activity in recent years.\textsuperscript{3}

Fig. 1 Photography of micro channel and Pt heater formed on the 4 inch silicon wafer.
Micro fabrication technology such as photolithography has been used for manufacturing a small and precise product like a semiconductor. Like this, the MEMS (Micro Electro Mechanical System) technology can be used to make micro reformer which has a same function of the conventional fuel processor but the volume is dramatically reduced. In this research, a miniature reformer was made on the silicon wafer by MEMS fabrication technology as showed in Fig 1. Substantially, a novel process of coating steam reforming catalyst on silicon wall was developed.

**Fabrication procedure**

A schematic of the steps followed in fabricating the micro channel reformer on 4 inch silicon wafer are given in Fig. 2. Standard photolithography steps followed by deep-reactive ion etching (DRIE) are used for etching features on a silicon substrate to form micro channels and cavity. For the passivation layer, Si₃N₄ is deposited as 1500 Å thickness by low pressure chemical vapor deposition (LPCVD). Dry film resist (DFR) layer is used to prevent the coated Al₂O₃ or Cu/ZnO/Al₂O₃ steam reforming catalyst from making the trouble in glass bonding steps and to remove catalysts perfectly. Platinum is sputtered on wafer’s back side to embed electrical resistance for the heater. The SiO₂ layer is formed between wafer and Pt heater for blocking the electrical conduct. Finally, pyrex glasses are bonded to both side of wafer by anodic bonding.

![Fabrication procedure diagram](image)

**Catalyst coating procedure**

The commercial Cu/ZnO/Al₂O₃ catalyst for steam reforming could be coated on a silicon wafer by specially invented process. Fig. 3 shows the steps of coating process.

![Catalyst coating procedure diagram](image)

First of all, a pretreatment of the micro-channel on silicon wafer is needed to increase the adhesive force between Al₂O₃ layer and wafer. For this, the silicon wafer is dipped into the 20 wt% KOH solution of 80 ~ 90 °C for few seconds. Fig. 4 shows the state of the wafer after dipping into the 20 wt% KOH solution of 90 °C for 10 seconds.

![Catalyst coating microscopic image](image)
Secondly, Al₂O₃ sol-gel is sprayed in the channel as seed layer under coating of the steam reforming catalyst. Thirdly, make the slurry that binders like PVA etc is mixed in the fine power of Cu/ZnO/Al₂O₃ - a commercial steam reforming catalyst. Finally, coat the catalyst on the channels and dry them in high temperature 300 °C for about 3 hours.

**Experimental set-up**

Fig. 5 shows the experimental set-up for the performance test of the micro reformer. The feed rate of a methanol water mixture is controlled by a syringe pump as 0.01 or 0.02 ml/min. An unconverted methanol and water vapor in the reacted gas are condensed through the cooling unit and trapped in bubbler. The final reformed gas is analyzed by micro gas chromatography (Agilent Micro-GC 3000A). And maximum operating temperature of reactor is 260 °C.

![Experimental set-up](image)

**Results and discussion**

The novel catalyst coating process on the silicon wafer is successfully completed and the coated catalyst image is showed in Fig. 6. And the XRD patterns of the coated catalyst prove it to be effective for steam reforming reaction because just CuO, ZnO, and Al₂O₃ peaks are observed.

![Microscopic image and XRD patterns](image)

Fig. 6 Microscopic image of the coated in channel and the X-ray diffraction (XRD) patterns of coated catalyst

Fig. 7 shows the complete micro reformer with wall coated catalyst and Pt heater after glass bonding and dicing. The dimension of the reformer is 3 x 3 x 0.1 cm, so total volume is just 0.9 cc (ml).
Fig. 7 the micro reformer after completing the glass bonding and the dicing

The methanol conversion rate is showed in table 1 as results of the performance test at different fuel supply rate and operating temperature of the reformer. Methanol conversion of 55% was observed at 0.01 ml/min, 260°C. The peak production rate of hydrogen is about 16 cc/min. The mol concentration of CO is below 3%, which is acceptable to high temperature membrane fuel cell operating at 180 degrees around.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Fuel supply rate (0.01ml/min)</th>
<th>Fuel supply rate (0.02ml/min)</th>
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<tbody>
<tr>
<td>240 °C</td>
<td>43.5%</td>
<td>35.4%</td>
</tr>
<tr>
<td>260 °C</td>
<td>55.0%</td>
<td>39.6%</td>
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</table>

**Conclusion**

In our research, MEMS fabricated micro reformer that can supply hydrogen sufficient for operating a 2W fuel cell was developed as a state-of the-art size. And completely novel method for coating a reforming catalyst on silicon micro channel was suggested.

**References:**