LOW TEMPERATURE POM MICRO-REFORMER WITH SILICON NANO-WIRE SUPPORTED NANO CATALYSTS

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Abstract: In this paper, we proposed a new design of a high performance methanol micro-reformer for hydrogen production which integrated low temperature catalysts supported by silicon nano-wires inside micro-channels with multi-inlet and in-parallel channel. Without complicated fabrication process, the reforming performance of micro-reformer with Silicon nano-wire grew on channel-sides (first -generation design) compared to that without nano-wires supported has 1.6 folds and 5.3 folds more methanol conversion and hydrogen yield. Furthermore, we want to enhance methanol-conversion percentage by growing nano-wires fully and partially filled channel-passageways in height and length (second-generation design) to force reactive-gases contact with catalysts and is expected to have the best methanol-reforming performance.

Keywords: hydrogen, methanol-reforming reactor, silicon nano-wires

INTRODUCTION

Reforming-type fuel cells have attracted much attention since they can in-situ transforming gas or liquid type fuels into hydrogen [1] without troublesome issues such as hydrogen storage or transportation [2]. Our system adopted partial-oxidation-methanol (POM)-type catalysts having lower reacting temperature (approach 200℃) much closer to the operating temperature for proto-exchange-membrane fuel cell (PEMFC) and more appropriate being an portable power source rather than often developed steam-reforming-methanol (SRM) type catalysts (exceed 300℃). Hydrogen yield loss resulting from catalytic activity decreased by hot-spot [3] and the formation of byproducts such as H_2O or CO also got improved due to the lower operating temperature of this miniature reformer. Regarding an excellent flow field design for the micro reactor, it must allow reactive gases distribute uniformly and react completely without a great deal of byproducts reformed. For this reason, our system adopts multi-inlet and in-parallel wander channels design which combined silicon nano-wires as catalytic supporters in order to enhance the methanol-reforming area and assist catalysts uniform coating whether on channel-sides or center, as shown in Fig. 1.

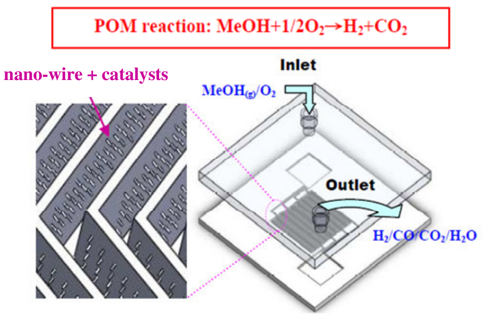


Figure 1. Schematic diagram of the methanol micro-reformer with multi-inlet micro-channels incorporated with nano-wire.

The first generation design of micro reformer fabricated the silicon nano-wires in the channel-sides in order to get better catalytic-coating morphology, the improvement of the methanol reforming efficiency for this reactor also shown afterward. However, the result also indicated that we should try to reform the reactor of first generation to be a new one, which allows considerable quantities of reactive gases react simultaneously and hydrogen moved out quickly, the new reactor was called second generation reactor. The concepts and the fabrication processes of the first and second generation reactor are shown in Fig. 2.

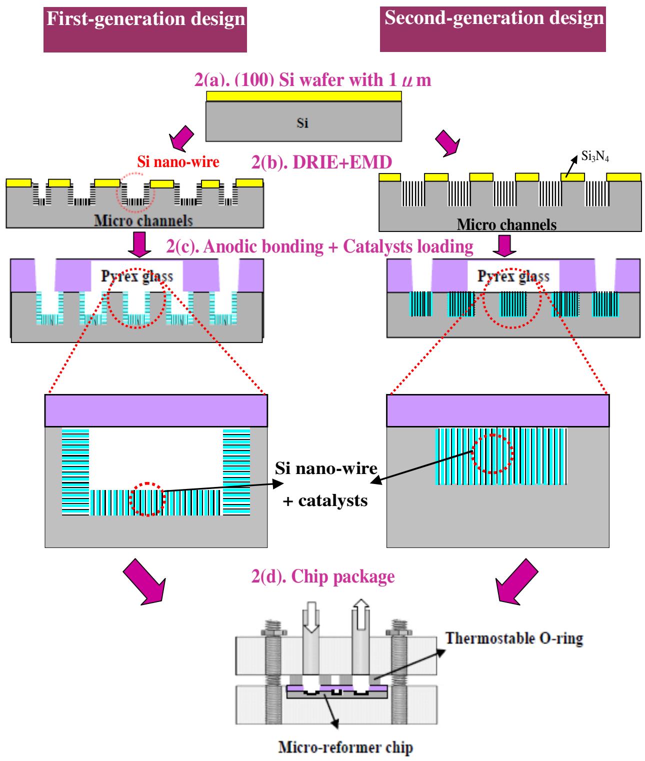


Figure 2. Fabrication process of the micro-reformer

EXPERIMENTAL

First, we used deep silicon RIE (reactive ion etching) and EMD (Electroless-Metal-Deposition) method to obtain micro-channels with nano-wire grew on channel-sides (first-generation design) or fully and partially filled channel-passageways in height and length (second-generation design) on region which defined by lithography previously, then immersing the fabricated chip in the catalytic-solution prepared by sol-gel method at 70℃ for 24h after bonded the chip with Pyrex-glass, drying and calcining for 4h to form the catalysts. Finally, the efficiency of the POM (Partial-oxidation-Methanol) reaction was measured by TCD/GC through connecting the gases pipes and the fixed-chip in the stainless-steel-jig.

The electroless metal deposition (EMD) [4] [5] method was chosen to grow nano-wire in <100> direction by immersing silicon substrate in a mixing aqueous-solution of $AgNO_3$ and HF at 50℃, followed by HNO_3 washing to strip nano-clusters, then the nano-wires with 8 μ m and 150nm in length and diameter was formed on the sides of channel-passageway in first generation reactor. But in second generation design, nano-wires must fully filled channel in height which was about 25 μ m and the spacing between nano-wire should be enlarged to reduce the resistance to gases flow, that is the reason why we do some experimental parameter adjustment in growing nano-wires as in Fig. 5. Due to its sensitivity to precise crystal direction, <100>, the more uniform growth morphology of silicon nano-wires can obtain by KOH pre-treated on silicon substrate to modify the lattice plane deviation which caused by deep silicon RIE. The mechanism is that Ag^+ will receive an electron given out by silicon and deposits when it approach the substrate surface, then SF_6^{2-} was formed and removed by solvent. According to this, it is obvious that the region with Ag nano-cluster covered would etch downward, and the other region being left behind called silicon nano-wires.

Sol-gel method was chosen to prepare the POM (Partial oxidation methanol) Cu-Mn-Zn based catalysts which converse methanol and oxygen into hydrogen and carbon-dioxide, there are chances for hydrogen reformed into water again if excessively high operating temperature or being held in channels too long. Reformer was supplied with methanol and oxygen in a ratio of 2:1 and the total flow rate was 0.5sccm, this exothermic reaction equation is shown blow:

$$CH_3OH + 1/2O_2 \rightarrow 2H_2 + CO_2$$
$$\triangle H_{298} = -192.6kJ/mole$$

It is easier for POM reaction (exothermic reaction) processing spontaneously compared to SRM reaction (endothermic reaction), so the micro reactor can be operated in the lower temperature more approach to room temperature.

RESULTS

Silicon substrate and aqueous catalytic solution prepared by sol-gel method had poor wettibility when catalysts loading, the catalysts aggregated at the corner and sides of the channels-passageways. This phenomenon not only wastes catalysts but also decreased the reactive areas exposed to reactive gases. Silicon nano-wires were introduced into our system to improve the catalytic-coating morphology owing to the decreasing contact angle between silicon and catalytic solution. Channels with nano-wires had more even catalytic distribution whether on channel sides or corners, and the catalysts were able to permeate into the cracks of nano-wires to increase reactive areas [6] [7] as shown in Fig. 3. The reforming performance of first generation micro-reformer with silicon nano-wires on channels sides compared to that without nano-wire had 1.6 folds and 5.3 folds more methanol conversion and hydrogen yield shown in Fig. 4. However, the hydrogen selectivity decreased from 225℃ to 250℃ and only 45% methanol conversion (reactive-gases bypass) means we should propose a new design (Fig. 2, the second-generation design) which allows large mount methanol reforming simultaneously (fully filled nano-wires) and departs from reactive-region right away (shorter channel length) to prevent hydrogen changed into water again.

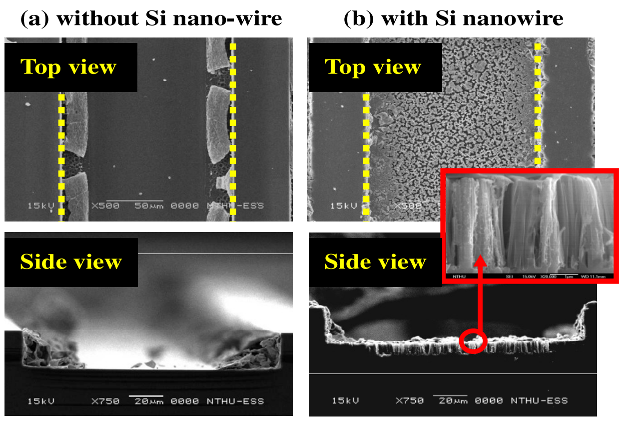
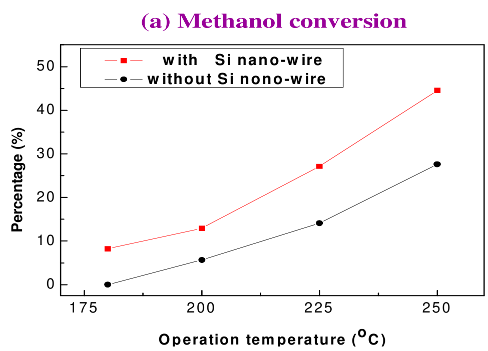
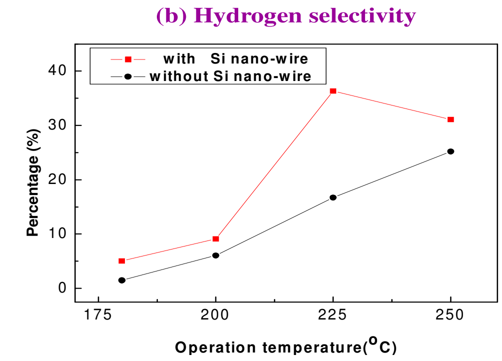


Figure 3. The SEM top and cross-sectional views of the micro-channels deposited by catalysts without (a) / with (b) silicon nano-wire supported.





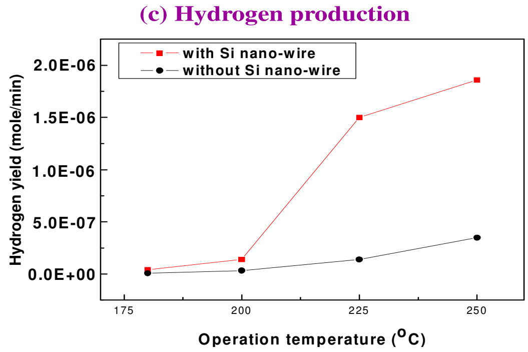


Figure 4. (a) Efficiency of the methanol reforming and (b) the analysis of hydrogen selectivity, and (c) hydrogen yield. The inlet conditions of POM reaction: the ratio and the total flow rate of nO2/nMeOH are 0.5 and 0.5sccm, respectively.

To obtain nano-wires fully filled channels in height and suitable spacing between nano-wires, we modified the experimental parameter (concentration of the reactive solution and the react time) of EMD method. The higher concentration of reactive solution had severe oxidative and reductive reaction, so the spaces between nano-wires are bigger and the cutting down in length are obvious; lower concentration had more uniform and shorter spacing between nano-wires, it also need more time to achieve the same wire length as shown in Fig.5.

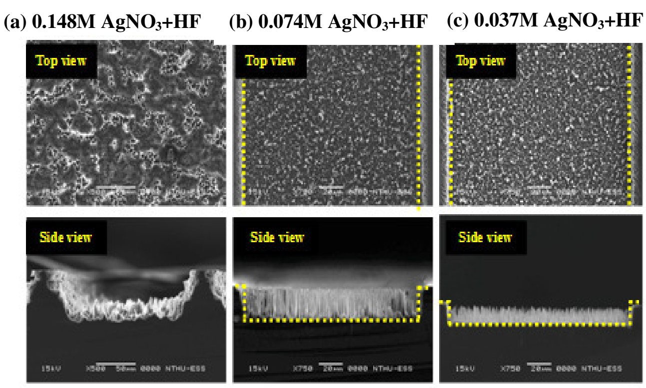


Figure 5. The SEM top and cross-sectional views of the micro-channels with silicon nano-wire grew in various concentration reactive-solution for 3 min.

The cutting down of silicon is disadvantageous for forcing reactive gases pass through nano-wires covered with catalysts and the compact spacing between silicon raising a high flow resistance for gasses. In the other word, we have to find out a most suitable experimental parameter (including the concentration and the reaction time) to get the silicon nano-wires we need in second generation reformer design, that was 0.074M silver nitrate ($AgNO_3$) aqueous solution mixing with HF (Fluorohydric acid) in actually.

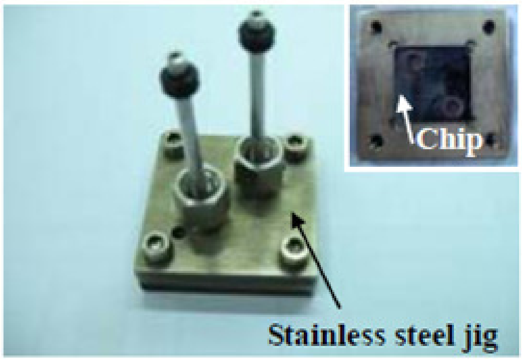


Figure 6. Package pictures of the methanol micro-reformer. Inset shown an integrated micro-reformer chip with the dimention of 2cm×2cm×0.1cm placed in the center of the fixture.

CONCLUSION

The reforming efficiency of the first generation micro-reformer which integrated silicon nano-wires on channel-sides compared to without one had 1.6 folds and 5.3 folds more methanol conversion and hydrogen yield respectively. However, there were large amount of reactive gases by-pass according to first generation design, second generation design was proposed to create more reactive area and forcing reactive gases contact with catalysts in limited channel volume. So far, we have already demonstrated that growing silicon nano-wires fully filled channels height is achievable by tuning experimental parameters. This means that the second generation methanol micro-reformer design is practicable, we will fabricate the second-generation reformer actually and testing the reforming-efficiency very soon.

ACKNOWLEGEMENT

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