A LOW TEMPERATURE, HIGH DURABILITY AND EFFICIENCY OF POM MICRO-CHANNEL METHANOL REFORMER

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Abstract: In this study, a long-operating period, low temperature and high efficiency of micro-channel methanol reformer has been designed and fabricated. In order to solve the low reproducibility resulted from the asymmetrical distribution of catalyst, the pre-developed centrifugal coating process is still adopted but the direction of centrifugal force was changed from parallel to perpendicular to the surface of micro reformer. The experimental result showed that all the performance including methanol conversion rate, hydrogen selectivity and hydrogen yield keep a comparatively steady trend after 3.5 days running, and 97.1 and 97.6% of the expected COV. and S_{H2} can be achieved even after 7 days operation.

Keywords: methanol reformer, hydrogen energy, high durability.

INTRODUCTION

To solve the crisis of energy, fuel cells have emerged alternative power sources for a myriad of applications in transportation, portable electronics, and residential power sources owing to its high overall system efficiency, high energy density and eco-friendly nature. Among the wide variety of areas in which fuel cells can be employed, one of the promising applications is its use as portable devices, especially for small proton-exchange membrane fuel cells (PEMFC), because it has attracted much attention for high efficiency, high volumetric energy densities which is up to 2500 Whl^{-1} for liquid hydrogen or 5000 Whl^{-1} for methanol (DMFC), compared to 400 Whl^{-1} provided by lithium-ion batteries [1]. DMFC can be operated at lower temperature and have high volumetric energy densities as its advantages but have the problem of methanol crossover through the membrane and the low reaction rate of methanol oxidation at anode. On the contrary, PEFMC have few phenomenon of fuel crossover and it requires H_2 as a fuel. Hence, a system capable of providing a stable and economical supply of pure H_2 gas is a prerequisite before any other challenges in the development of PEMFCs. Recently, it's reported that micro-PEMFC may have a considerable small size system through using MEMs technique and equipping with a micro-channel reformer to generate hydrogen from liquid fuels [2]. Methanol has gained interest due to its availability and high hydrogen-to-carbon raio. Generally the micro methanol reformer produces hydrogen via catalytic action of the Cu/Mn/Zn catalyst coated in the micro-channel of reformer. So far, there are several reactions that can efficiently transform methanol into hydrogen, and among all the reactions steam reforming reaction (SRM) and partial oxidative reforming reaction (POM) are mostly attracted attentions owing to their characteristics. SRM can theoretically produce a hydrogen-rich gas with a composition of 75% H2 and 25% CO2, but it's an exothermic reaction:

$$CH_3OH\ (g) + H_2O \rightarrow CO2 + 3H_2,\ \Delta H = +49\ kJ/mol \qquad (1)$$

So, SRM will increase the needs of power via needing an extra heating resource to reach a suitable operating temperature.

The POM reaction of methanol over the Cu/Mn/Zn catalyst can be expressed as the following reactions [3-5]:

$$CH_3OH\ (g) + 0.5O_2 \rightarrow CO2 + 2H_2,\ \Delta H = -192\ kJ/mol \qquad (2)$$

$$CO + 0.5O_2 \rightarrow CO_2,\ \Delta H = -283\ kJ/mol \qquad (3)$$

$$CO + H_2O\ (g) \rightarrow CO_2 + H_2,\ \Delta H = -41\ kJ/mol \qquad (4)$$

Eq. (2) shows POM is a highly exothermic reaction, which can which can be used to construct highly dynamic and fast reforming systems; the preferential oxidation reaction(PROX) (Eq. (3)) and the water gas shift reaction (Eq.(4)) are clean-up steps to reduce the CO concentration in the productive gas. In methanol reformer, its performance depends on many factors, such as temperature, pressure, catalyst type, water to methanol ratio, reactor geometry, flow pattern, etc. but the conditions that decide micro-PEMFC whether will be successfully commercialized is not only the performance of methanol reformer but its durability. Because, the durability will have influence on the fact that how much often consumer will change the device.

In this work, we adjust the direction of spin during the coating process to solve the problem of the block of catalyst to increase the reproducibility and the content of catalyst to enhance the performance of the methanol reformer and test its durability.

Experimental method

Preparation of micro channel

The general fabrication step has been published in our previous work, [6]. Finger-shaped grooves were first fabricated on silicon (100) wafer by photolithography and deep silicon reactive ion etching (DRIE) process. Then, hydrophilic groove-walls were obtained by oxygen plasma manner. Pyrex glasses with inlet/outlet holes were machined by laser dripping process and then bonded on the chips to obtain micro-channels by using anodic bonding process.

The fabrication of micro methanol reformer

We use liquid metallic precursors, including Cu-$5H_2O$-NO_3, Mn-$5H_2O$-NO_3 and Zn-$5H_2O$-NO_3, to mix all the together to prepare the catalyst loaded into the micro channel with the ratio of the 30% of Cu, 20% of Mn and 50% of Zn. Then, the $CaCO_3$ will be added into the precursor solution to start the reaction of crystallization with keeping PH value at 7 till the precursor solution is completely used up, and stop adding the $CaCO_3$ to let the PH value raise to 8. Afterward, the catalyst solution is filtered with 2 liter water and dried it for one night. The preparation of catalyst will be finished after calcining the dried catalyst. We prepared catalyst solutions containing 15% of solid content and 0 % of binder, meaning that there's not any binder in the catalyst solution. First, 10ml DI water was mixed with a constant content of catalyst, and well mingled catalyst solutions were then mixed by stirring and sonicating for one hour; the mixed solutions were injected into the fabricated micro channel, and then put in a centrifugal apparatus for packing self-assembled catalysts into the micro channels. During the loading process, we introduce different direction of centrifugal force to solve the the block of catalyst resulted from the original loading process. The solvents in the catalyst slurries were dried out at 105^oC for 30 min. The catalyst preparation was repeated ten times by the above-mentioned steps and then finally obtained after annealing at 400^oC for 2 hr.

The analytic and testing system of micro-channel methanol reformer

The schematic diagram of whole testing system has been set up successfully. At the beginning, argon, oxygen and steam methanol were well mingled in the mixing chamber as reactive gaseous in the ratio of 81.7 (ml/min), 6.1(ml/min) and 12.2(ml/min), respectively. Then, the fabricated micro-channel methanol reformer was operated on a stainless stage and put on the hotplate to be heated to the required temperature for testing. Afterward, reactive gaseous were sent in the inlet hole of micro-channel methanol reformer in the flow rate of 2 (ml/min) via mass flow controller to transform methanol into hydrogen accompanying with some of carbon dioxide, carbon monoxide and water, and then these productive gas would be analyzed through gas chromatography (GC) to indentify the performance of micro-channel methanol reformer. The catalyst content and cross-section image of the tested micro-channel methanol reformer will be confirmed via Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) and field emission gun scanning electron microscopy (FEGSEM, JEOL-6330F, Japan).

RESULTS AND DISCUSSION

The influence of different direction of spin process

The Figure 1 (a) showed that there's still a serious problem about the asymmetrical distribution of catalyst resulted from the obstruction of catalyst at the entrance of micro channel as the former coating step, and in order to modify the problem of catalytic block, the pre-developed centrifugal coating process is still adopted but the direction of centrifugal force was changed from parallel to perpendicular to the surface of micro reformer as shown in fabrication diagram. Then, the Figure 1 (b) showed that the uniform

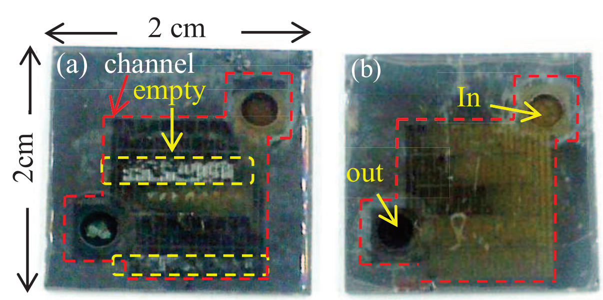

Figure1. The image of the fabricated of micro-channel reformer. (a) the reformer with old productive process. (b) the reformer with new productive process.

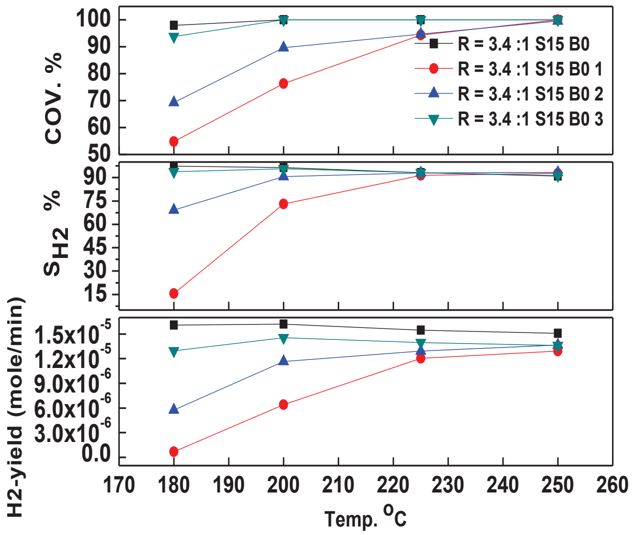

Figure 2. The reproducibility of the micro-channel methanol reformer with the new fabrication process.

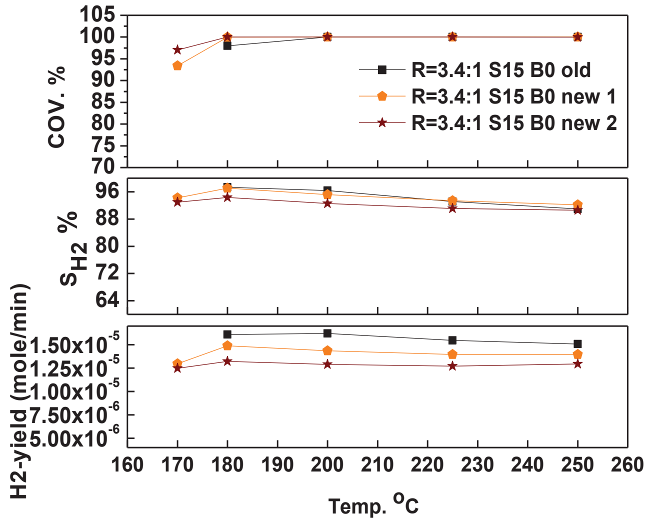

Figure 3. The reproducibility of the micro-channel methanol reformer with the new fabrication process, and the performance of the new one and the old one.

distribution of catalyst in micro reformer is much improved via new fabrication process. By introducing the perpendicular direction of centrifugal force, the catalyst will be forced to deposit on the bottom of channel layer by layer so that all the surface of channel will be coated the catalyst at first, and there's not ununiform catalytic distribution which has bad influence on the performance of methanol reformer.

The experimental result showed the reproducibility had been much improved from only 20-30% to nearly 90% when the new productive course was adopted to solve the block of catalyst at the entrance of micro channel, as shown in Figure.2 and 3. and the Figure 3. also showed that the performance keep a high property where the methanol conversion rate still can reach up to 95.5% by average even though the testing temperature was cooled down to 170℃. Among the operating temperature, the performance of reformer at 180℃ which the 99.9% of conversion rate and 94.8% of S_{H2} could be observed is the best one, consequently the long-term period of operation was tested at this temperature.

The enhancement of reproducibility is resulted from the modification of the obstruction of the catalyst so that it will cause the uniform distribution and raise the rate of collision between the catalytic particle and steam methanol to ameliorate the performance of micro reformer with high reproducibility.

Another reason for the improvement of reproducibility is the augmentation of the catalyst amount in the micro reformer, so the active site is modified.

The durability test

According to the result of the previous experiment, the temperature set at 180 ℃ has the much better performance, and the condition of durability test, hence, is kept at this temperature. The experimental result showed all the performance including methanol conversion rate (COV.), hydrogen selectivity (S_{H2}) and hydrogen yield keep a comparatively steady trend after 3.5 days running, and 97.1 and 97.6% of the expected COV. and S_{H2} can be achieved even after 7 days operation, respectively, as shown in Fig.4. This result means that the reformer has long lifespan and economical superiority, therefore consumers don't need to spend so much cost on changing the reformer system so that there will be more chances to commercialize the whole fuel cell system.

Discussion

In order to solve the low reproducibility resulted from the problem of the obstruction of catalyst via the original loading process, the new spin loading process with different centrifugal direction, including parallel and perpendicular direction, was adopted to deal with this phenomenon. The experimental result showed that the uniform catalytic distribution and high reproducibility were obtained. As catalytic particle can deposit on the bottom of channel layer by layer by applying the centrifugal process with the perpendicular force compared to those process with the force which direction is parallel to the surface of the chip. According to the GC analyzing diagram, the more uniform catalytic distribution, the higher the performance of methanol reformer, and a high

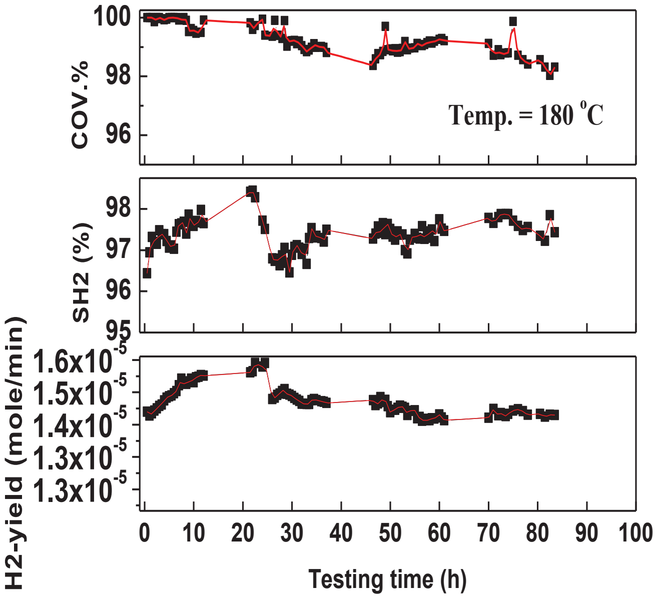

Figure 5. The performance of the long-lasting operation of micro-channel reformer tested at 180℃

durability and efficiency of micro methanol reformer has been obtained in this work

CONCLUSION

Briefly, the characteristic of high reproducibility and steady operation, which is affected by the distribution of catalyst, is important to raise the potential of commercializing for micro methanol reformer. Hence, we provide, in this article, a new fabrication way with various direction of centrifugal force to modify the obstruction of catalyst so that each reformers has the similar performance, and the identity of long-lasting operation is prominent.

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