

AUTOTHERMAL REFORMER USING HYDROGEN PEROXIDE FOR MICRO FULL CELLS

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Abstract: Development and performance evaluation of the on-board hydrogen generator by autothermal reforming process were carried out. A reformer that extracts hydrogen from liquid fuel is an essential subsystem of the power pack. The device is called autothermal reformer. Typical product gas of ATR still contains a large amount of carbon monoxide that poisons electro-catalyst of the MEA. In the present study we used the decomposition of hydrogen peroxide as a parallel exothermic reaction in the same reactor as the reformer. For fabricating ATR reformer, we choose the material as photosensitive glass. Using the present concept we could reduce the concentration of carbon monoxide in the product gas of the reformer. We can be possible to load the methanol-hydrogen peroxide ATR system without any devices.

Keywords: Reforming process, Methanol, Hydrogen Peroxide, Fuel cell

INTRODUCTION

Fuel cells have drawn attention as an ideal alternative solution to the existing power engine in portable power applications.[1] Internal combustion produces high power, but there has vibration, noise and low heat efficiency problem in portable scale. Battery has low energy density and short operation time. But fuel cell has no vibration and noise also high energy density. But a major constraint in the successful development of a fuel cell power system has been difficulties and hazards involved in the storage and handling of hydrogen, the fuel for fuel cells. On-board hydrogen production is a key issue for development of a portable fuel cell power system. [2] There are some ways of hydrogen storage like compressed hydrogen tank, liquid hydrogen tank and metal hydride. Among hydrogen storage ways, fuel reforming, as a reaction to extract gaseous hydrogen from a liquid fuel, is an essential process for because a fuel is stored and used in liquid phase. Methanol is a good option as a fuel source for reforming because of low boiling point, easy to get, high hydrogen to carbon ratio. [3]

The mechanism of autothermal reforming involves a combination of steam reforming and partial oxidation. [4] Steam reforming is endothermic, while partial oxidation is an exothermic reaction. The total heat balance in autothermal reforming can be controlled by changing the degree of exothermic and endothermic reactions. Autothermal reforming requires no additional external heat source. Furthermore, autothermal reforming uses simple, small reactors with relatively high efficiency. Oxygen facilitates a fast reforming reaction causing the content of hydrogen in the reformat gas to be higher

than that of partial oxidation. However, autothermal reforming requires additional air supply to provide oxygen, and the concentration of hydrogen in reformat gas is lower than in steam reforming due to nitrogen in the air (see Fig. 1). [5]

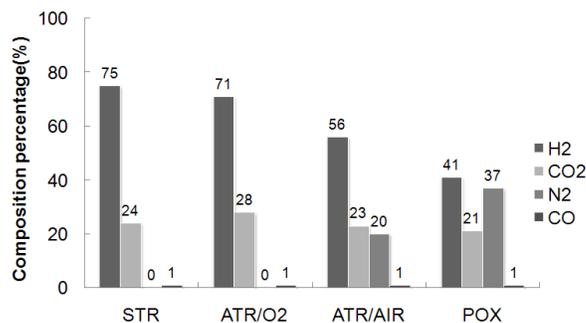
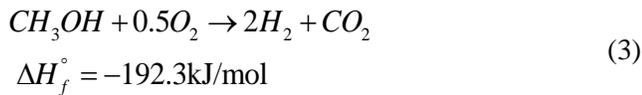
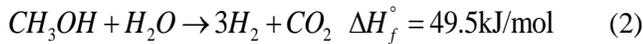
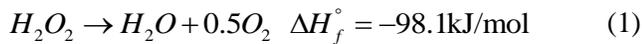


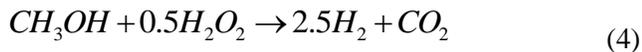
Fig. 1: Composition of product gas for various reforming methods

METHODOLOGY

Decomposition of hydrogen peroxide for autothermal reforming of methanol is presented in this study. The decomposition of hydrogen peroxide is a highly exothermic reaction; the resultant heat can be used effectively to vaporize methanol. The decomposition of hydrogen peroxide also generates oxygen with steam, making autothermal reforming with methanol possible. The substitution of oxygen for air fed by an additional pump makes the concentration of hydrogen increase as high as in the steam reforming technique (see Fig. 1). Three reactions take place in a reactor, in sequence:



Decomposition of hydrogen peroxide, (1), takes place in the fore part of the reactor, generating oxygen with steam. Methanol is partially oxidized as (2) to generate sufficient amount of heat for steam reforming of methanol (3). The overall reaction is expressed below:



Ideally, 1 mole methanol with 0.5 mole hydrogen peroxide generates 2.5 moles hydrogen and 1 mole carbon dioxide. However, the catalytic process in a reactor is complex. The characteristics of methanol autothermal reforming reaction with the decomposition of hydrogen peroxide were investigated in this study.

DESIGN AND FABRICATION

Design of reformer

The shapes of micro reformers using MEMS technology are usually flat because of high bonding surface and space. In this research the reformer made of six glass wafers. The photosensitive glass (MEG2) wafer selected as the structural material had such properties as hardness for sustaining the product gas and resistance to strong acid like hydrogen peroxide. [6] Also it has good thermal insulation and gas sealing can be achieved easily with a material. The dimension of each wafer was 30mm X 30mm with 1mm thickness and reaction zone is 10mm X 10mm X 4mm.

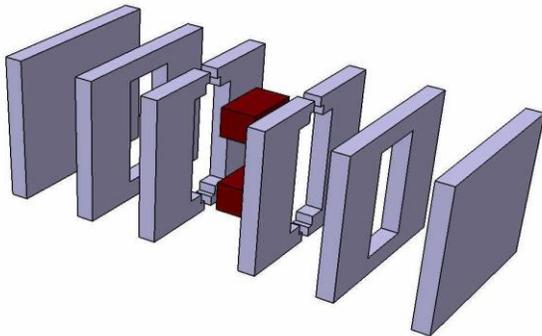


Fig. 2: The construction of the micro reformer

Catalyst preparation

Cu/ZnO was selected as a catalyst for hydrogen peroxide decomposition and methanol autothermal reforming, respectively. [7] γ -Alumina was selected as support. γ -Alumina is high porous material, and stable at high temperature within reactor. Cu/ZnO alumina catalyst was prepared by wetness impregnation method.

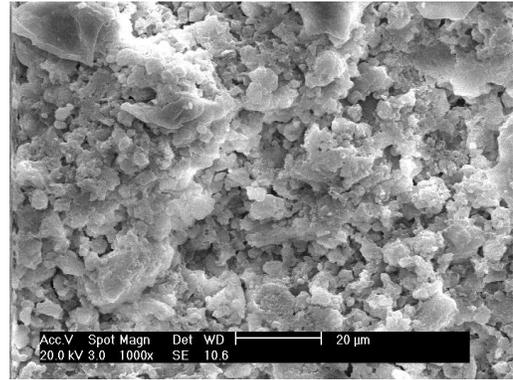


Fig. 3: SEM image of Cu/ZnO catalyst

Fabrication process

The overall fabrication process is as follows. Fabrication process for an individual glass wafer consists of 7 steps: (1) exposure to UV light under a chrome mask at the intensity of 2J/cm^2 , (2) heat treatment at 585°C for 1 hour to crystallize the portion of the glass that was exposed to UV. (3) The crystallized portion of the glass dissolved in the 10% hydrofluoric solution to result in the membrane for making one assembly and the etching rate was $20 \mu\text{m}/\text{min}$. (4) After etching, the surface of glass was uneven so polishing process was needed for bonding. The best bonding condition was determined with pressing the wafers against each other at 1000N/m^2 in a furnace held at 500°C . (5) After bonding process, membranes were removed by 10% hydrofluoric solution. (6) The alumina catalyst supports were inserted in the reformer layer respectively. Ni foam was chosen for mixing. Because methanol and hydrogen peroxide were injected as liquid phase. As the reaction is occurred at over 200°C so the conventional injection method is needed. In this research, 1/16 inch SUS tube was connected to micro glass reformer. 1/16 inch SUS tubes were fitted to front and end ferrules. And the fitted

SUS tubes were locked with the reactor. (7) The complete device was constructed by thermally bonding the etched glass layers. The gap between SUS tubes and glass was filled with PDMS (Polydimethylsiloxane) which is transparent, non-toxic, non-flammable and good heat resistance is widely used as the sealant for MEMS devices.

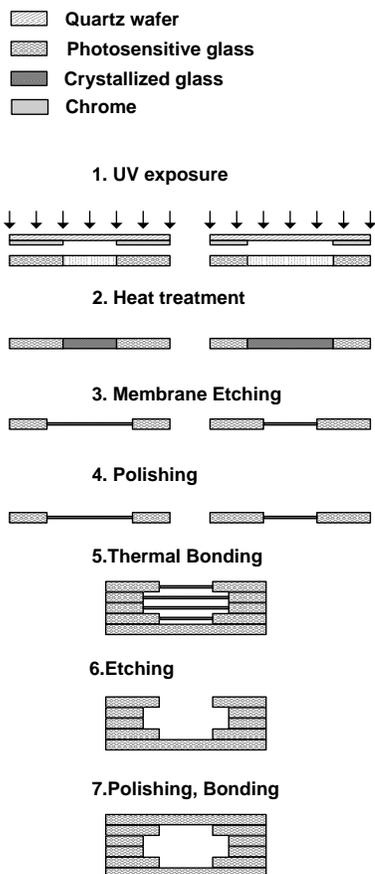


Fig. 4: Procedure for fabrication of micro ATR reformer

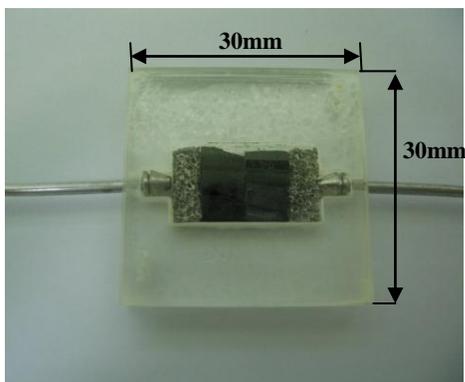


Fig. 5: The fabricated micro ATR reformer connected with 1/16 inch SUS tubes

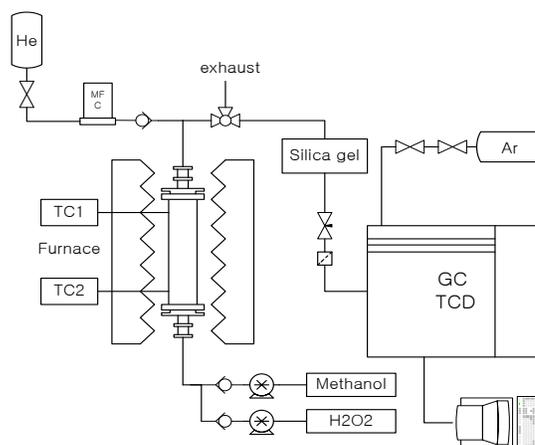


Fig. 6: Schematic of micro reformer experiment

EXPERIMENTAL RESULTS

Comparison of conventional ATR

To compare with conventional ATR and ATR using hydrogen peroxide, compositions of methanol, water and oxygen are used in both cases. In conventional ATR and ATR using hydrogen peroxide, methanol was injected by 4cc/hour rate. Water and oxygen was injected by same rate which is that flow rate of water is 1cc/hour both cases to compare to same amount composition condition

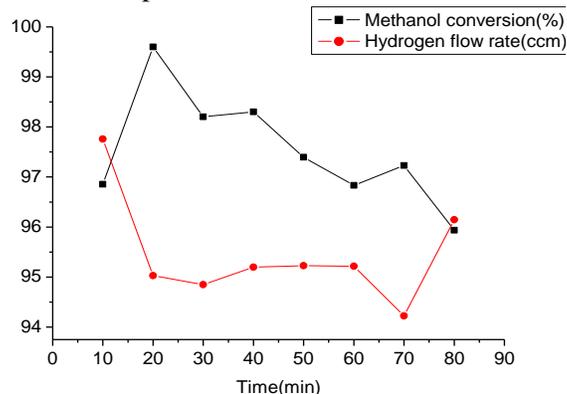


Fig. 7: Conversion and flow rate graph of conventional autothermal reforming

In conventional case, the temperature decrement of inlet and outlet is from 30 to 40 degree of Celsius because of oxidation is occurred near the inlet. This tendency is shown by that steam reforming process is slower than partial oxidation. The methanol conversion rate is almost 100%. It means that the catalyst is suitable for this system.

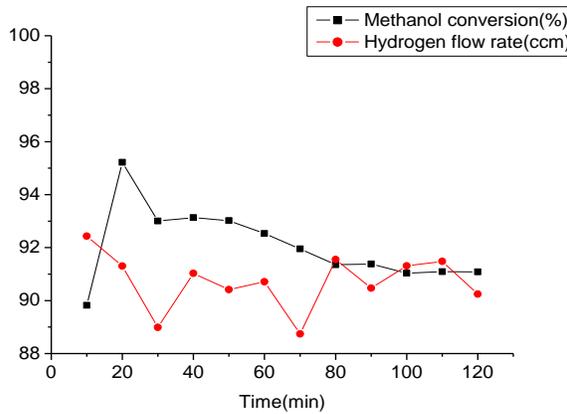


Fig. 8: Conversion and flow rate graph of autothermal reforming using hydrogen peroxide

In ATR using hydrogen peroxide, the temperature decrement of inlet and outlet is from 10 to 20 degree of Celsius. This temperature decrement is appeared because the decomposition of hydrogen peroxide is more uniformly spread. And it is shown by 4~5% lower methanol conversion than conventional ATR caused by catalyst.

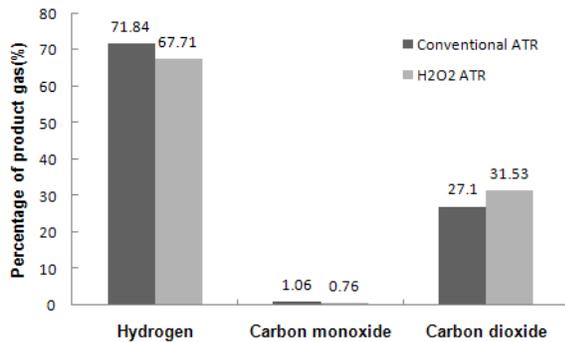


Fig. 9: Composition of product gas for conventional ATR and ATR using H₂O₂

Comparing to component of product gas in both cases, carbon monoxide is reduced by ATR using hydrogen peroxide by 30%. This result is caused by small temperature decrement of ATR using hydrogen peroxide. Carbon monoxide is important in fuel cells system. In fuel cell, there is MEA to convert electricity by electrochemistry way that is covered with Platinum as catalyst. But carbon monoxide makes membrane above Platinum by oxidation.

CONCLUSION

The micro methanol reformer was fabricated using photosensitive glass using thermal bonding with new connecting concepts for sustaining high reaction

temperature.

There are some differences between Conventional autothermal reforming and autothermal reforming using hydrogen peroxide.

First, autothermal reforming using hydrogen peroxide produced less carbon monoxide about 30% compared with conventional one. Carbon monoxide is usually produced by temperature gradient in reformer. Autothermal reforming using hydrogen peroxide had low temperature gradient because of decomposition of hydrogen peroxide.

Second, considering conversion rate, conventional autothermal reforming was better than autothermal reforming using hydrogen peroxide because of catalyst. In autothermal reforming using hydrogen peroxide Cu/ZnO alumina catalyst didn't give effects for decomposition of hydrogen peroxide, so hydrogen peroxide decomposed a lot of portion of water by heat.

By the results, autothermal reforming using hydrogen peroxide is suitable for portable PEMFC systems because of the simplicity and low carbon monoxide contents.

ACKNOWLEDGE

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