

A STUDY ON MICRO CATALYTIC REACTOR FOR AUTOETHERMAL REFORMING USING METHANOL AND HYDROGEN PEROXIDE WITH BUILT-IN CHROME SILICIDE THERMOCOUPLE

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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. 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 with built-in chrome silicide thermocouple for temperature measuring.

Keywords: Autothermal reforming, Methanol, Hydrogen peroxide, Chrome silicide thermocouple

INTRODUCTION

An ideal alternative solution of power system is studied by many researchers because of economic and environmental problem. 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 with high energy density and efficiency. 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 subsystem of fuel cell power system. Condensed phase fuel such as hydrocarbon is suitable for a compact power generation because a fuel is stored and used in liquid phase. Especially 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]

There are several ways of hydrocarbon fuel reforming process. Steam reforming is the most common method of producing commercial hydrogen.[3] And Partial oxidation (POX) is a type of chemical reaction that is partially combusted in a reformer, creating a hydrogen-rich syngas which can then be put to further use, for example in a fuel cell.[4] Autothermal reforming is a combination of steam reforming and partial oxidation.[5]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]

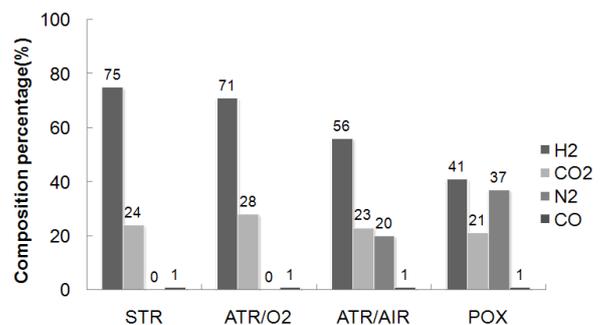
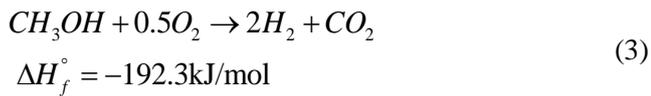


Fig. 1: Composition of product gas for various reforming methods

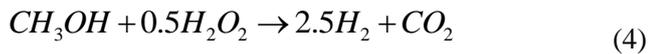
METHODOLOGY

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. 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.

To figure out the reaction mechanism of micro system, the temperature of reactor should be measured. It is hard to measure the temperature in micro system. So in this paper, the built-in thermocouple is suggested to measure the reaction temperature of the micro system. Before fabricating a micro reactor, numerical simulation was accomplished by fluent. The temperature distribution of reactor was calculated and the design parameters of micro reactor were confirmed by simulation results. To ensure the results of simulation, chrome silicide ($CrSi_2$) thermocouple module which we were fabricated were used in experiment setup.

DESIGN AND FABRICATION

Design of built-in chrome silicide thermocouple

An implantable hybrid temperature sensor for a micro scale space in a power MEMS device is proposed using chrome silicide which has a very high electromotive force, and nickel as a base metal. [6]

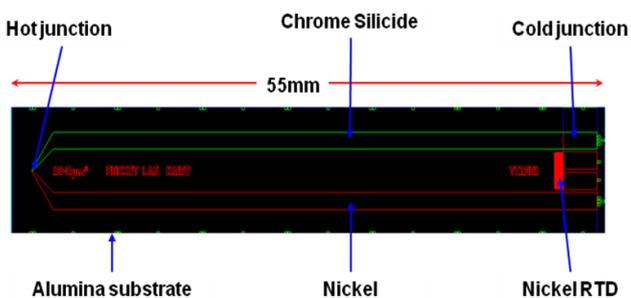


Fig. 2: Design concept of the $CrSi_2$ -Ni thin film thermocouple

Design of reformer system

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 30 mm with 1 mm thickness and reaction zone is 10mm X 10mm X4 mm.

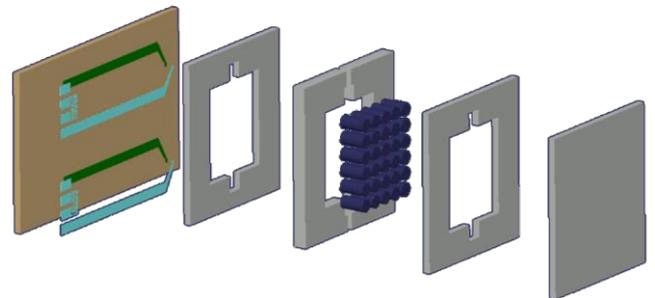


Fig. 3: Concept of the built-in thermocouple in a micro ATR system

Catalyst preparation

Cu/ZnO was selected as a catalyst for hydrogen peroxide decomposition and methanol autothermal reforming, respectively. 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.

Fabrication of chrome silicide thermocouple

The fabrication procedure is performed as follows. The $CrSi_2$ was sputtered to a thickness of 5000 Å on the alumina substrate with 1 kW power in an 8 mmTorr vacuum condition. Before the lift-off process that patterns the film, the substrate should be annealed in 30 min at 400 °C, and then for 30 min at 450 °C. In the second step, the nickel film is deposited on the substrate using the same procedure as that used for the $CrSi_2$ deposition, and the contact hole for the junction was built. In order to insulate the whole metal areas excluding the electrode contact with the outer measurements, an oxide layer of 1 μm SiO_2 was fabricated in the final process. The thicknesses of the junctions were 1 μm. The RTDs have a thickness of 5000 Å, a length of 58 mm, and a width of 40 μm.

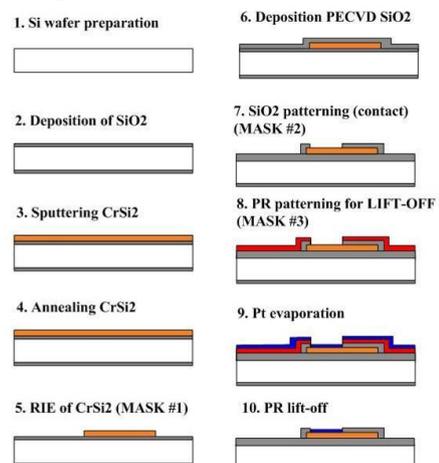


Fig. 4: Procedure for fabrication process of $CrSi_2$ Thermocouple

Fabrication of reformer 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 $2\text{J}/\text{cm}^2$, (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 $1000\text{N}/\text{m}^2$ 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.

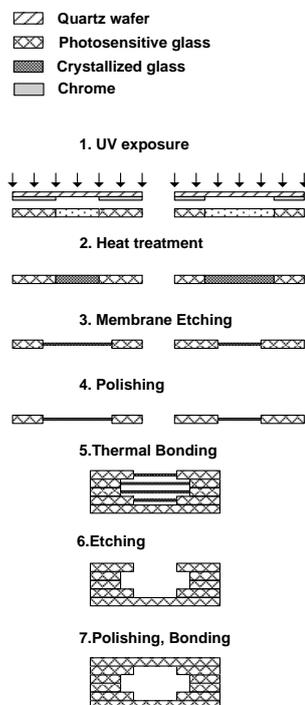


Fig. 5: Procedure for fabrication of micro ATR reformer

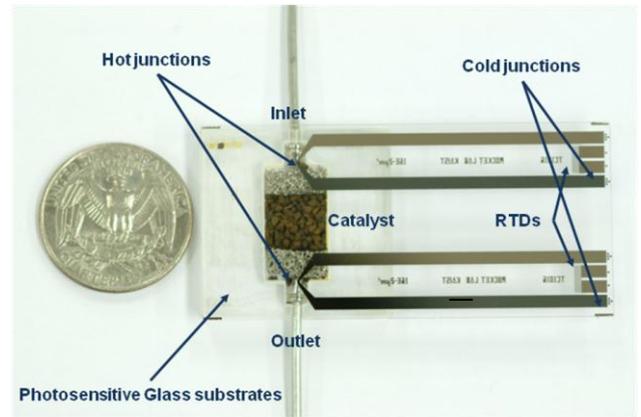


Fig. 6: Sample of the built-in thermocouple in a micro ATR system

EXPERIMENTAL RESULTS

Chrome silicide thermocouple

The sample RTD was calibrated in the temperature range from -10°C to 360°C . As shown in Figure 5(a), the slope of the normalized resistance according to the linear fit can express the TCR of the nickel RTD [14]. The value of the slope that is the nickel RTD TCR, α_{Ni} was $0.0063/^\circ\text{C}$ at 20°C , whereas the reference value of the nickel TCR, $\alpha_{\text{Ni-ref}}$ was $0.0067/^\circ\text{C}$ at 20°C . The resistance of the RTD was $913.668\ \Omega$, which has approximately 82% of the design value of the resistance of the nickel RTD ($1113.759\ \Omega$).

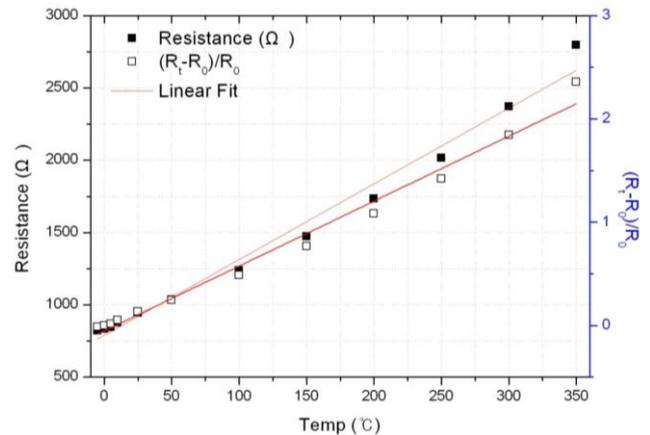


Fig. 7: Test results of the thermocouple

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 $4\text{cc}/\text{hour}$ rate. Water and oxygen was injected by same rate which is that flow rate of water is $1\text{cc}/\text{hour}$ both cases to compare to same amount composition condition

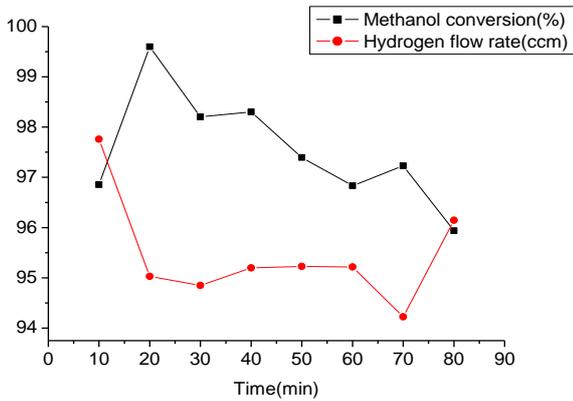


Fig. 8: Conversion and flow rate graph of conventional autothermal reforming

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.

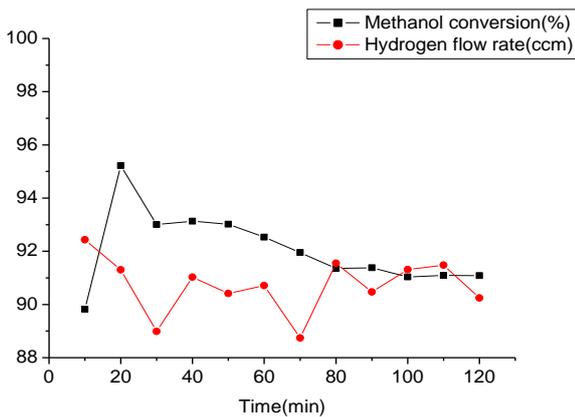


Fig. 8: Conversion and flow rate graph of autothermal reforming using hydrogen peroxide

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.

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 with built-in chrome silicide thermocouple was fabricated using photosensitive glass using thermal bonding with new connecting concepts for sustaining high reaction temperature. And the chrome silicide thermocouple for measuring reaction in micro system was fabricated.

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. And also the measured temperature using thermocouple is to be used as parametric data to figure out micro kinetics.

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