

FEASIBILITY STUDY ON MICRO PLASMA-CATALYTIC METHANOL REFORMER

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Abstract: Feasibility on micro plasma-catalytic methanol reformer was investigated in the present study. A micro methanol reformer was fabricated using photosensitive glass wafers. Cu catalyst layer was coated into microchannels of the reformer. Two electrodes were attached on both top and bottom side, respectively. The methanol conversion of the micro methanol reformer without electric discharges was measured as the temperature varied. The pulse wave discharge was loaded during the methanol reforming. The effect of electric discharges on the methanol conversion was investigated as various discharge conditions. The effect of electric discharges was observed at the temperature range of 220-240 °C, while the methanol conversion was not increased at temperature lower than 200 °C.

Keywords: Micro plasma; Methanol reforming; Microreactor; Non-thermal plasma; Plasma-catalyst reaction

INTRODUCTION

Micro fuel cell has called much attention as a source of micro-power because their energy density is higher than that of the batteries [1-2]. Direct methanol fuel cell (DMFC), solid oxide fuel cell (SOFC), and proton exchange membrane fuel cell (PEMFC) [1] have been tried as micro fuel cells in the last decade. Of various types of fuel cells, PEMFC came to the attention as the most promising fuel cell type for commercialization due to its excellent performance at low temperatures. There is a great body of research works dealing with implementation of the micro fuel cells. However, high-density hydrogen storage is required to meet the overall energy density for micro power sources [3-4].

There are several technologies for the hydrogen storage such as the compressed hydrogen, liquefied hydrogen, reforming of hydrocarbons, metal hydrides, chemical hydrides, and carbon nanotubes. Micro methanol reformer is a device to generate hydrogen from the reforming of methanol [5]. PEMFC can be a primary candidate for a micro power source if the reformer is realized in micro scale [2]. Many researchers have been developed a micro methanol reformer using MEMS technologies that is a useful tool to reduce a size of the reformer [5-7].

There are a number of reforming techniques available including steam reforming [8], partial oxidation [9] and autothermal reforming [10]. Steam reforming was selected for a micro methanol reformer because of its high attainable hydrogen concentration in the reformat gas. The methanol steam reforming reaction consists of two overall reactions; one is a primary process in the steam reforming of methanol and the other is the methanol decomposition to produce carbon monoxide (CO) [11].



The methanol steam reforming reactions require temperature higher than 250 °C to initiate the reactions on the catalysts. The micro electric heater and micro combustor were mainly used to supply heat to the micro reformer. In addition, the reformer needs thermal isolation integrated with the micro fuel cell because of its high operating temperature. Vacuum packaging technology could be used to this end, but it is difficult and expensive in micro-scale [12]. From above problems, it becomes apparent that a new catalytic process for methanol reforming is needed, which would be operable at a low temperature.

In the present study, non-thermal micro plasma was used to improve the catalytic activity on the catalyst at the low temperature. Feasibility on micro plasma-catalytic methanol reformer was investigated.

EXPERIMENTS

Micro Reformer Design

Figure 1 shows the schematic of the micro plasma-catalytic methanol reformer. The fabrication process of the micro reformer is as follows:

- (a) Photosensitive glass wafer was exposed to the ultraviolet (UV) light with a wavelength of 310 nm at the intensity of 2 J/cm² under a quartz wafer mask.
- (b) Heat treatment at 585 °C for 1 hour, then the exposed part of the glass to the UV light was crystallized.
- (c) The crystallized part was etched in the diluted 10% hydrofluoric (HF) solution in order to obtain the desired shape.
- (d) Each layer was bonded using thermal bonding at 1 kPa at 500 °C for 12 hours.
- (e) Cu/Al₂O₃ catalyst was coated on microchannels using slurry injection method.
- (f) ITO electrodes were attached on both top and bottom side of the micro reformer.

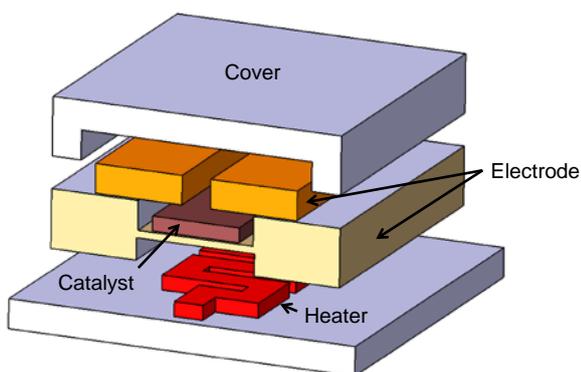


Fig. 1: Schematic of the micro plasma-catalytic methanol reformer.

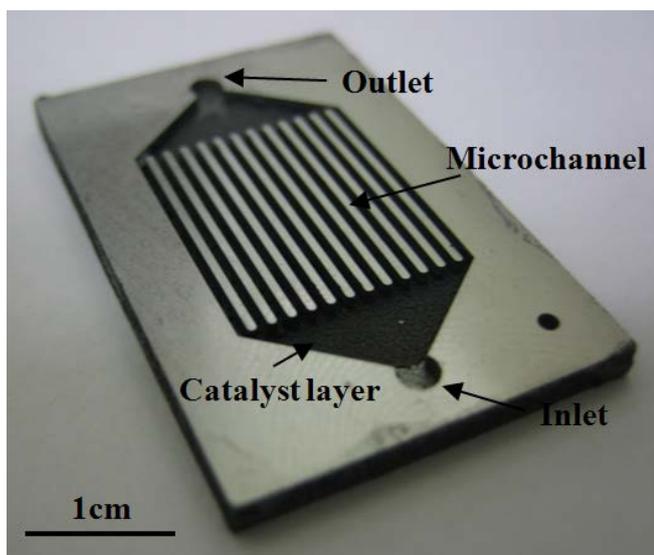


Fig. 2: The catalyst-coated microchannels of the micro methanol reformer.

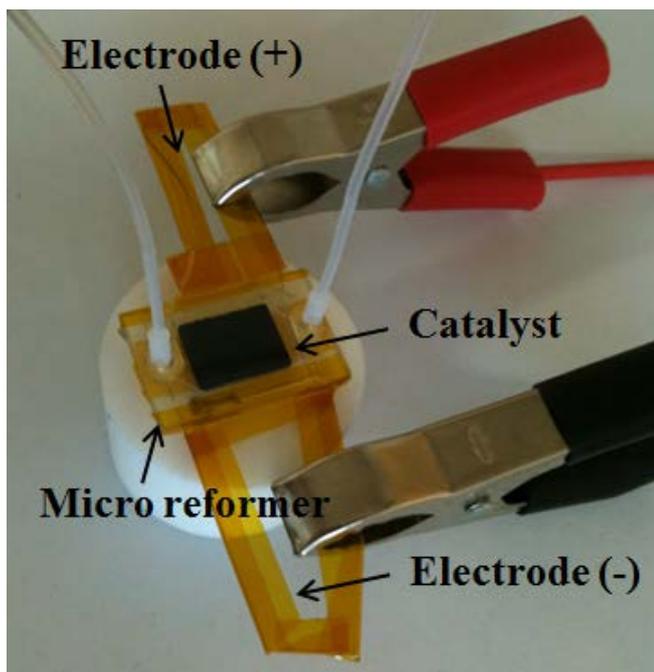


Fig. 3: The micro methanol reformer attached with ITO electrodes.

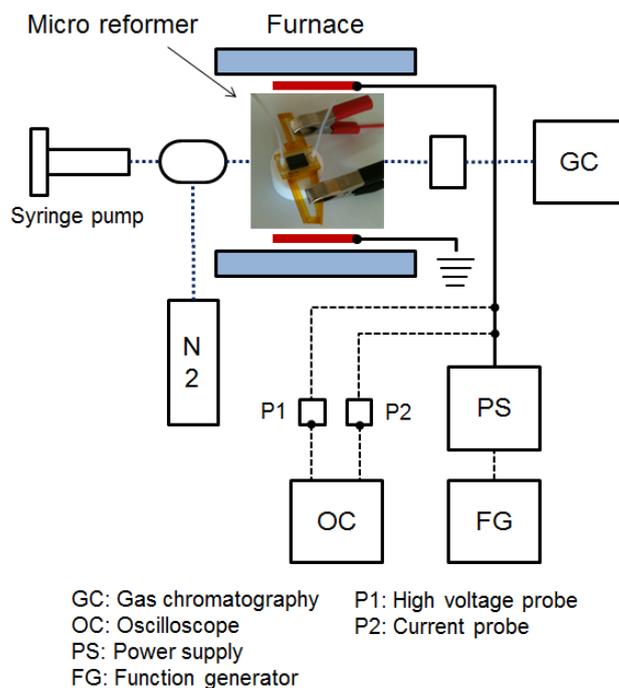


Fig. 4: Experimental apparatus for micro plasma-catalytic methanol reforming.

The catalyst-coated microchannels were shown in Fig. 2. The microchannel dimension was $500 \mu\text{m} \times 1000 \mu\text{m}$ and the catalyst thickness was $30 \mu\text{m}$. The area of the catalytic zone was 1.2 cm^2 . Figure 3 shows the micro methanol reformer attached with transparent ITO (Indium Tin Oxide) electrodes. The illumination induced by plasma discharge can be observed because the glass reformer and ITO electrodes are perfectly transparent.

Experimental method

The schematic of experimental apparatus for micro plasma-catalytic methanol reformer is shown in Fig. 4. High voltage power supply (HPS1200) was used to supply power for plasma discharge in the micro methanol reformer. The supply voltage and current were measured using high voltage and current probes (Tektronix). The voltage and current were recorded in oscilloscope (LeCoy) in order to calculate the power consumption.

The methanol and water were mixed and supplied to the micro reformer in the controlled flow rate using a syringe pump (KDS200). Nitrogen used as a carrier gas was supplied using a mass flow controller (BRONKHORST). The steam-to-carbon ratio (S/C) was fixed to 1.0 and the feed rate was 0.2 ml/h. The temperature was controlled using an electric furnace, ranging from 200 to 250 °C. A thermocouple was attached in the middle of the micro reformer in order to measure the reaction temperature.

The composition of products generated from methanol reforming was analyzed in the gas chromatography (YONGLIN) in order to calculate the methanol conversion.

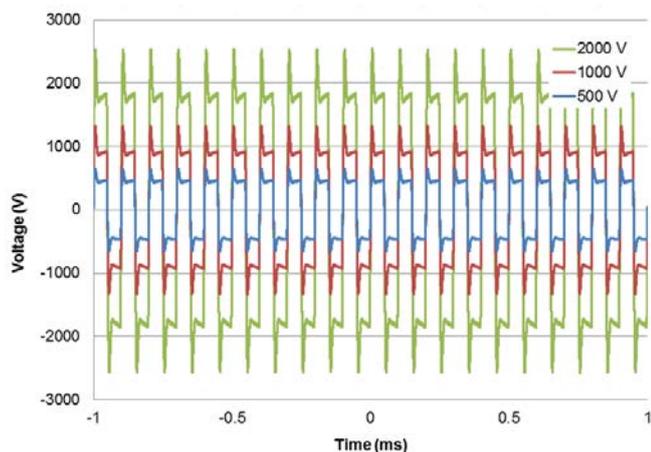


Fig. 5: Discharge voltage as a function of time; pulse wave with 20 kHz and 50 μ s pulse width.

RESULTS AND DISCUSSION

Methanol-steam reforming in micro plasma

The presence of Cu/Al₂O₃ catalyst in the discharge zone of the micro reformer may affect the discharge characteristics of the micro plasma due to surface discharge on the catalyst. In order to check this point, the plasma reaction with the same amount of Al₂O₃ in the micro reformer was carried out. The methanol reforming without discharge was also carried out. As a result, the effect of catalyst presence on the discharge characteristics was not observed.

The reforming reaction of micro reformer in the micro plasma without catalyst was carried out. The results showed that no reaction take place in the all of temperature range. It was found that the plasma energy is not sufficient to activate methanol-steam reforming without catalyst. Additionally, the reforming reaction of micro reformer without catalyst and plasma was carried out. The reaction did not take place because the glass material of the micro reformer was not active to the reaction.

Plasma-catalytic methanol-steam reforming

Figure 5 shows the discharge voltage as a function of time. The discharge voltage ranged from 500 to 2000 V. The various types of voltage signal are available such as sinusoidal, saw-tooth, triangular waves, and pulse waves. In this study, the pulse wave was used; the frequency was 20 kHz and the pulse width was 50 μ s.

Methanol conversion of the micro plasma-catalytic methanol reformer as the function of temperature and discharge voltages was shown in Fig. 6. The methanol conversion was defined:

$$\text{CH}_3\text{OH conversion} = \frac{\text{Mole of CH}_3\text{OH}_{\text{converted}}}{\text{Mole of CH}_3\text{OH}_{\text{feed}}} \quad (3)$$

The effect of electric discharges on the methanol reforming was observed at the temperature range of

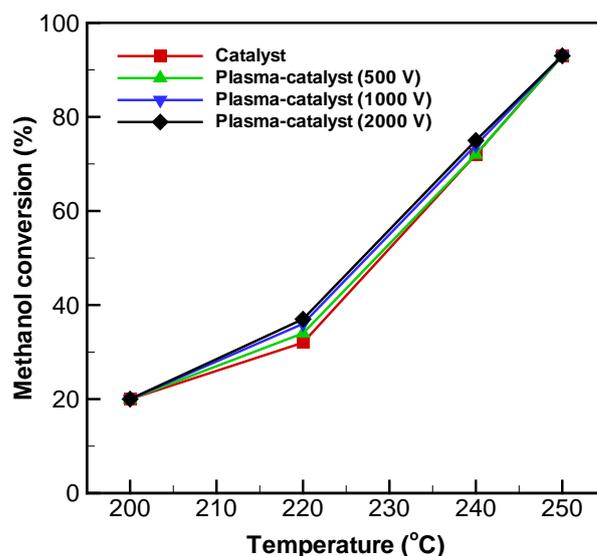


Fig. 6: Methanol conversion of the micro plasma-catalytic methanol reformer as the function of temperatures and discharge voltages.

220-240 °C. The methanol conversion increased with the discharge voltage because a higher discharge voltage provided more electrons with sufficient energy to activate the reactant molecules. The methanol conversion did not increase at 250 °C due to the decrease of discharge intensity with the increase of temperature. At temperature lower than 200 °C, the methanol conversion did not increase due to the low reaction rate on the catalyst surface.

The increase of methanol conversion was highest at 220 °C. The reactant molecules are activated to vibrational excited states by inelastic electron impact in the plasma. The excited molecules more easily arrive on the catalyst surface and absorb on the active site of the catalyst; thus, the reactant molecules participating in the catalytic reactions increased. Moreover, the interaction of plasma with the catalyst through the surface discharge induces the decrease of activation temperature of the catalyst.

CONCLUSION

A micro plasma-catalytic methanol reformer was fabricated using photosensitive glass wafers. The effect of the combination of plasma with the catalyst on the methanol conversion was investigated as the voltages and temperatures varied. The methanol conversion increased at the temperature range of 220-240 °C. The reactant molecules excited by the plasma was more reactive on the catalyst than those reacted without the plasma.

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