INTRODUCTION

Proton exchange membrane fuel cell (PEMFC) has drawn attention as a primary candidate for a micro power source because the energy density is higher than that of batteries [1]. There are considerable research works which are focused on the realization of micro fuel cells in the literature. However, the high density hydrogen storage is required to meet the overall energy density for micro power sources [2]. Recently, chemical hydrides have attracted a great attention for new hydrogen generation methods.

Of various hydrides, the sodium borohydride (NaBH₄) is stored in liquid phase, and is a stable and nonflammable alkaline solution. In addition, it has relatively high hydrogen content, and is a renewable and environmentally friendly fuel. It is easy to control the hydrogen generation rate and pure hydrogen can be obtained by hydrolysis reaction given below [3].

\[ \text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2 \] (1)

The hydrogen is only gas product in the reaction and therefore pure hydrogen can be obtained after separating the borate, which can be recycled into the sodium borohydride. No additional heat supply is required because the sodium borohydride hydrolysis is an exothermic reaction.

The PEMFC can be a primary candidate for a micro power source if the hydrogen generation device is realized in micro scale. Many researchers have been developed a microreactor using MEMS technologies that is a useful tool to reduce a size of the reformer.

In the present study, the sodium borohydride was used as a hydrogen source. The microreactor for the catalytic hydrolysis reaction was fabricated using MEMS fabrication technologies and the performance evaluation was carried out.

EXPERIMENTAL

Catalyst

The noble metals such as ruthenium (Ru) and platinum (Pt) have a high activity in the sodium borohydride hydrolysis reaction but a high cost [4]. Recently, cobalt (Co) and nickel (Ni) have been studied as an alternative to the noble catalysts [5]. The cobalt was selected as a catalyst for the sodium borohydride hydrolysis reaction and the nickel form was used as a catalyst support in the present study. The nickel form had the porosity of 90% and the average pore diameter of 200 µm. The electroless plating method was used to coat the cobalt catalyst on the surface of the nickel form support. The cobalt chloride and sodium borohydride were used as a cobalt precursor and a reducing agent, respectively.

Fabrication

The microreactor was made of three photosensitive glass layers; one for a bottom layer, one for a reaction chamber and the remaining for a cover with inlet and outlet ports. The fabrication process for an individual glass wafer included as shown in Fig. 1; (1) exposure to the ultraviolet (UV) light under a mask at the intensity of 2 J/cm², (2) heat treatment at 585 °C for 1 hour to crystallize the part of the glass that was exposed to the ultraviolet light, and (3) etching the exposed part in the 10% hydrofluoric (HF) solution to result in the desired shape [6]. With above process, the cover and the reactor layer bonded on the bottom, respectively.

The nickel form was cut as the size of the reaction chamber and washed in the ultrasonic bath with ethanol solution for 5 min. The nickel form was inserted in the reaction chamber made on the glass wafer, following the thermal bonding with the cover. The bonding process involved pressing the layers.
1. UV exposure
2. Heat treatment
3. HF glass etching
4. Bonding
5. Electroless plating

1 kN/m²

Fig. 1: Fabrication process of the microreactor.

Fig. 2: Fabricated result of the microreactor.

The microfuel cell was fabricated to perform the integrated test with the hydrogen generation microreactor. Membrane electrode assembly (MEA) was prepared by coating 0.3 mg/cm² Pt/C on both sides of a Nafion-112 membrane as an anode and a cathode, respectively. Carbon paper was used as a gas diffusion layer. Flow channels were fabricated by etching the photosensitive glass wafer, on which Ag/Ti layer were sputtered as the current collectors [7]. Figure 3 shows the micro fuel cell and the fabricated result.

Performance measurement

The hydrogen generation rate of the microreactor was measured at the various conditions. Experimental setup for the performance measurement is shown in Fig. 4. The sodium borohydride solution was supplied to the microreactor by a syringe pump. The sodium metaborate (NaBO₂), a byproduct of sodium borohydride hydrolysis reaction, was filtered through the condenser and the pure hydrogen flow rate was measured by a flow meter. The temperature of microreactor was recorded during the reaction.

The microreactor was connected with the microfuel cell and the power output was measured. The performance of micro fuel cell was compared with the result of the pure hydrogen test.

Fig. 3: Fabrication of micro polymer electrolyte membrane fuel cell.

Fig. 4: Experimental setup for the performance measurement of microreactor.
RESULTS AND DISCUSSION

Characterization of Co-B/Ni-form catalyst

Figure 5 shows a SEM image of the electroless plated Co-B/Ni-form catalyst for the plating time of 1 min. The cobalt particles were detected on the surface of nickel form by EDS analysis. As the electroless plating was repeated, the amount of catalyst was increased. The final weight fraction of catalyst was 11.65 wt% at 5 time plating processes.

The catalytic hydrolysis reaction of sodium borohydride depends strongly on the temperature. It was reported that the hydrogen generation rate is faster at high temperature and the reaction kinetics is a zero-order reaction. Figure 6 presents the Arrhenius plot of the sodium borohydride hydrolysis reaction on the Co-B/Ni-form catalyst. The activation energy was calculated to be 51.5 kJ/mol from the straight slope of ln r versus 1/T. This is comparable with the activation energy of ruthenium and platinum catalysts.

Hydrogen generation rate

The hydrogen generation rate and the generated hydrogen amount as a function of time are presented in Fig. 7. The peak of hydrogen generation rate occurred at the start of reaction and the hydrogen generation rate was decreased gradually due to the formation of sodium borate on the surface of Co-B/Ni-form catalyst as the reaction time elapsed. The total amount of generated hydrogen was 1,223 ml for 30 min.

Figure 8 shows the effect of temperature on the hydrogen generation rate. The hydrogen generation rate increased with the temperature. At temperature higher than 35 °C, the hydrogen generation rate increased sharply. The hydrogen generation rate at 30 °C was 50 ml/min and this amount of hydrogen can produce 4.5W electric power on a typical PEMFC.
Integrated performance of micro fuel cell

The hydrogen generation rate was approximately 20 ml/min and maintained its value when 30 min elapsed after the initiation of reaction. Figure 9 shows the performance curve of the micro fuel cell at the hydrogen flow rate of 20 ml/min. The maximum power output was 157 mW at the current of 0.5 A.

There is no the performance difference between the integrated test and the pure hydrogen test of micro fuel cell. It means that the microreactor generates the pure hydrogen from the sodium borohydride solution.

CONCLUSION

The catalytic microreactor was fabricated for hydrogen generation from sodium borohydride. The microreactor was made of three photosensitive glasses and the cobalt boride catalyst coated on the nickel form by the electroless plating method was prepared and inserted in the microreactor. The formation of the cobalt catalyst on the surface of nickel form was validated by SEM image and EDS analysis. The activation energy was calculated to be 51.5 kJ/mol from the Arrhenius plot for the sodium borohydride hydrolysis reaction on the catalyst.

The hydrogen generation rate of the microreactor was measured in 50 ml/min that is the sufficient amount to operate 4.5 W PEMFC. The micro fuel cell was fabricated and operated with the hydrogen generated by the micro-reactor. The maximum power output was 157 mW at the current of 0.5 A that is comparable with the performance of micro fuel cell with pure hydrogen. The next challenges are the fully integrated fabrication and test of the microreactor, micro fuel cell, micro pump and fuel storage chamber.

REFERENCES


