MICRO PDMS HYDROGEN GENERATOR USING HYDROLYSIS OF SODIUM BOROHYDRIDE OVER COBALT NICKEL-FOAM CATALYST AND IMMOBILIZED COBALT-PH3PO/PDMS/SIO2 CATALYST

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Abstract: Development and performance evaluation of micro PDMS hydrogen generator using hydrolysis of sodium borohydride were carried out. Important points of hydrolysis of sodium borohydride are choosing catalyst and reactor material. The synthesis processes of cobalt nickel foam catalyst and immobilized cobalt-$Ph_3PO/PDMS/SiO_2$ catalyst were established. Micro PDMS hydrogen generator was fabricated using Teflon fitting process and borate was less shown in reactor because of characteristics of PDMS. We can possible to load PDMS hydrogen generator with low fabrication cost and high performance in fuel cell system.

Keywords: PDMS, Sodium borohydride, Hydrolysis, Cobalt catalyst

INTRODUCTION

Many researchers studied Proton exchange membrane fuel cell (PEMFC) 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.

Sodium borohydride is one of chemical hydrides and an inorganic compound with formula $NaBH_4$. [3] It has characteristics of good solubility at water, good stability at solution state and inflammability. Especially sodium borohydride is good choice for fuel due to high density when stored at liquid solution state compared to other solution. When hydrolysis of sodium borohydride occurred, the content of hydrogen is 10.6%. In addition, it is easy to control the hydrogen generation by catalytic hydrolysis in terms of system management. Hydrogen is the only gas product from hydrolysis. Through the separation of filter pure hydrogen is obtained and there are no carbon products which induce the poison effect on PEMFC.

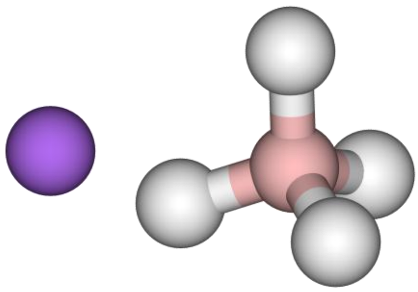

Fig. 1: Modeling of sodium borohydride

METHODOLOGY

Hydrolysis of NaBH4

The mechanism of hydrolysis of sodium borohydride is like below chemical reaction.

$$NaBH_4(l) + 2H_2O(l) \rightarrow NaBO_2(l) + 4H_2(g) + 217KJ/kmol$$

There is no heat supply needed because the sodium borohydride hydrolysis is an exothermic reaction. Sodium borohydride alkaline solution has high reactivity over usually ruthenium, platinum, cobalt catalyst. The noble metal such as ruthenium has a high activity in hydrolysis but high cost. So recently cobalt has been studied as an alternative to the noble catalyst. In this research, we choose two ways of cobalt catalyst production.

Co-P/Ni foam catalyst

First way of catalyst production is electroless plating. Cobalt/Alumina catalyst has good catalytic activity but the durability of support is weak. Stronger support like metal is needed. To load cobalt material on metal, coating method is needed. Electro plating has characteristics like good adhesion and non-uniform coating. But electroless plating has several advantages like no electricity, uniform coating, non-conductive material but very sensitive process. So we choose the coating method as electroless plating. [4]

Co-$Ph_3PO/PDMS/SiO_2$ catalyst

The other way of catalyst production is immobilized Co-$Ph_3PO/PDMS/SiO_2$ catalyst. Co-Ph_3PO complex immobilized on polydimethylsiloxane (PDMS) functionalized SiO_2 was prepared by sol-gel method. Immobilization of inorganic materials, such as silica, has advantages due to the physical strength and chemical inertness. The entrapment of catalysts inside the porous system of silica matrices prepared by the sol–gel method appears to be a promising strategy for catalyst recovery [5]. Several groups have studied such hybrid inorganic-organic matrices and polysiloxane-bound transition metal complexes were extensively studied.

Material selection

Polydimethylsiloxane is chosen as hydrogen generator material. PDMS is considered to be inert, non-toxic and non-flammable. Fully cured PDMS is very flexible and durable. The low gas permeability of the gases produced in the reaction through PDMS material also makes this material attractive.

CATALYST PRODUCTION

Manufacture of Co-P/Ni foam catalyst

Co-P/Ni foam catalyst was manufactured based on previous researches [1-2], and pretreatment of nickel foam was performed before electroless plating. Nickel foam of 40 pores per inch (PPI) was used for manufacture of Co-P/Ni foam catalyst. First of all, nickel foam was washed with detergent to remove impurities, and ultrasonic cleaning (JAC-1505, Kodo Technical Research, Korea) was performed in ethanol solution (C_2H_5OH, OCI, Korea) during 5 min. Nickel foam was etched in hydrochloric acid (HCl, OCI, Korea) solution of 10 vol% for 1 min after cleaning. Tin chloride ($SnCl_2$•$2H_2O$, Samchun Chemical, Korea) was used for sensitization and sensitization was carried out with $SnCl_2$ (1 g/L) + HCl (1 ml/L) solution for 3 min. Palladium chloride ($PdCl_2$, Kojima Chemcal, Japan) was used for activation, and activation was carried out with $PdCl_2$ (0.1 g/L) + HCl (1 ml/L) solution for 2 min. Sodium hydroxide (NaOH, Junsei Chemical, Japan) solution of 1 m was used for acceleration and acceleration was carried out for 1 min after sensitization and activation. Nickel foam was finally washed with distilled water (H_2O, OCI, Korea) and dried at atmosphere.

Co-P/Ni foam catalyst was manufactured by electroless plating after pretreatment of nickel foam. Coating bath was made of cobalt chloride ($CoCl_2$•$6H_2O$, Junsei Chemical, Japan), sodium phosphinate (NaH_2PO_2•H2O, Junsei Chemical, Japan), glycine (NH_2CH_2COOH, Samchun Chemical, Korea). Composition of coating bath was 0.1 m ($CoCl_2$), 0.4 m (NH_2CH_2COOH), 1.0 m (NaH_2PO2) based on previous study. After coating bath was made, pH of coating bath was adjusted to 12.0 with NaOH. Because pH of solution is affected by temperature, pH was adjusted and measured at 22 ℃. A thermostat (RBC-10, JEIO TECH, Korea) was used to maintain temperature of coating bath. The pH meter (77P, iSTEK, Korea) was used to measure pH of coating bath, and pH meter was calibrated by pH buffer solution (pH 4, 7, 10, Samchun Chemical, Korea) before experiment. Electroless plating was performed for 30 min at 50 ℃ after adjustment of the pH of coating bath. Coating bath was agitated with a magnetic stir at 100 rpm during electroless plating. A hot plate (RET control-visc C, IKA, Germany) was used for heating and agitation. Co-P/Ni foam catalyst was washed with distilled water to remove impurities and dried at atmosphere after electroless plating.

Weight measurement was carried out before and after electroless plating, and weight percent of deposited catalyst was calculated by Eq. (1). In Eq. (1), m_catalyst and m_nickel foam are weight of Co-P/Ni foam catalyst, and weight of nickel foam respectively.

$$\text{Weight percent of deposited catalyst (wt\%)} = \frac{m_{catalyst} - m_{nickel\ foam}}{m_{nickel\ foam}} \times 100 \qquad (1)$$

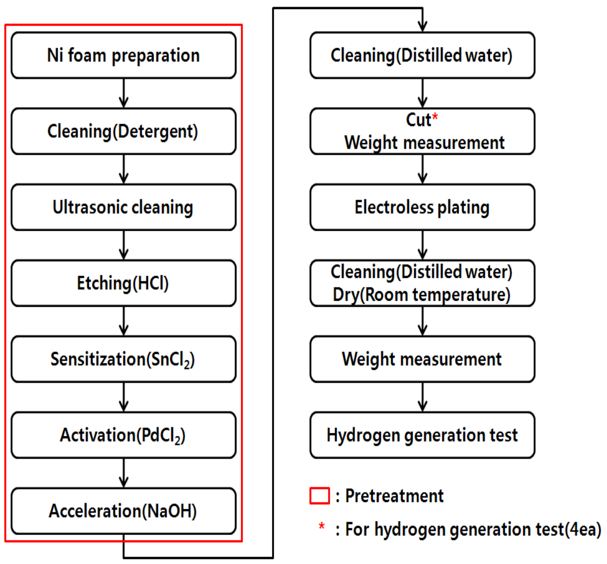

Fig. 2: Procedure of electroless plating cobalt Ni-foam catalyst manufacture

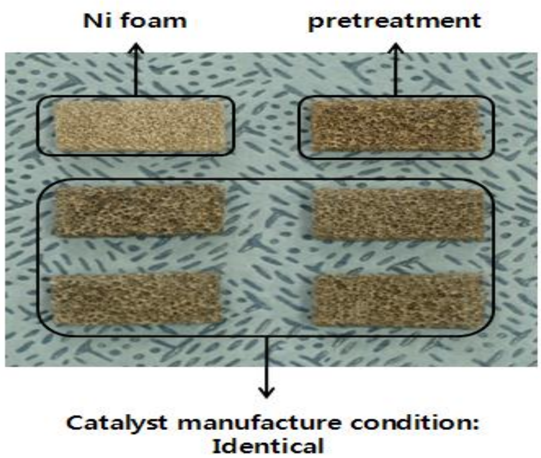

Fig. 3: Picture of electroless plating cobalt Ni-foam catalyst

Manufacture of Co-Ph_3PO/PDMS/SiO_2 catalyst

The preparation of immobilized catalysts refers to the procedures described in literature [11]. A typical procedure: 1 mmol $[Co(CH_3COO)_2)]\cdot 4H_2O$ and 2 mmol of the triphenyl phosphine oxide were dissolved in 6 ml of tetrahydrofuran $(CH_2)_4O$ in a 50 ml Schlenk flask. After 15 min stirring, 2.0 ml (11.10 mmol) of deionized water, 2.0 ml(13.56 mmol) of TEOS (tetraethylorthosilicate), 1.0 ml(24.69 mmol) of methanol and 1 ml polydimethylsiloxane were added to the blue solution. The resulting solution was stirred for 15 min and then allowed to stand for at least overnight until gelation. The gel was washed with CH_2Cl_2 three times and dried at 353 K. The resulting materials were stored under air at room temperature.

Fig. 4: Picture of pretreatment of Co-Ph_3PO/PDMS/ SiO_2 catalyst

Design of reactor

The shapes of micro hydrogen generator using MEMS technology are usually flat because of high bonding surface and space. In this research the hydrogen generator made of six PDMS wafers. PDMS selected as the structural material had such properties as hardness for sustaining the product gas and resistance to strong acid. To feed the sodium borohydride fuel, the Teflon fitting was used. The dimension of each wafer was 30mm X 30 mm with 1 mm thickness and reaction zone is 10mm X 10mm X 2 mm.'

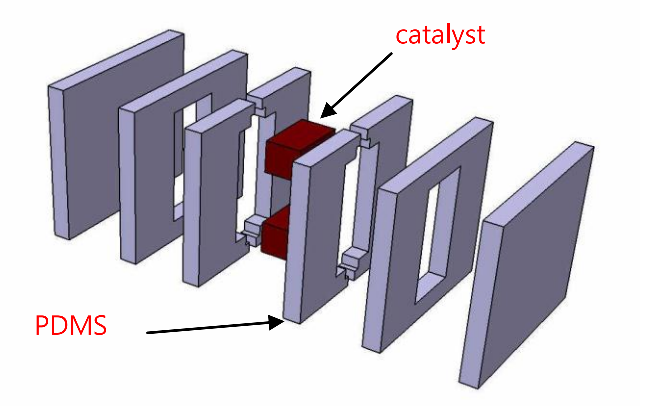

Fig. 5: Construction of micro PDMS hydrogen generator

RESULTS

Fabrication of hydrogen generator

PDMS is not toxic but should be be taken not to expose the vapors outside of the fume hood. The PDMS oven is typically at a temperature of 60℃ and care should be taken to avoid burns. Operating procedure is for casting PDMS into microfabricated molds. PDMS is used to replicate features from wafer molds which are commonly fabricated from photosensitive glass. Usually PDMS mold has high aspect ratio like SU-8. Photosensitive glass has highly aspect ratio for MEMS application. In this research, photosensitive glass is chosen by PDMS mold.

Fabrication of reactor has five steps: mixing, degassing, pouring, baking, cleaning and bonding process.

(1) Mixing: Curing agent such that the ratio of elastomer base to curing agent is 10:1 by weight. The mixing generates a lot of bubbles and a homogeneous distribution of bubbles is an indicator of good mixing. Poor mixing may lead to clumps in the PDMS texture while curing. (2) Degassing: During the mixing step, gas is captured in PDMS. So in degassing step, the bubble in the PDMS should be removed in vacuum chamber with valve. (3) Pouring: Pour PDMS from the beaker to achieve the required thickness. (4) Baking: Poured PDMS baked during 2hrs at 60 ℃ in oven. (5) Cleaning: Cleaning is often the most important step for smooth PDMS handling to remove spills and discard them. (6) Bonding: Before the bonding process, the catalyst is inserted in PDMS which is cleaned. The PDMS is bonded by PDMS or handling plasma.

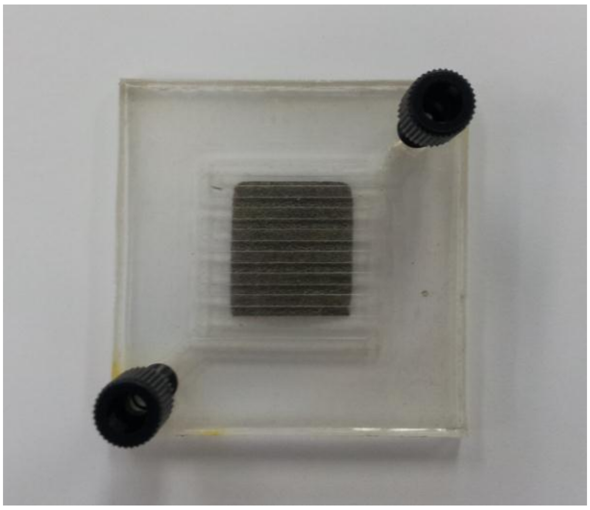

Fig. 6: Fabricated micro PDMS hydrogen generator with Teflon fitting

Experiment setup

Performance evaluation of micro PDMS hydrogen generator is measured by mass flow meter and data acquisition board. Moisture of generated hydrogen gas was removed by silica gel (SiO_2, Junsei Chemical, Japan) in another conical flask. Volume flow rate of dehydrated hydrogen gas was measured by volume flow meter (FVL-1606A, Omega Engineering, USA), and data of hydrogen generation rate was stored on personal computer by personal data acquisition board (Personal Daq/54, IOtech, USA).

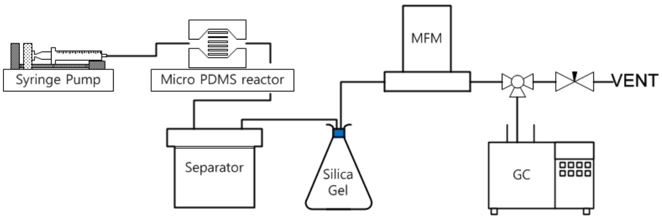

Fig. 7: Schematics of micro PDMS hydrogen generator flow test experiment

Experiment results

Hydrogen generation tests of Co-P/Ni foam catalysts and Co-Ph_3PO/PDMS/SiO_2 were performed to investigate effect of bath composition on catalytic activity of Co-P/Ni foam catalyst. 5 wt% NaOH and 15 wt% sodium borohydride were dissolved in 80 wt% distilled water to make sodium borohydride solution for hydrogen generation test. Flow rate of sodium borohydride fuel is 0.12cc/min by syringe pump.

The results of hydrogen generation of each catalyst are below the table 1.

Table 1: Hydrogen generation table

Catalyst	Fuel flow rate(cc/min)	H2 production (cc/min)
Cobalt Nickel foam	0.12	63.64
Cobalt Ph_3PO/PDMS/SiO_2		52.12

Hydrogen generation of cobalt nickel foam catalyst is higher than cobalt-Ph_3PO/PDMS/SiO_2 catalyst. The catalyst of cobalt nickel foam has high porosity than cobalt-Ph_3PO/PDMS/SiO_2 catalyst. Usually after the reaction of hydrolysis of sodium borohydride, the borate was deposited in catalyst. But PDMS has characteristics of hydrophilic, so the borate was less shown at PDMS hydrogen generator.

CONCLUSION

In this research, the hydrolysis reaction of sodium borohydride was studied. The catalyst of hydrolysis was manufactured. We established the process of cobalt nickel foam catalyst and cobalt Ph_3PO/PDMS/SiO_2 catalyst.

For MEMS process, PDMS has many advantages which are easy to get, handling and chemical stability. So PDMS hydrogen generator is fabricated by Microfabricated photosensitive glass mold.

The results of hydrogen generation were 63.64 cc/min at cobalt nickel foam catalyst and 52.12 cc/min at cobalt Ph_3PO/PDMS/SiO_2 catalyst. Because of the material characteristics of hydrophilic, the reactor has good performance of borate problem. And this hydrogen generator is suitable for micro fuel cell because of simplicity, low fabrication cost, high performance.

ACKNOWLEDGE

This work was supported by the Korea Science and Engineering Foundation(KOSEF) grant funded by the Korea government(MEST) through NRL (No. R0A-2007-000-20065-0)

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