

FABRICATION AND EVALUATION OF A NaBH_4 HYDROGEN MICROREACTOR ASSEMBLED BY TRIPLE STACK GLASS BONDING

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Abstract: This work is a part of a joint research project aiming at the development of an integrated micro power supply system comprising a PEM micro fuel cell, a microreactor for the generation of hydrogen, a micropump, microvalves, a fuel/waste tank, as well as a power processing circuit. A microsystem-technology-based, batch process compatible fabrication concept for a catalytic microreactor generating hydrogen from a base-stabilized solution of aqueous sodium borohydride (NaBH_4) was investigated. The major aim of this attempt is increasing the energy density of the system by a smaller package. The reactor is designed for continuous operation by pumping the fuel solution through a channel containing a ruthenium-based catalyst. Hydrogen is separated from the fuel solution directly at the reaction site via a porous PTFE (polytetrafluoroethylene) membrane. Since the fuel solution is stabilized by sodium hydroxide (NaOH , pH 14), all materials and interconnections are designed to be stable under harsh alkaline conditions. The microreactor with a size of $20 \times 20 \times 1.7 \text{ mm}^3$ was successfully fabricated and delivered a constant H_2 rate of 3.5 sccm when supplied with a solution of 10 wt% NaBH_4 and 5 wt% NaOH in water at a pump rate of 20 $\mu\text{l}/\text{min}$.

Keywords: hydrogen generation, sodium borohydride, harsh environment, Cytop bonding, fuel cell, microreactor

INTRODUCTION

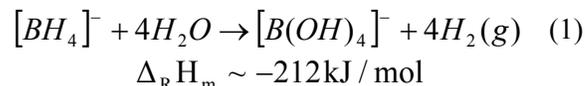
The goal of micro fuel cell development is achieving a higher energy density compared to batteries, resulting in longer runtimes for portable electronics or microsystems. Most activities focus on direct methanol fuel cells (DMFC) because of their high energy density and the ease of handling small amounts of fuel. Nevertheless, there are still several issues concerning DMFCs, e.g. low power density. Planar self-breathing PEM hydrogen fuel cells are delivering a high power density and system reliability sufficient for many electronics and microsystem applications. However, hydrogen fuel cells suffer from difficulties in storing small amounts of hydrogen. Especially for portable small fuel cells, compressed gas or liquid hydrogen cannot be practically used.

Alternatively, hydrogen-containing chemical compounds, such as chemical hydrides, have recently started to attract more attention as hydrogen storage materials. The storage of hydrogen in chemical hydrides has the potential of a high gravimetric and volumetric storage density at room temperature and atmospheric pressure. Also, in contrast to reforming processes, hydrogen is released at room temperature. This means that neither a heavy tank nor high temperatures or thermal insulation are needed. Thus, this study focuses on on-demand hydrogen generation in a microsystem using sodium borohydride (NaBH_4).

References [1-3] are introducing different reactors for the hydrolysis of NaBH_4 . However, except for [3], discussing a silicon-based passive device for the generation of relatively small hydrogen rates, there seems to be no publication introducing a concept for an on-demand hydrogen generation microreactor by microsystem fabrication technology. To provide a high-energy-density on-demand power source using NaBH_4 and a fuel cell, small packaging is important, though.

THEORY

Hydrogen is released from NaBH_4 by catalytic hydrolysis in the following reaction (1).



1 mole of NaBH_4 reacts with 4 moles of water to form 4 moles of hydrogen gas, whereat half of this hydrogen comes from the water. The molar reaction enthalpy of (1) accounts for -212 kJ/mol by calculation based on [4]. I.e., the reaction is exothermic and thus no energy input is required to generate hydrogen. The hydrolysis of NaBH_4 occurs to some extent even without the presence of catalyst (self hydrolysis). Without a catalyst, reaction (1) is strongly pH-dependant, its speed increasing with decreasing pH values. Therefore, stable fuel solutions are obtained by the addition of sodium hydroxide

(NaOH) to the aqueous borohydride solution. Sodium borohydride fuel solutions usually consist of about 10 to 30 wt% of NaBH₄ and 4 to 10 wt% of NaOH dissolved in water. According to the work of Kreevoy and Jacobson [5], a base-stabilized, aqueous NaBH₄ solution has a shelf half-life of about two years at room temperature and a pH of 14 (4 wt% of NaOH).

FABRICATION

Design of the device

The microreactor is a stacked structure of 4 layers as shown in Fig. 1: (4) bottom layer with temperature sensors, (3) layer with the fluid channel / catalyst, (2) nanoporous PTFE gas-liquid-separation membrane, and (1) lid with H₂ collection structure serving as an interface to the fuel/waste tank and the fuel cell.

Layer (2) provides gas separation and prevents the caustic NaBH₄ solution from entering the fuel cell. The catalyst-filled fluid channel of layer (3) is realized in form of a meander connecting the openings for the in- and outlet. Layers (1), (3), and (4) are made of borosilicate glass, but it can be replaced by any ceramic without changing the fabrication process described below.

Structuring of the glass substrates

Figure 2 shows the fabrication process of glass substrates of the device. *Substrate (1)* was fabricated from a 500 μm thick borosilicate glass wafer. First, three non-penetrating holes on the topside of the substrate were produced at the position of fuel inlet, fuel outlet and hydrogen outlet. Then a 200 μm deep H₂ collection structure was formed on the downside of the substrate by sandblasting. This gas collection structure was realized in form of a 300 μm thick bar structure following the outer shape of the fluid channel of substrate (3) to keep the PTFE membrane in place by pressure and sealing it during and after bonding. The opening of holes for fuel in- and outlet and hydrogen outlet was achieved during the same step (steps 1-6 of Fig. 2).

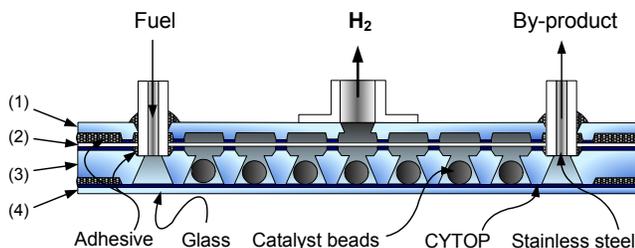


Fig. 1: Cross sectional view of the microreactor (diagonal cross section)

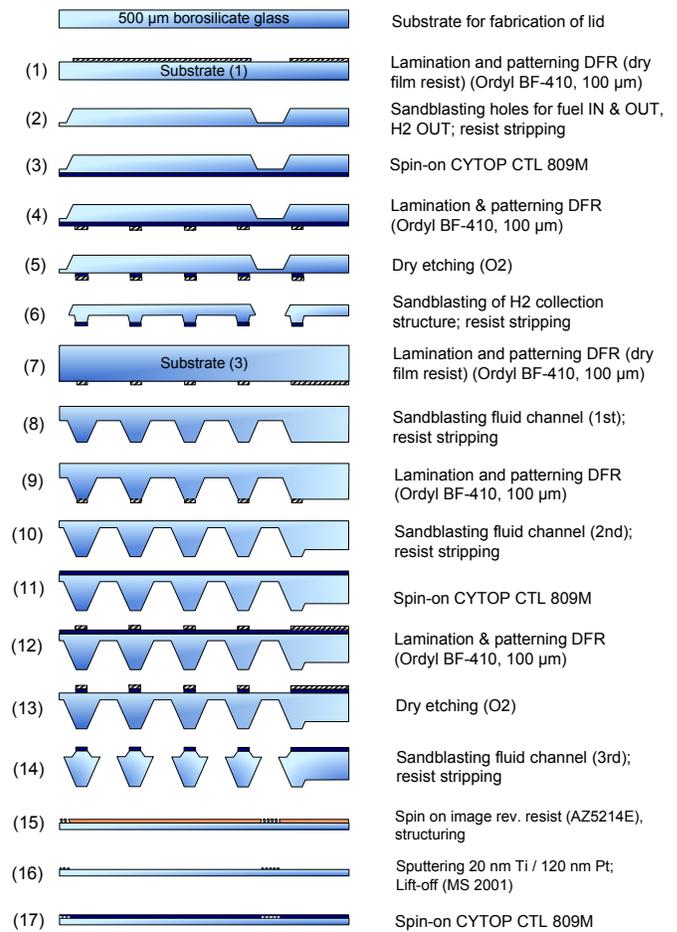


Fig. 2: Process steps for the fabrication of all glass substrates (diagonal cross section middle to edge)

Substrate (3) was fabricated from a 1 mm borosilicate glass wafer and consists of the penetrating fluid channel structure, which also provides space for the catalyst and stoppers to prevent the catalyst beads from being pushed out of the channel or against the PTFE membrane. Because the diameter of the catalyst beads is 540 μm in average, substrate (3) must be thick and thus structured by a high-speed fabrication method, i.e. sandblasting (steps 7-14 of Fig. 2). To prepare substrate (4), a 150 nm thick Ti/Pt layer was deposited on a 200 μm borosilicate glass wafer by sputtering and patterned by a lift-off process. Hereby, 3 temperature sensors located at the inlet, mid and outlet of the fluid channel were fabricated on the topside of the substrate (steps 15-17 of fig. 2).

Bonding

After preparation of all single substrates, the device was assembled by two proceeding bonding steps. *In the first bonding step*, substrates (4) and (2) were bonded to each other, hereby integrating the PTFE gas liquid separation membrane. Given the creep behavior of PTFE and its maximum operation

temperature of 260 °C, this bonding step must be conducted at a low temperature. Because of its low bonding temperature (glass transition temperature $T_g=108$ °C) and chemical inertness, we chose CYTOP (Cyclic Transparent Optic Polymer, Asahi Glass), a cyclized perfluoro polymer based on perfluoro butyl vinyl ether components, as the bonding material. CYTOP is provided at different viscosities and thus can be applied by spin-coating, spray-coating and dip-coating. To obtain a uniform and sufficient layer thickness, we chose spin-coating. Since the deep structures of substrates (1) and (3) make spin-coating difficult, CYTOP CTL 809M was spun on substrates (1) and (3) twice at 1500 rpm for 30 s prior to sandblasting the interconnection-faced surfaces of these substrates. To remove the solvent, the coating was cured for 90 min at 180 °C. This treatment resulted in a CYTOP layer thickness of about 2 μm . For the following sandblasting steps, tape resist must be coated on CYTOP. Sufficient adhesion between dry film resist (Ordyl BF-410, Tokyo Ohka Kogyo) and the low surface energy polymer CYTOP was achieved after activation by O_2 plasma (10 s, 130 W).

Before bonding substrate (1) to substrate (3), the 60 μm thick porous PTFE membrane (FP-010-60, Sumitomo Denko) was attached to the CYTOP-coated side of substrate (3) and fixed by heating for 5 min at 160 °C. Chemically similar to PTFE, CYTOP enters the pores of the PTFE membrane easily at a temperature above its glass transition point of 108 °C, resulting in a relative strong interconnection of the materials after cooling down. The same effect was utilized when bonding substrate (3) with the PTFE membrane to substrate (4), resulting in a glass-CYTOP-PTFE-CYTOP-glass interface. The bonding process was conducted under vacuum (< 1 Pa) by applying a temperature of 160 °C and a pressure of 4 MPa for 30 min. After bonding we observed a colour change of the porous PTFE membrane from white to transparent, indicating that its pores are sealed (Fig. 3a). The bonding strength was measured by tensile strength testing. When applying a pressure beyond 1.15 MPa, the assembly was separated between PTFE membrane and substrate (1).

During the second bonding step, the fluidic channel was closed by joining substrate (4) to the already assembled part of the device with the through-patterned fluidic channel. This bonding step was undertaken in order to provide a good transparency, i.e. visibility of the catalysis process, as well as a minimum distance between temperature sensors and reaction site. Because of its chemical inertness, capability of height compensation, and transparency, again CYTOP was chosen as the intermediate

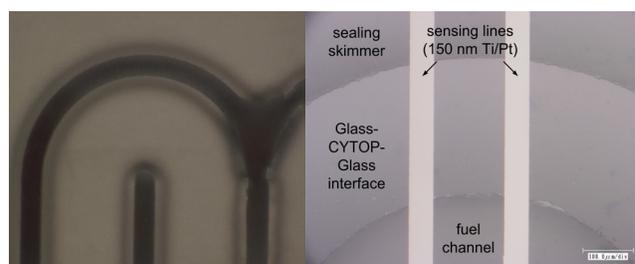


Fig. 3: a Bond interface between (1) and (3); b: Bond interface between (3) and (4)

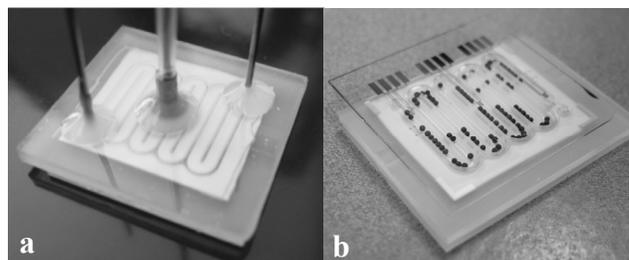


Fig. 4: Fabricated microreactor (a topside, b downside)

bonding material and applied by spin-coating similar as for substrates (1) and (3). To enable electrical contacting, the cured CYTOP layer was removed from the contact pads of the temperature sensors by dry O_2 etching. After filling the channel with catalyst, the second bonding was performed at a pressure of 4 MPa at 160 °C for 30 min. Figure 3b shows the interface between substrates (3) and (4) at the location of two sensing lines. It can be seen that the height difference due to the 150 nm thick metal lines is compensated by the CYTOP layer. The bonding strength of the interface was measured to be stronger than 4 MPa.

Glass-CYTOP-glass as well as glass-CYTOP-PTFE-CYTOP-glass interface were found to be liquid tight. To improve the gas tightness of both interfaces, the spacers between substrate (1) and (2) as well as (2) and (4) were additionally filled with a sealant after assembly of the device. The fabricated microreactor has an overall volume of 0.68 cm^3 that can be further decreased to 0.4 cm^3 . Its channel length of 96 mm is sufficient to store approximately 160 catalyst beads.

MEASUREMENT AND EVALUATION

A fuel solution of 10 wt% NaBH_4 and 5 wt% NaOH dissolved in water was supplied to the microreactor by a high precision syringe pump (neMESYS, Cetoni GmbH). Hereby, a measurement of the hydrogen rate decoupled of potential influences by an unsteady fuel pump rate due to back pressure sensibility of the pump was achieved. The product solution leaving the device was collected in a product solution container. The hydrogen being separated

from the fuel solution via the gas-liquid separation membrane was measured using a flow meter (Flow Tracker 1000, Agilent).

Table 1: Reactor performance for diff. catalyst loads

m_{cat} [% of max]	T_{max} [°C]	r_{max} [sccm]	r_{avg} [sccm]	H_2 yield [%]
32	30.5	4.9	3.5	74
51	31.0	6.3	3.4	72
90	37.0	8.9	4.77	100

Hydrogen rate was measured for three reactors with different catalyst loadings supplied with fuel solution at a pump rate of 20 $\mu\text{l}/\text{min}$. Given this pump rate, at complete chemical conversion of the fuel, a maximum constant hydrogen rate of 4.75 sccm would be expected. The data actually obtained is outlined in Table 2. r_{avg} indicates the average hydrogen rate over a time of 15 min after startup. r_{max} and T_{max} are the maximum measured hydrogen rate and reactor temperature, respectively.

As shown in Fig. 5, the startup time for the reactor (i.e. the time needed for establishment of a steady state of rate and temperature) accounts for about 10 min. For a catalyst load of 32 % (graph QS04), we observed a uniform hydrogen rate over time. In contrast to that, two kinds of rate fluctuations were observed for higher catalyst loads (QS07, QS08). Fluctuations within the frame of seconds were caused by the temporary formation of bubbles inside the fuel channel and therefore temporary dewetting of the catalyst. Rate fluctuations within several minutes are considered to be due to the complete consumption of the fuel inside of the catalyst channel, i.e. higher pump rates are necessary to avoid these fluctuations. With a catalyst content of 32 % as well as 51 % about the same hydrogen yield was obtained (Tab. 1).

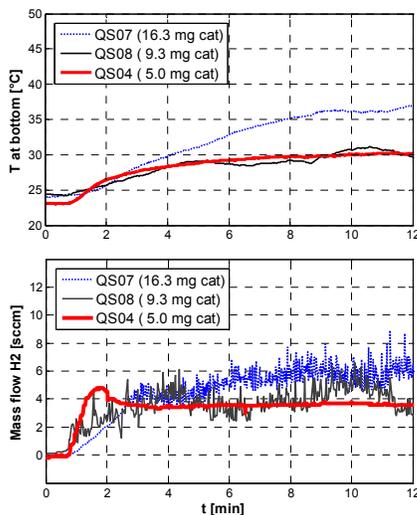


Fig. 5: Hydrogen rate for different catalyst loadings

This is probably due to distribution differences of the catalyst beads that were able to move within the channel to some extent, especially at lower catalyst loads. This result shows that distribution and fixation of the catalyst within the channel is of importance.

CONCLUSION

Previously we introduced a concept for the fabrication of a NaBH_4 hydrogen microreactor [6]. That concept included the formation of a cavity for the integration of a porous, 60 μm thick PTFE gas-liquid separation membrane, resulting in the need for a difficult height compensation step and a limited applicability of the process for batch fabrication. In this study, a process for the integration of the membrane enabling fabrication of the device completely by batch processing was successfully applied and tested. When supplied with 10 wt% NaBH_4 fuel solution at a rate of 10 $\mu\text{l}/\text{min}$, a constant hydrogen rate of 3.5 sccm sufficient to supply a 350 mW class fuel cell was generated by the microreactor with a catalyst load of 32 %. Testing at higher pump rates and other fuel concentrations as well as investigating catalyst distribution effects will be subject of further study.

ACKNOWLEDGEMENT

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