

## NABH<sub>4</sub> HYDROGEN MICROREACTOR FABRICATED BY MICROSYSTEM TECHNOLOGY

**K. Hoeppe**<sup>1,2</sup>, **R. Hahn**<sup>3</sup>, **H. Reichl**<sup>1,3</sup>, **M. Esashi**<sup>2</sup>, **S. Tanaka**<sup>2</sup>

<sup>1</sup>Berlin Center of Advanced Packaging, Berlin University of Technology, Berlin, Germany

<sup>2</sup>Department of Nanomechanics, Tohoku University, Sendai, Japan

<sup>3</sup>Fraunhofer Institute for Reliability and Microintegration (IZM), Berlin, Germany

**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 fabrication concept for a catalytic microreactor generating hydrogen from a base-stabilized solution of aqueous sodium borohydride (NaBH<sub>4</sub>) 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 the catalyst. Hydrogen is separated from the fuel solution directly at the reaction site via a porous PTFE (polytetrafluoroethylene) membrane, allowing for less restrictive back pressure requirements for the fuel pump. 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.

**Key words:** hydrogen generation, sodium borohydride, fuel cell, microreactor, Cytop bonding

### 1. 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. Their system reliability is sufficient for many electronics and microsystem applications. But hydrogen fuel cells suffer from difficulties in storing small amounts of hydrogen. Especially for the supply of portable small fuel cells, compressed gas or liquid hydrogen cannot be practically used.

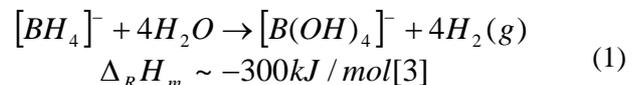
Alternatively, hydrogen-containing chemical compounds, such as chemical hydrides, have recently started to attract more attention as hydrogen storage materials. The storage of hydrogen in chemical hydrides has the potential of a high gravimetric and volumetric storage density at room temperature and 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 the on-demand hydrogen generation in a microsystem using sodium borohydride (NaBH<sub>4</sub>).

There has already been work done on reactors for the hydrolysis of NaBH<sub>4</sub> [1-3]. However, currently there seems to be no publication introducing a continuous flow microreactor based on microsystem fabrication technology. To provide a high-energy-density power source using NaBH<sub>4</sub> and a fuel cell, the down-sizing of each system component and packaging are important, though.

### 2. FUEL AND HYDROGEN RELEASE

#### 2.1 Fuel Solution

Hydrogen is released by catalytic hydrolysis from NaBH<sub>4</sub> as shown in the following reaction (1):



1 mole of NaBH<sub>4</sub> reacts with four moles of water to form 4 moles of hydrogen gas, whereat half of this hydrogen comes from the water. Reaction (1) is exothermic; therefore no energy input is required to generate hydrogen. At a fuel cell efficiency of 60 %, 500 ml H<sub>2</sub> from a NaBH<sub>4</sub> solution volume of 1 ml would result in an energy density of 900 Wh/l; more than double the energy density of state of the art Li ion batteries. Of course, especially in small systems, a high total energy density can only be achieved, if a hydrogen generator and a fuel cell are sufficiently small.

The hydrolysis of  $\text{NaBH}_4$  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  $\text{NaBH}_4$  and 4 to 10 wt% of NaOH dissolved in water. According to the work of Kreevoy and Jacobson [4], a base-stabilized, aqueous  $\text{NaBH}_4$  solution has a shelf half-life of about two years at room temperature and a pH of 14 (i.e. 4 wt% of NaOH).

### 2.2 Catalyst

There are several materials known to catalyse the hydrolysis of  $\text{NaBH}_4$ , e.g. cobalt, nickel and ruthenium. Within previous work [5], Ru was deposited on several different support materials and the obtained catalysts investigated with respect to chemical resistance under caustic conditions and hydrogen generation rate. The investigated materials include ceramics, carbon, ion exchange resin membranes and spherical beads of ion exchange resin. The choice of the support material showed a remarkable influence on the reaction rate. The best result was obtained with Ru supported by the ion exchange resin beads (Room&Haas), which are, having an average diameter of 540  $\mu\text{m}$ , relatively large. We obtained a specific hydrogen generation rate of up to 10 sccm per milligram of Ru. This is higher than the specific rates quoted in previous reports, where up to 6 scc  $\text{H}_2$  per minute and milligram Ru were achieved [3]. We therefore chose this material as the catalyst for our reactor.

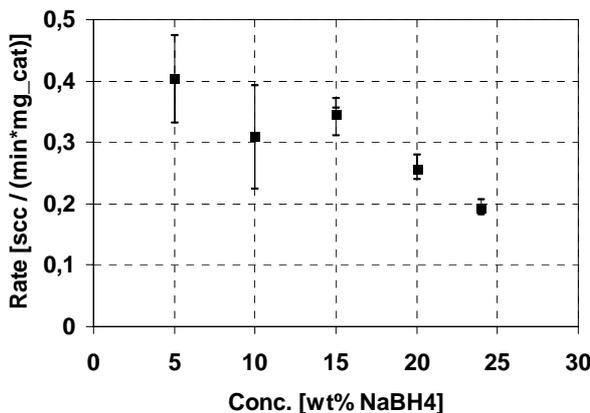


Fig. 1: Performance of the developed catalyst

The resin material was washed, dried, and soaked with a 2 wt% aqueous  $\text{RuCl}_3$  solution for 24 hours. The aqueous  $\text{RuCl}_3$  solution was acidified with HCl to

support the formation of negatively charged Ru-Cl-complexes. After that, the Ru-loaded resin beads were separated from the remaining  $\text{RuCl}_3$  solution by filtering and dried at room temperature, followed by reduction in a 5 wt% solution of  $\text{NaBH}_4$ . Figure 1 shows the hydrogen generation rate of the developed catalyst at 4 different fuel concentrations [5]. For each concentration 3 measurements were done and the 3 obtained values as well as their mean plotted against  $\text{NaBH}_4$  concentration.

## 3. DESIGN AND FABRICATION

### 3.1 Structure

The microreactor is a stacked structure of 4 layers as shown in Figure 2: (1) bottom layer with temperature sensor, (2) layer with the fluid channel, (3) nanoporous PTFE gas-liquid-separation membrane, and (4) lid with  $\text{H}_2$  collection structure serving as an interface to the fuel/waste tank and the fuel cell. Layer (3) provides gas separation and prevents the caustic  $\text{NaBH}_4$  solution from entering the fuel cell. Layers (1), (2), and (4) are made from borosilicate glass. The catalyst-filled channel is realized in form of a meander connecting the openings for the in- and outlet.

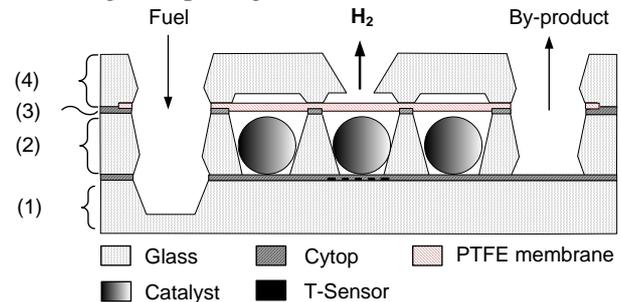


Fig. 2: Cross sectional view of the microreactor

### 3.2 Fabrication process

Figure 3 shows the fabrication process of the  $\text{NaBH}_4$  microreactor made of glass. First, substrates (2) and (4) are spin coated with Cytop and afterwards structured by sandblasting (steps 1-12). Substrate (2) is fabricated from a 600  $\mu\text{m}$  borosilicate glass wafer and consists of the penetrating fluid channel structure, which also provides space for the catalyst, as well as a stopper to prevent the catalyst beads from being pushed out of the channel. Because the diameter of the catalyst beads is 540  $\mu\text{m}$  in average, substrate (2) must at least be as thick as 600  $\mu\text{m}$ , and thus structured by a high-speed batch fabrication method, i.e. sandblasting. The gas collection structure of layer (4) is 200  $\mu\text{m}$  deep. The same meandering layout as for the fluidic channel has been used. Hereby the PTFE membrane is kept in place by pressure.

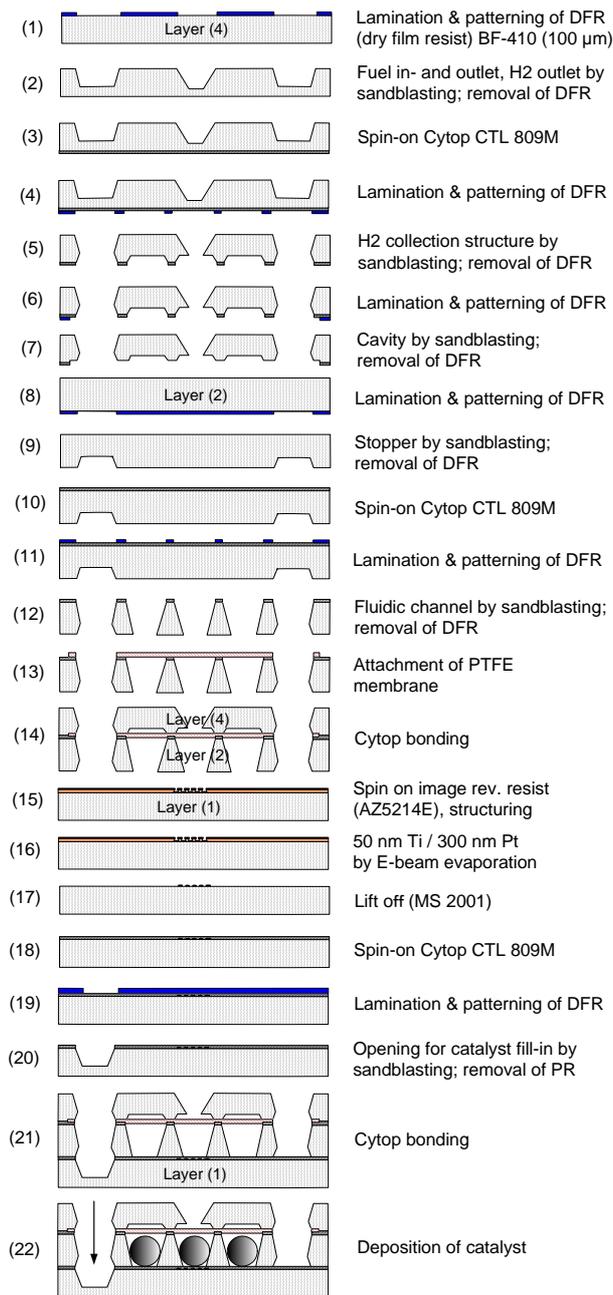


Fig. 3: Process steps for the fabrication of the microreactor made of glass

Since PTFE has a maximum operation temperature of 260 °C, substrate (4) must be bonded to substrate (2) at a low temperature. Providing a low bonding temperature and chemical inertness we chose Cytop as the intermediate bonding material. Cytop (Cyclic Transparent Optic Polymer) is a cyclized perfluoro polymer (CPFP), which is commercially available (Asahi Glass). The material is provided at different viscosities and thus can be applied by spin-coating, spray-coating and dip-coating. It shows good adhesion on glass. To obtain a uniform and sufficient layer thickness, we chose to spin coat the polymer. The deep structures of substrates (2) and (4) make spin coating

impossible after structuring by sandblasting. Cytop CTL 809M was thus spun on substrates (2) and (4) at 1500 rpm for 30 s prior to sandblasting the interconnection-faced surfaces of these substrates (steps 3, 10). To remove the solvent, the coating was cured for 30 min at 90 °C. This treatment resulted in a Cytop layer thickness of about 1 μm. For the following sandblast steps tape resist must be coated on Cytop. PTFE (Cytop) is well known for its non-adhesive property. However, after activation by O<sub>2</sub> plasma (10 s, 130 W), the tape resist used (BF-410, Ordyl) could be laminated on Cytop with sufficient adhesion for sandblasting (steps 4-7, 11-12).

Before bonding substrate (4) to substrate (2), the porous PTFE membrane was attached. We chose a 60 μm thick, porous PTFE membrane (FP-010-60, Sumitomo Denko) as the material for the gas separation layer. To prevent H<sub>2</sub> leakage through its pores, the membrane was structured to pieces of 15 × 20 mm by a fs-laser prior to attachment. Hereby a 2.5 mm wide sealing frame on the outside of the wafer was provided for the next bonding step sealing the device. The membrane pieces were cleaned by ultrasonic treatment in acetone for 30 min, aligned to the Cytop-coated side of substrate (2) and fixed by heating for 5 min at 160 °C (step 13). Chemically very 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.

Next, substrate (2) was bonded to substrate (4) by Cytop bonding (step 14). To find suitable process parameters for bonding, we referred to the work by Oh *et al.* [7], where was reported that bonding at a pressure of 4 MPa and a temperature of 160 °C for 30 min resulted in the best bonding performance. These conditions were confirmed to be applicable to our device. Bonding pressure and a uniform Cytop layer thickness turned out to be the most significant parameters for successful bonding.

A temperature sensor was fabricated on the topside of substrate (1) by electron beam evaporation of Ti/Pt and lift-off patterning (steps 15-17).

The fluidic channel was closed by bonding substrate (1) to the already assembled part of the device with the through-patterned fluidic channel. This bonding step is undertaken in order to provide a good transparency, i.e. visibility of the catalysis process within the device, as well as a minimum distance between the temperature sensor and reaction site. Because of its chemical inertness, capability of height compensation, and transparency, again Cytop was chosen as the intermediate bonding material and applied by spin coating like for substrates (4) and (2). To provide a structure for filling the catalyst into the

channel after completion of the device, also substrate (1) must be processed by sandblasting (**steps 19-20**) before bonding at a pressure of 4 MPa at 160 °C for 30 min (**step 21**). Finally the catalyst can be filled into the microchannel of the reactor (**step 22**).

### 3.3 Bonding

Several options for the fabrication of a microreactor have been investigated with the aim of realizing a small package. The key for miniaturization is an appropriate bonding technique, since this makes an external clamping structure, e.g. bolted clamping plates, unnecessary. Besides the requirement for hydrogen and liquid tightness, the bonding interface and all used materials must be stable under harsh alkaline conditions. Because of its excellent chemical resistance, a PTFE membrane was chosen as the gas separation layer. But the maximum operating temperature (260 °C) and creep behavior of PTFE limit the usable bonding technologies after attaching the membrane to low temperature processes. Cytop bonding technique fulfilling all requirements was found. We investigated the liquid tightness of the bonding interface by pumping a solution of ethanol dyed with Malachite green through the Cytop-sealed catalyst channel (Fig.4a). No leakage could be found during 30 min of pumping. Bonding strength was measured to be higher than 4 MPa.

### 3.4 Fabrication result

Figure 4b shows the first prototype of the microreactor. The fabricated reactor prototype has a channel length of 1.2 cm, which is sufficient to store approximately 180 catalyst beads inside the microchannel. From our experimental data [5], it is expected that this amount of catalyst will produce 7 sccm of hydrogen. The overall volume of the reactor is 0.8 cm<sup>3</sup>. At a more improved state of development, this volume may also include the fuel cell, since the lid of the reactor may be exchanged by a self breathing fuel cell [8]. This fuel cell would then directly be supplied with H<sub>2</sub> generated in the catalyst channel.

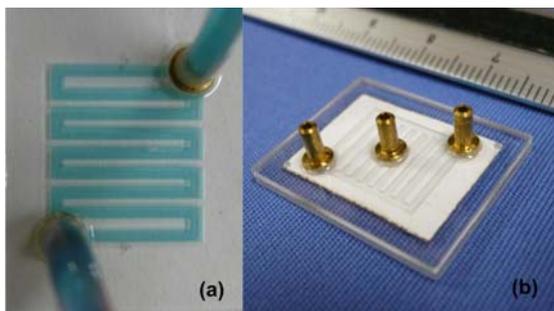


Fig . 4 a) Liquid tightness after 30 min of pumping  
b) Microreactor prototype made of glass

With the process outlined above, a separate PTFE membrane has to be bonded to each reactor individually. Future work will focus on a wafer level process where a simultaneous bonding of the membrane as a batch process is required.

## 4. CONCLUSION

A continuous-flow microreactor to produce hydrogen from sodium borohydride (NaBH<sub>4</sub>) solution using Ru-loaded ion exchange resin beads as a catalyst was prototyped. First, the hydrogen generation performance of the catalyst was described. The experimental results suggest that the microreactor with 180 catalyst beads will produce 7 cc/min of hydrogen, which is sufficient for 0.6 W class fuel cells.

Next, the first version of the microreactor was fabricated by joining borosilicate glass substrates and a porous PTFE gas separation membrane. The main processing techniques are sandblasting with a high abrasion rate and low temperature adhesive bonding. In the next step, the fabricated microreactor will be tested with regards to hydrogen generation rate under different conditions, and the design revised according to the test results.

## ACKNOWLEDGEMENT

This study was partly supported by a scholarship of the Japanese MEXT and partly by a fuel cell research grant of the German BMBF (Project PemGen).

## REFERENCES

- [1] Gervasio D et al 2005 Room temperature micro-hydrogen-generator *J Power Sourc.* **149** 15–21
- [2] Richardson B S et al 2005 Sodium borohydride based hybrid power system *J Power Sourc.* **145** 21-29
- [3] Amendola et al 2000 A safe, portable, hydrogen gas generator using aqueous borohydride solution and Ru catalyst, *Int J Hydrogen Energ.* **25** 969-975
- [4] Kreevoy M M et al 1979 The rate of decomposition of NaBH<sub>4</sub> in basic aqueous solutions *Ventron Alembic* **15** 2-3
- [5] Hoepfner K et al 2007 Hydrogen Generation for Micro Fuel Cells *Proceedings 'Mikrosystemtechnik Kongress 2007'*, Dresden, Germany, Oct.-15-17<sup>th</sup>, 2007
- [7] Oh K W et al 2002 A low-temperature bonding technique using spin-on fluorocarbon polymers to assemble microsystems *J Micromech. Microeng.* **12** 187-191
- [8] Hahn R et al 2004 Development of a planar micro fuel cell with thin film and micro patterning technologies *J Power Sourc.* **131** 73-78