

AN INTEGRATED MICROFLUIDIC SELF-REGULATING AND SELF-CIRCULATING HYDROGEN GENERATOR FOR FUEL CELLS

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ABSTRACT

This paper introduces a micro-hydrogen generator with self-circulation and self-regulation mechanisms for delivering alkaline sodium borohydride solution without parasitic power consumption. The self-circulation of the sodium borohydride solution was achieved by using directional growth and selective venting of hydrogen bubbles in microchannels, which leads to agitation and addition of fresh solution without power consumption. The pumping rate can be automatically regulated by the pressure at the gas outlet, which directly corresponds to the current output of the fuel cell, and thus the electrical load. Design, fabrication, and testing results of a prototype system are described. A maximum hydrogen generation rate of 0.5 sccm and self-circulation/self-regulation mechanisms have been demonstrated in this paper.

KEYWORDS

Micro-fuel cell, hydrogen generator, microfluidics, self-circulation, self-regulation

INTRODUCTION

Research and development of micro power sources have been spurred by recent fast growth of portable customer electronics, such as cell phones, global positioning systems (GPS), personnel digital assistants (PDA), digital cameras, and laptop computers [1]. Electronic devices with more functions and smaller volumes demand small power sources with high power and energy densities to support a better performance and a reasonable working time.

Micro-hydrogen proton exchange membrane fuel cells (μH_2 -PEMFC) have received considerable attention over the past decade as a promising solution to the increasing demands on micro-power sources [2]. However, significant technical challenges for μH_2 -PEMFCs still exist on the microscale, such as high energy density on-board hydrogen storage, and control mechanisms that have little or no parasitic power consumption. Hydrogen generation using a catalytic hydrolysis reaction of alkaline sodium borohydride (NaBH_4) solution has been reported previously, due to high energy density and ease of control [3-6]. But most of the reported systems use active pumps, valves, and gas-liquid separators, which can cause significant parasitic power consumption and difficulties to miniaturize them to a small scale. Gervasio *et al.* reported

a micro-hydrogen generator in 2005, which utilized a Celgard membrane to separate NaBH_4 solution and hydrogen [7]. However, an external active piezo-pump and valves have to be used to regulate hydrogen generation.

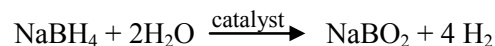
In order to build a micro-hydrogen generator based on hydrolysis of NaBH_4 solution with little or no parasitic power consumption, a passive micro-pump, valve and micro gas-liquid separator have to be developed and integrated into the micro hydrogen generation system. In this paper, we present a fully integrated microfluidic self-regulating and self-circulating hydrogen generator using alkaline NaBH_4 solutions with no parasitic power consumption.

In this design, a nanoporous hydrophobic membrane was used to separate the NaBH_4 solution and hydrogen gas. The hydrogen gas bubbles generated in the reaction microchannels were employed to circulate the NaBH_4 solution in a microfluidic loop. Hydrogen generation is regulated by the hydrogen pressure at the venting port, which self-regulates to generate only the required amount of hydrogen. By eliminating the need for active pumps, valves, and gas-liquid separators, this design enables the miniaturization of hydrogen generators based on a catalytic hydrolysis reaction of alkaline NaBH_4 solutions.

OPERATION MECHANISMS

Hydrogen Generation Reaction

The hydrogen storage solution was made by preparing a 10 or 20 wt% solution of NaBH_4 (Aldrich chemical company, St. Louis, MO) in 5 wt% sodium hydroxide (NaOH) (Aldrich) water (Millipore 18M Ω) solution. This solution is safe and stable at room temperature. It releases hydrogen only in the presence of catalyst [8], such as ruthenium, platinum, ruthenium salt, and cobalt chloride (CoCl_2), as



In this work, high surface area platinum black was used as the catalyst to facilitate hydrolysis reactions.

Self-Circulation and Self-Regulation Mechanisms

As depicted in Fig. 1 (a), a group of small hydrophilic channels were fabricated on the left side of the reaction channel to serve as a virtual check valve for gas bubbles. Hydrogen generation reaction happens when the alkaline NaBH_4 solution is brought into contact with a platinum

black catalyst inside the reaction channel. When a hydrogen bubble (b1) grows at a location close to this virtual check valve, expansion of the left meniscus of the bubble is hindered due to its capability to provide a higher capillary pressure than the right meniscus does. Consequently, the bubble only grows to the right and pushes the liquid rightward. The bubbles generated in the middle of the reaction channel can be pushed by the leftmost one to the right. By making the reaction channel hydrophilic (e.g., SiO_2), a surface energy difference between its hydrophilic surface and the hydrophobic membrane can make the latter a “bubble trap” [9]. Once a bubble (b2) reaches the hydrophobic nanoporous membrane, it will be drawn into the membrane region. Through the vent holes in the membrane, the bubble (b3) is removed without liquid loss. The liquid then fills into the section symmetrically to replace the vacancy left by the gas bubble. A pumping cycle is thus completed and a net pumping to the right is achieved.

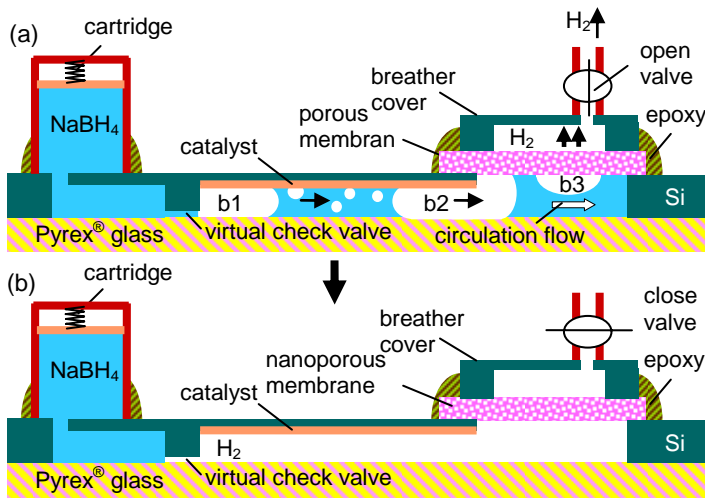


Fig. 1 Schematic of the microfluidic hydrogen generator. (a) The self-circulation mechanism when hydrogen is constantly consumed. (b) The self-regulation mechanism. When hydrogen is not being consumed by the fuel cell or the outlet valve is closed, NaBH_4 solution will be forced out of the catalyst channel to stop the reaction.

Hydrogen generation is regulated by virtue of NaBH_4 solution being allowed into or forced out of the catalyst channel. When hydrogen is consumed by the fuel cell during periods of load, the fuel is circulated by hydrogen bubbles to generate the required amount of hydrogen, as Fig. 1 (a) shows. Our preliminary test in this paper releases the gas freely *via* an open gas outlet to represent this operation condition. The flow rate of liquid circulation can be regulated by the pressure or flow rate at the gas outlet. When the gas is released from the outlet at a flow rate lower than its generation rate, pressure starts to build up, which will decrease the gas removal rate as well as the pumping rate until the equilibrium is reached. In other

words, a lower hydrogen consumption as a result of a smaller load (low current) in a fuel cell will result in a lower pumping rate. When external load is completely removed and hydrogen is not being consumed at the anode, as Fig. 1 (b) shows, the catalyst channel will be pressurized and eventually filled with hydrogen gas. NaBH_4 solution will thus be forced out of the catalyst channel to stop the reaction. This effect can be observed by closing the valve at the gas outlet.

FABRICATION

The device was fabricated from a 375 μm thick silicon wafer using MEMS fabrication processes, as shown in Fig. 2. 90 μm wide, 64 μm deep V-shaped channels (virtual check valve), 600 μm wide, 200 μm deep trapezoidal channels (reaction channel), and venting windows were patterned by anisotropic KOH etching. A 0.5 μm silicon dioxide was grown on the surface as an electrical insulation layer in an 1100°C oxidation tube furnace for 12 hr. Au/Cr was deposited in the reaction channels as a seed layer for electroplating platinum using a shadow mask. A thin layer of photoresist (AZ 1518, Clariant Co.) was transferred to the top surface of the device to cover the Au/Cr layer to prevent the catalyst from being electroplated. But the reaction channels were left open. A catalytic layer of Platinum black was electroplated on the bottom and the side walls of the reaction channels. The plating bath consisted of 120 ml of

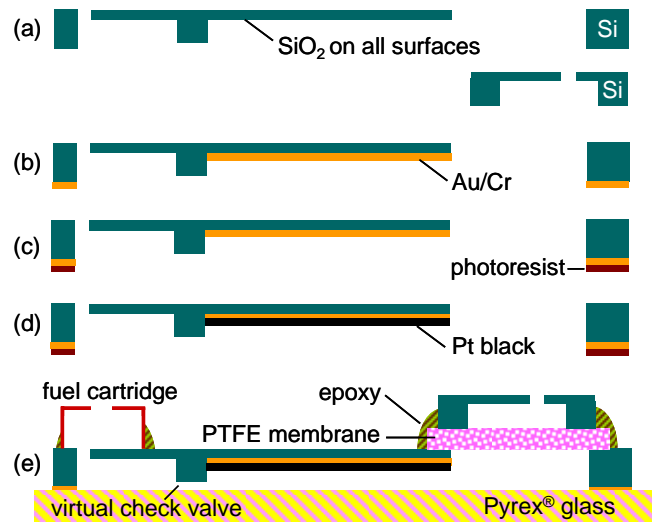


Fig. 2 Microfabrication processes: (a) KOH etching and SiO_2 growth in an 1100°C oxidation tube furnace for 12 hr; (b) deposit and pattern Au/Cr layer in the reaction channels using a shadow mask; (c) transfer a thin layer of AZ 1518 photoresist to the surface of the silicon chip to cover the Au/Cr layer but leave the reaction channels open; (d) electroplate Pt black on the bottom and side walls of the reaction channels; (e) bond the fabricated silicon chip, a Pyrex[®] glass plate, a hydrophobic porous PTFE membrane, and a silicon cover chip together by adhesive bonding. Glue the cartridge with epoxy.

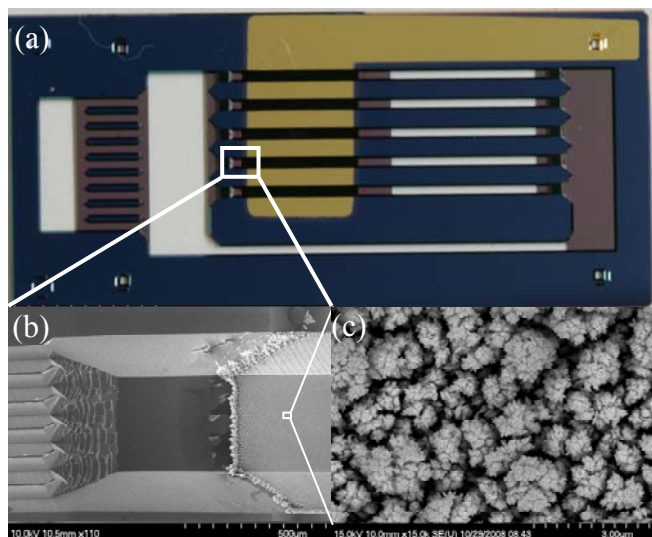


Fig. 3 (a) Optical and (b, c) SEM images of the fabricated silicon chip with V-shaped virtual check valves, reaction channels, venting windows, and (c) Pt-black catalyst.

DI water, 5 g of dihydrogen hexachloroplatinate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Alfa AESAR, Ward Hill, MA). As shown in Fig. 3 (b) and (c), high surface area nanostructures were achieved by carrying out the deposition for 30 sec at relatively high current densities of about 0.4 A/cm^2 [10]. After removing the photoresist in acetone, the fabricated silicon layer, a Pyrex glass plate, a hydrophobic porous PTFE membrane (GE osmonics labstore, Minnetonka, MN), and a silicon cover layer were bonded together by adhesive bonding [11]. Finally, the fuel cartridge was fixed on the device by epoxy.

RESULTS AND DISCUSSION

A fabricated device was tested using two different NaBH_4 solutions, 10 and 20%, respectively. A mass flow meter (FMA-1615A, Omega, Stamford, CT) was used to measure the hydrogen generation rate. The hydrogen generation profiles are shown in Fig. 4. The 10% NaBH_4 solution has higher generation rate than the 20% solution, which is consistent with the reported results showing that NaBH_4 solution with 5% NaOH has maximum catalytic reaction rate at 10% concentration [12]. Figure 4 also shows that the generation rate continuously decreased from 0.5 and 0.2 sccm to about 0.05 sccm in one hour. In the current design, NaBH_4 solution is only circulated and exchanged with on-chip reservoir of about $11 \mu\text{L}$. After the fresh NaBH_4 solution is used out in the on-chip reservoir, NaBH_4 only can be delivered to the circulation loop by diffusion. In addition, the reaction byproduct, sodium borate (NaBO_2), can accumulate in the circulation loop to increase the pH value of the solution, thereby decreasing the reaction rate. A future design with an out-of-plane circulation loop and bigger reaction channel is expected to maintain stable hydrogen generation rate at a relatively high level over a longer period.

In order to verify the self-circulation mechanism, NaBH_4 solution circulation rates at different hydrogen flow rates are compared and shown in Fig. 5. The hydrogen flow rate was controlled by a needle valve and measured by an Omega[®] mass flow meter. The liquid flow rate was measured by tracking the movement of small gas bubbles in the channels. Figure 5 demonstrates that the circulation rate of the solution can be automatically regulated by the outlet hydrogen flow rate. When the gas outlet is closed, the catalyst microchannels are filled with hydrogen gas to stop the catalytic reaction.

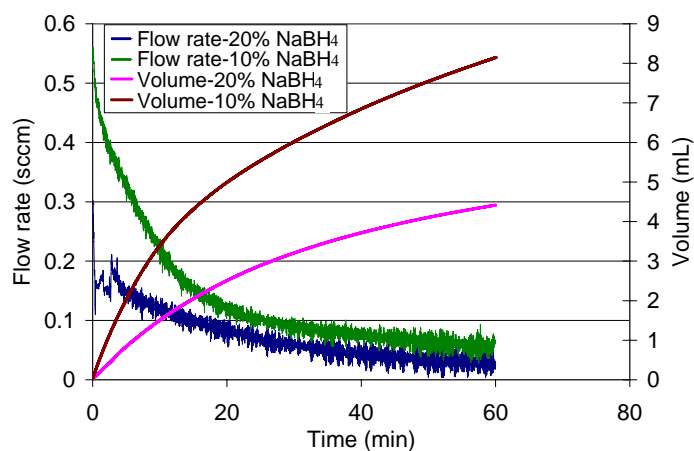


Fig. 4 Hydrogen generation profiles with a solution of 10% NaBH_4 and 5% NaOH and a solution of 20% NaBH_4 and 5% NaOH . The hydrogen flow rate was measured by an Omega[®] mass flow meter.

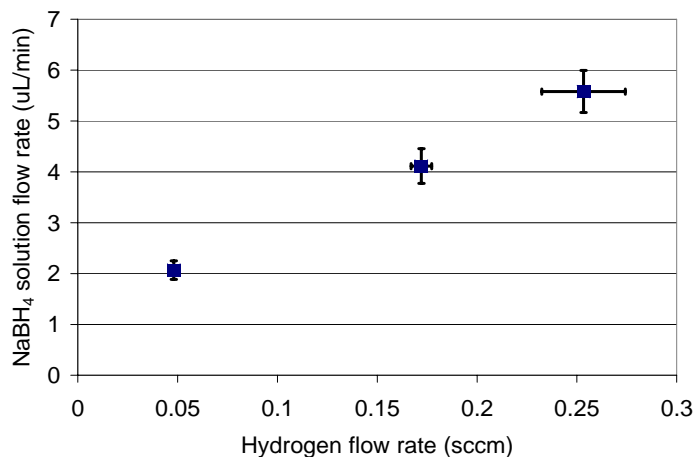


Fig. 5 Comparison of NaBH_4 solution circulation rate at different hydrogen flow rates.

However, it is observed that when the device is over-pressurized, gas may reenter the device through the vent membrane covering the on-chip reservoir. Consequently, some extra liquid will be pushed into the catalyst microchannels to continue the reaction for another short period (extra cycle). In Fig. 6, this extra cycle is marked by a temporary pressure drop in the closed outlet and an elongated stopping time. Although the reaction eventually stops, it is desirable to eliminate the extra cycle so as to

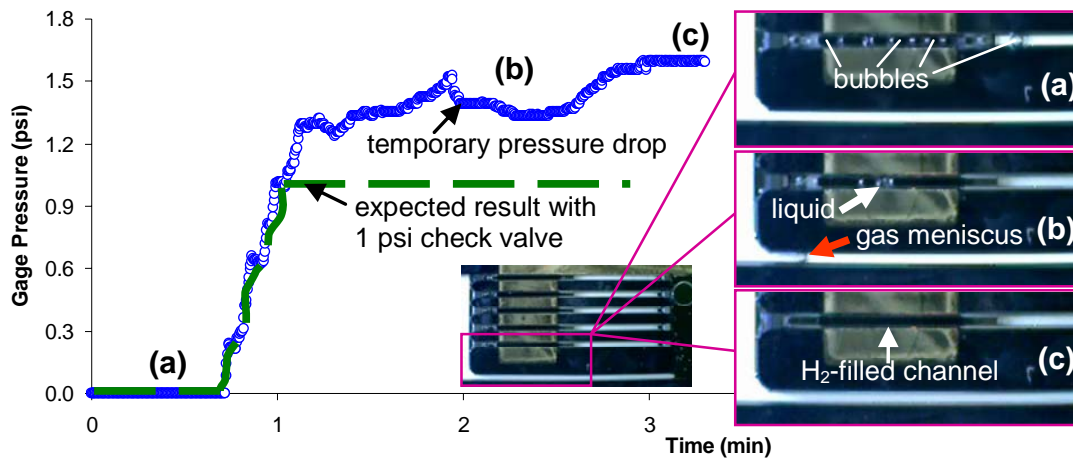


Fig. 6. Hydrogen pressure at outlet during stop-process. Insert (a) shows the hydrogen bubbles pumping liquid without power consumption during normal operation. Manual valve at outlet closes at ~45 seconds to stop the generator. Insert (b) shows gas entering the on-chip reservoir and pushing liquid into the already cleared reaction channel. Insert (c) shows a reaction microchannel completely filled with hydrogen. The reaction is stopped at ~3 minutes. With the addition of a 1 psi check valve, the pressure was observed (but not recorded yet) to reach 1 psi maximum in ~ 30 seconds and remain stable.

shorten the shutoff time, which can be achieved by adding a 1-psi check valve to the outlet to prevent overpressure and speed up the shutoff process. This effect has been observed in our testing, although the data were not recorded yet. Further analysis of operation with check valve can be conducted to optimize the stop-process.

CONCLUSION

In this paper, we have successfully demonstrated an integrated microfluidic hydrogen generator with self-circulation and self-regulation mechanisms for micro-fuel cells. Prototype devices have been fabricated using MEMS fabrication processes and tested with two different NaBH_4 solutions, 10% and 20% respectively. A maximum hydrogen generation rate of 0.5 sccm has been achieved with 10% solution. The results demonstrate that the hydrogen bubbles can be used to pump NaBH_4 solution along the circulation loop and the circulation rate of the solution can be automatically regulated by the outlet hydrogen flow rate without parasitic power consumption.

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