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A self-regulating hydrogen generator for micro fuel cells

Saeed Moghaddam[a,*], Eakkachai Pengwang[a], Richard I. Masel[b], Mark A. Shannon[a]

[a] Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, 1206 West Green Street, Urbana, IL 61801, United States
[b] Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, 213 Roger Adams Lab, 600 S. Mathews, Urbana, IL 61801, United States

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ABSTRACT

The ever-increasing power demands and miniaturization of portable electronics, micro-sensors and actuators, and emerging technologies such as cognitive arthropods have created a significant interest in development of micro fuel cells. One of the major challenges in development of hydrogen micro fuel cells is the fabrication and integration of auxiliary systems for generating, regulating, and delivering hydrogen gas to the membrane electrode assembly (MEA). In this paper, we report the development of a hydrogen gas generator with a micro-scale control system that does not consume any power. The hydrogen generator consists of a hydride reactor and a water reservoir, with a regulating valve separating them. The regulating valve consists of a port from the water reservoir and a movable membrane with via holes that permit water to flow from the reservoir to the hydride reactor. Water flows towards the hydride reactor, but stops within the membrane via holes due to capillary forces. Water vapor then diffuses from the via holes into the hydride reactor resulting in generation of hydrogen gas. When the rate of hydrogen consumed by the MEA is lower than the generation rate, gas pressure builds up inside the hydride reactor, deflecting the membrane, closing the water regulator valve, until the pressure drops, whereby the valve reopens. We have integrated the self-regulating micro hydrogen generator to a MEA and successfully conducted fuel cell tests under varying load conditions.

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1. Introduction

The increasing demand for high energy density power sources driven by advancements in portable electronics and MEMS devices has generated significant interest in development of micro fuel cells and batteries [1,2]. In terms of energy density, metal hydrides (e.g. $NaBH_4$), methanol, and most hydrocarbon fuels have an energy density up to an order of magnitude higher than the competitive battery technologies. Micro fuel cells, however, can potentially outperform the batteries only if their fuel to device volume ratio can be maximized and the power consumption of their auxiliary systems to regulate fuel delivery and power output is significantly reduced. While fabrication of small-scale membrane electrode assembly (MEA) is widely reported in literature [3–8], shrinking the size of the auxiliary systems (pump, valves, sensors, distribution components, and power and control electronics for these components) has remained a challenge. While this might be somewhat feasible in centimeter-scale fuel cells, fitting all the auxiliary components within a few cubic millimeters volume is quite a challenge. Developing a new means of fuel delivery and control that can be scaled downed and consume little to no power opens an opportunity for fabricating millimeter-scale fuel cells and realizing new devices that are tied to the existence of such power sources.

Despite the advancements in fuel cell components and fabrication processing, there has been very little progress made on micro fuel cell system integration. Integrated micro fuel cell architectures suggested in literature (e.g. in [9–12]) are scaled-downed versions of large-scale systems with numerous auxiliary components. These components can be much larger than the membrane electrode assembly, greatly reducing the overall device energy density. In addition, they consume power, which reduces available output power from the micro fuel cell for a further reduction of the device energy density. Additionally, auxiliary components normally require numerous microfabrication steps and have integration difficulties that can result in higher production costs and added complexity of micro fuel cells operation.

Examples of fuel delivery and control systems can be found in [13–18]. Sarata et al. [13] proposed a pressure-based control system for a hydrogen generator comprising of a hydride reactor and water for hydrolysis. The hydrogen generation rate is controlled by monitoring the reactor pressure and then stopping the pumping of water to the hydride chamber when the hydride chamber pressure increases above a reference value. The pressure sensor, pump, valve, and electronics to conduct this control operation occupy significant space, which directly translate to lower energy density and

* Corresponding author. Tel.: +1 217 244 5136; fax: +1 217 244 6534.
E-mail addresses: saeedmog@uiuc.edu (S. Moghaddam), epengwa2@uiuc.edu (E. Pengwang), r-masel@uiuc.edu (R.I. Masel), mshannon@uiuc.edu (M.A. Shannon).

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high cost for micro fuel cells. In another approach [18], the pressure increase in a macro-scale hydride chamber was used to automatically push the water out of a conduit that connected the water reservoir to the hydride reactor. This results in an increase in the diffusion length between the water front and the hydride and consequently slows down the hydrogen generation rate. This passive approach may be more suitable for miniaturization (e.g. fabrication of a microchannel between the water and hydride reservoirs and so on). But, unfortunately, since water diffusion and thereby hydrogen generation is not completely stopped, pressure continues to rise such that failure can occur. Furthermore, the movements of the water front inside the microchannel (i.e. dynamics of the advancing and receding contact lines) and the pressure of the excess hydrogen inside the device that pushes against the water front can be complicated to predict and control.

In this manuscript, we present the development of a micro hydrogen generator with a self-regulating control mechanism. The control scheme enables the hydrogen generator to automatically stop generating hydrogen when it is not consumed by the micro fuel cell. The volume of the control mechanism is less than 50 nL (approximately 0.5% of the device volume) and requires no energy input. This technology has enabled fabrication of the first fully integrated millimeter-scale fuel cell that operates much like a battery. This technology can also be implemented in centimeter-scale micro fuel cells to enhance their energy density and reliability and reduce their complexity and cost. Details of the control mechanism and development of a self-regulating micro hydrogen generator and its integration with a MEA are discussed in this manuscript.

2. Operation principle

The no-power, self-regulating hydrogen generator consists of a hydride reactor and a water reservoir, with a regulating valve separating them, as shown in Fig. 1. The regulating valve consists of a port and a membrane with via holes in it. Water flows through the port towards the hydride chamber, but stops within the membrane via holes due to capillary forces. Water vapor then diffuses into the hydride chamber resulting in hydrogen generation (metal hydrides such as LiH, $LiAlH_4$, and CaH_2 react with water vapor to produce H_2 [19]). When the rate of hydrogen consumption by the fuel cell is lower than generation rate, gas pressure builds up inside the hydride reactor and deflects the membrane towards the water port, blocking the port and ceasing the water flow to the hydride after the water evaporates. This regulation action, however, assumes that the membrane deflects under a smaller pressure than needed to break into the liquid meniscus formed inside the membrane via holes. Under such conditions, complete isolation of the hydride reactor from the water reservoir can occur. When hydrogen consumption by the fuel cell is faster than the generation rate, the reverse happens, opening the membrane to allow water to diffuse into the hydride reactor, increasing the hydrogen generation. Essentially, the control mechanism is a passive valve that automatically regulates hydrogen production based on the hydride reactor pressure. Details of the valve operation and testing are discussed in the following sections.

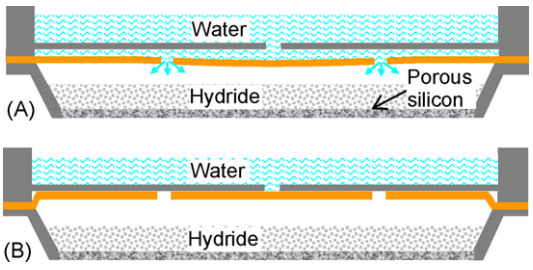

Fig. 1. Schematic cross-section of the self-regulating hydrogen generator and its principle of operation. (A) Membrane in release mode: water exits the reservoir and diffuses into the hydride reactor through the membrane holes. (B) Membrane in closed mode: small pressure buildup in the hydride reactor, when hydrogen is not used, bends the membrane and closes off the water port.

3. Valve fabrication and testing

3.1. Valve and water reservoir assembly

The membrane separating the water reservoir and the hydride reactor was made of polyimide (PI) through spinning and curing PI 5878G (from HD Microsystems) on a 100 mm diameter 500 μm thick glass wafer. The final thickness of the PI layer was 5 μm. A circular 1.3 mm diameter area at the center of the membrane was sputter coated with a 0.2 μm thick Cr/Au layer to prevent water diffusion through the membrane when it is closed. A circularly distributed array of 30 μm diameter holes was etched through the Cr/Au (wet etched) and PI (reactive ion etched) layers close to the perimeter of the Cr/Au coated area. Fig. 2 shows the front view of the membrane. The membrane was then transfer-bonded (process is described in [20]) to the bottom of the water reservoir fabricated from ⟨1 0 0⟩ *p*-doped silicon through deep reactive ion etching (DRIE) process (cf. Fig. 3). Note that the 3 μm deep recess seen in the bottom view of the reservoir is the separating gap between the PI membrane and the bottom of the water reservoir, as depicted in the schematic of Fig. 1.

3.2. Membrane bulge test

A test piece was fabricated to determine the membrane deflection with pressure. The test piece was a silicon die (10 mm × 10 mm) with 2.4 mm × 2.4 mm opening at its middle, over which the PI membrane was bonded. The PI membrane was similar to that of the device in every aspect (i.e. size and microfabrication process) except that it did not have the 30 μm holes. A bulge test setup was used to measure the membrane deflection at different pressures (cf. Fig. 4). The test piece was installed on the pressure chamber of the setup, as depicted in Fig. 4. The chamber pressure was increased using a piezoelectric actuator. As the results in Fig. 5 show, an applied pressure of approximately 150 Pa is sufficient to deform the

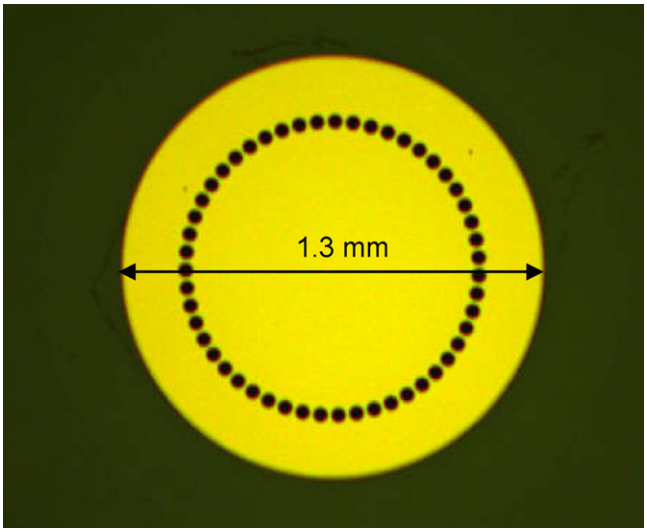

Fig. 2. Top view of the center of the polyimide membrane coated with Cr/Au to prevent water diffusion through the membrane. The holes are 30 μm in diameter.