A FULLY-ENCLOSED MICRO PEM FUEL CELL WITH SELF-REGULATED FUEL DELIVERY AND SHUT-DOWN

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Abstract: A fully-integrated, self-regulated micro fuel cell (µFC) system is reported to power implanted, under-water, or on-flight devices in anaerobic environments. Using silicon micromachining processes, we have fabricated hydrogen and oxygen generators and demonstrated their capability to automatically deliver reactants to a µFC with self-regulation. Hydrogen gas is generated by catalyzed hydrolysis of an aqueous sodium borohydride solution, while oxygen is generated from a dilute solution of hydrogen peroxide. During normal operation of the µFC, gas bubbles generated by the reactions are employed to circulate the liquid reactants automatically without consuming any electrical power. Once the µFC is shut down, the gases will automatically empty the reaction channels to stop the reactions. The gas generation rate is found to be positively correlated to the fuel cell current output, revealing the self-regulation nature of the system. Repeatable automatic shut down is also demonstrated.

Keywords: micro fuel cell, self-circulation, self-regulation, fully-enclosed devices.

INTRODUCTION

Micro-fuel cells (µFCs) [1] continue to show promise as high-energy-density power sources for portable electronics and MEMS. We have previously demonstrated a MEMS-based self-regulating device that generates high-purity pre-hydrated hydrogen gas by hydrolysis of an aqueous Sodium Borohydride (NaBH$_4$) solution [2]. In this paper, we expand upon the capability of the device by demonstrating, for the first time, the self-driven delivery of both hydrogen and oxygen to power a µFC, as well as the autonomous shut-down of reactant generation when the µFC is not being operated. The reported technology opens up the door for a fully-integrated µFC in anaerobic environments, thus enabling µFCs for implantable, under-water, and on-flight (e.g. outer space) applications.

Self-circulation of liquid fuel during gas generation, as depicted in (Fig. 1), is initiated when the aqueous fuel/oxidant (NaBH$_4$ or H$_2$O$_2$) contacts the platinum black catalyst and starts to generate gas bubbles. Directional growth of these gas bubbles (H$_2$ or O$_2$) adjacent to the virtual check valve is followed by symmetric venting at the hydrophobic nanoporous membrane (Fig. 1a), resulting in rightward pumping of the liquid reactants (previously demonstrated for micro direct methanol fuel cell [3]). The embedded pumping structure draws fresh solution into the reaction channel with neither parasitic power nor significant packaging penalty. Moreover, the gas generators can be automatically shut down when the gas is not being consumed. In this case, the excess gas

can fill up the reaction channels to repel the liquid reactants, thus stopping the reaction (Fig. 1b). When the µFC restarts, the circulation and gas generation resume automatically. The concept of this self-circulating, self-regulating gas generator has been proven previously with a NaBH$_4$-H$_2$ system as an example.
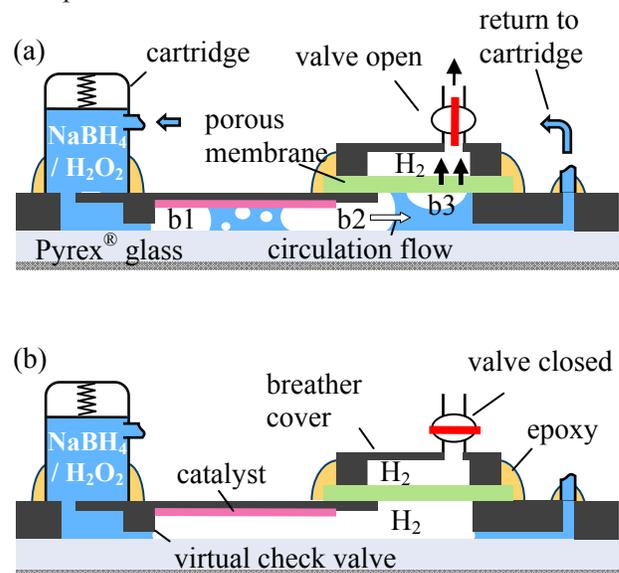

Fig. 1: Schematic of the microfluidic H$_2$/O$_2$ generators. (a) self-regulated fuel delivery and (b) automatic shut-down.

In this paper, we demonstrate a complete µFC system with both hydrogen and oxygen generators to deliver reactants, as well as its capability of self-circulation, self-regulation, and automatic shut-down.

EXPERIMENTAL SETUP

Fabrication of gas generators

Microfabrication of the gas generators was achieved by KOH etching of a 375μm-thick silicon wafer. The etched reaction channels were then coated with an Au/Cr seed layer to aid in electroplating of the Platinum black catalyst. The fabricated silicon chip was then bonded to a Pyrex glass slide. Lastly, the PTFE nanoporous membrane, venting covers, and tube fittings were glued to the chip with epoxy. More details of the fabrication process can be found in [2].
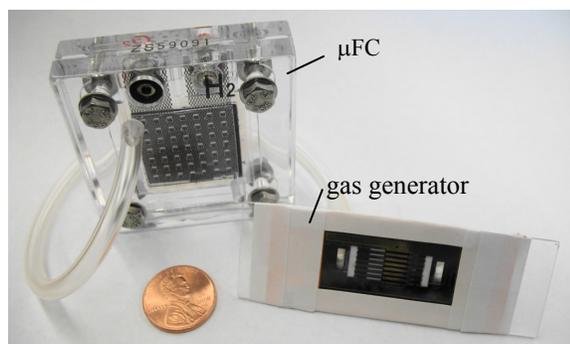

Fig. 2: μFC and a gas generator

Fully-Enclosed μFC

To demonstrate the feasibility of a self-regulating μFC system, the H_2/O_2 generators were assembled with a commercially-obtained micro PEM (polymer electrolyte membrane) fuel cell (FuelCell Store) (Fig. 2). The gas outlet of the hydrogen generator was connected by tubing to the anode inlet of the fuel cell, with the oxygen generator similarly connected to the cathode inlet, as exemplified in Fig. 2. The outlets at the anode and cathode where closed off by a valve. An electronic mass flowmeter (OMEGA, FMA-1602) was used to measure the hydrogen and oxygen flowrates. The flowmeter was placed in-line between each gas generator and the fuel cell. The length and inner diameter of the tubing used was kept at a minimum to reduce the storage volume of each gas (discussed below). The full assembly, consisting of a H_2 generator, an O_2 generator, and the μFC, is schematically shown in Fig. 3. To simulate a removable external electric load, a 150 ohm resistor and a toggle switch were connected to the μFC. In this configuration, the μFC powers the load when the external electrical circuit is closed by the toggle switch. Gas consumption within the fuel cell will initiate the self-circulation of liquid reactants within the generators (Fig 3a). Reactions in the generators continue as long as H_2 and O_2 are consumed. However, once the circuit is opened, the gas
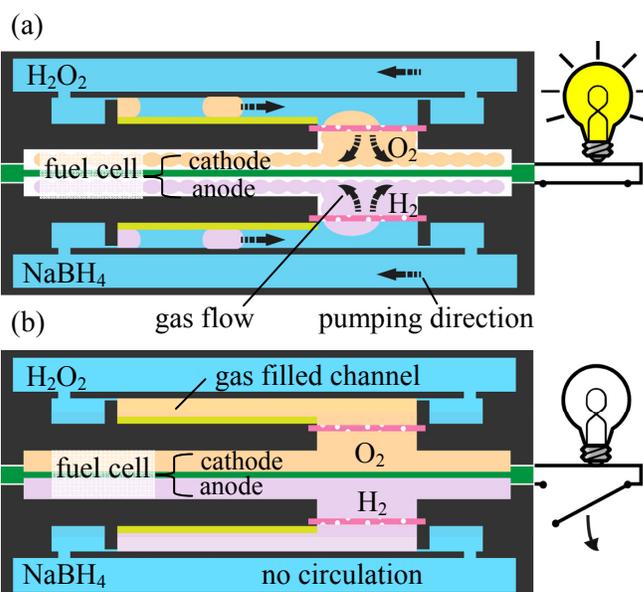

Fig 3: Schematic of the fully-enclosed μFC and generator assembly. (a) External current is drawn and (b) external current is interrupted

generators will be stopped automatically to conserve the liquid fuel/oxidant until its next usage (Fig 3b).

It is noted that the reported generators haven't been optimized to tolerate concentrated reactants yet. For hydrogen generation, 10 wt% $NaBH_4$ was used based on [4]. To increase the shelf life of the fuel, 5 wt% NaOH was added to increase the pH and make the solution basic. For oxygen generation, a 5 wt% solution of H_2O_2 was used as the oxidant.

EXPERIMENTAL RESULTS

Open Circuit and Start Up

The fully-enclosed μFC with on-board gas generators was cycled between "open" and "closed" states for several times (Fig. 4a). Open circuit voltage (OCV) of the μFC is measured as ~1V. Immediately after connecting an external load at t_1, the voltage starts to drop until it stabilizes at 0.9V. Two factors may contribute to this voltage drop, including overpotential of the μFC and drop of the pressures at the anode and the cathode due to the consumption of the gas reactants. The latter is also revealed in the initial peak of the current (~6.8 x 10^{-3} amps), which eventually stabilizes at 6 x 10^{-3} amps. The active area of the fuel cell used in this experiment is 1 cm^2. The current density (6 mA/cm^2) measured in this experiment is far below the maximum current density of this fuel cell, which reveals that the current was determined by the fuel generation rate. Overall it takes
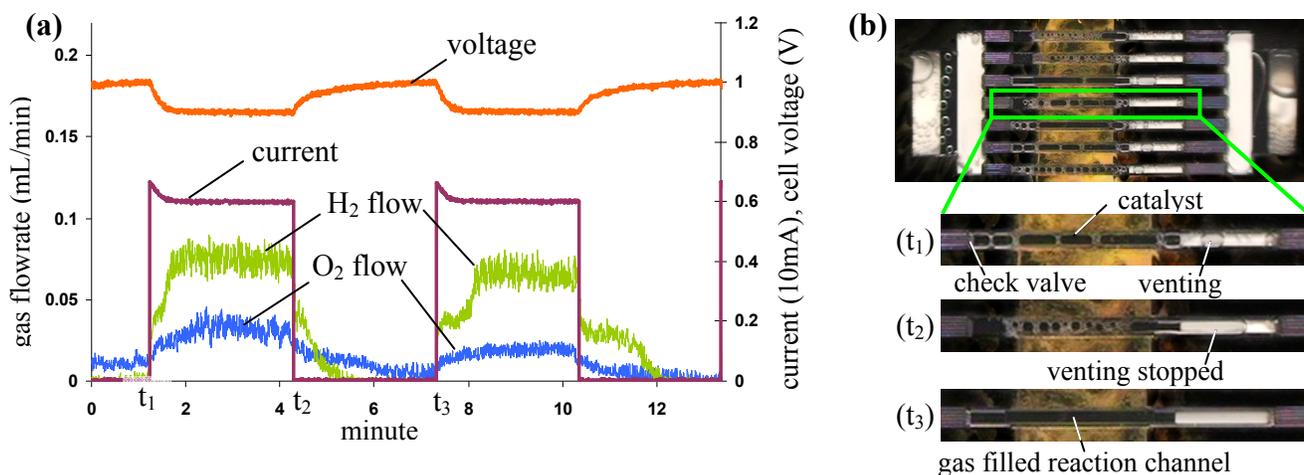
Fig. 4: Cyclic performance of μFC with on-board fuel/oxidant storage. (a) gas generation rates as a response to turning the fuel cell "on" and "off" and (b) synchronized video sequence of hydrogen generator

about 37 seconds for the current and voltage to reach steady state. However it appears that the gas flowrates take longer to reach a steady flow. This can be explained by the excess gas stored within the fuel cell, the tubing, and the reaction channels of the gas generators, which can serve as a gas reservoir and buffer the pressure/flow. During open circuit measurements this space is filled with gas and is slightly pressurized by the gas generators. After the external load is connected at t_1 (Fig 4a), the gas consumption of the μFC is first supplied by the pressurized gas stored in this space, which is reflected in the initial rapid increase of gas flow rate. The gas generators will then start to pick up the reactant delivery and eventually stabilize the gas generation. In other words, the gas generation lags behind the quick gas consumption (the reverse is seen during shut-down). On average, gas flowrates stabilize after ~50 seconds.

Closed Circuit Steady State

Average gas flow rates during steady state gas generation (Fig 4b) are measured as ~0.075 mL/min for hydrogen and ~0.027 mL/min for oxygen. It is still unclear at this point why the hydrogen flowrate was not exactly twice the flowrate of oxygen. But it is suspected to be related to the accuracy of the flow meter and the fact that the hydrogen and oxygen flow rates are not measured in the exact same experiments, although the same electrical load is used.

Shut-down

At time t_2 the external load was removed and gas flowrates start to decrease. As mentioned before, the space within the fuel cell, the tubing, and the reaction

channels of the gas generators must first fill with gas and become slightly pressurized before the gas generators come to a complete stop. As seen in Fig 4b at t_2, the gas has stopped venting and started to fill up the reaction channel. At time t_3, the gas completely fills the reaction channel and forces the liquid reactants out of the channel to stop gas generation. On average it takes ~80 seconds for hydrogen gas generation to stop and ~180 seconds for oxygen gas generation to stop. Once again, gas pressures increase as the generators shut down and the voltage restores to the OCV (~1V). The cyclic performance results have been reliably repeated for more than 20 times.

Self-regulation

To verify the self-regulation of reactant delivery, gas flowrates were measured at various output currents (Fig. 5). The increase in gas flowrates as a function of current verifies self-regulation. Therefore, the reactant delivery self-adjusts to the power output of the fuel cell. For reasons unknown the H_2 flowrates are not exactly twice as much as O_2 flowrates. The ratio of hydrogen to oxygen flowrates ranges from 1.79 at point (a) to 2.73 at point (b).

Orientation

For portable applications the gas generators must be able to function in multiple orientations. This is especially critical if the device is in the upright position and the reactant delivery must work against gravity. Our observations conclude that the hydrogen gas generator will work in all orientations. However, the oxygen gas generator shows some sensitivity to orientation. The orientation dependence of the oxygen generator is believed to be related to the reduced

difference in the H_2O_2 contact angles on the venting membrane and the surface of the reaction channel. A plausible solution is to further decrease the size of the reaction channels to reduce the effect of gravity on the liquid reactant.
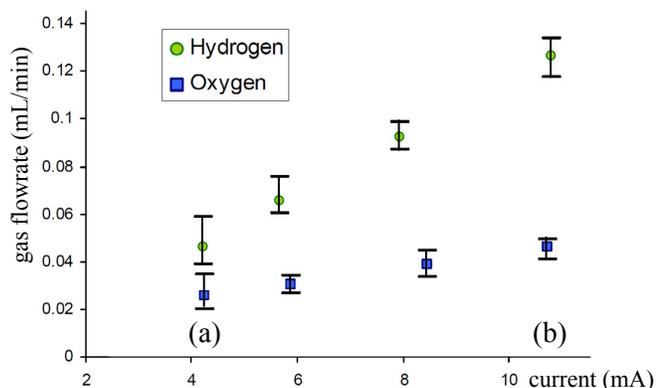

Fig. 5:self-regulation as a function of current drawn

Water Management

We have observed clear water accumulation on the cathode, as shown in Fig. 6. Water management in this closed configuration will be an important issue. As noted above, in order for the self-regulation to function, both the anode and cathode of the fuel cell should be closed off from the ambient air. To effectively shut-down, the anode/cathode must fill up with gas first and then proceed to fill up the generators. Closing off the outlet port on the anode side is not a problem. However, closing off the outlet port on the cathode side will cut off the water outlet as well. In order to avoid flooding of the cathode, an effective water management approach will be an essential component of the fully-closed µFC system.
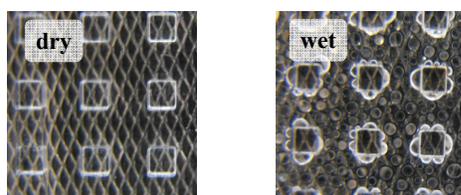

Fig. 6: cathode when dry and wet

Both active and passive methods have been developed to address the water management issue of µFCs. Electroosmotic pumps [5] and hydrophilic water storage medium (e.g., hydrogel) [6] are among the most promising techniques to mitigate or solve the flooding problem for the proposed device. Water management is anticipated to be a focus of future investigation.

CONCLUSION

A micro PEM fuel cell system is demonstrated by employing two self-regulated micro gas generators. When coupled together, the assembly represents a fully-enclosed power source suitable for applications in anaerobic environments. The self-regulation mechanism includes 1) the self-circulation of liquid reactants in the gas generator during the normal operation of µFC, 2) automatic shut-down of the gas generation when the fuel cell is turned off, and 3) self-regulation of pumping rate to adapt to the demand of gas by the fuel cell under different output currents. All three types of regulation have been demonstrated in this paper. Cyclic operation between the on and off state of the µFC is also performed to verify the reliability of the system. Future investigations include: tailoring the gas generation devices to tolerate higher reactant concentrations, optimizing the channel dimensions for greater orientation independence, and effectively removing water from the cathode to avoid flooding.

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