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Miniature fuel-cell system complete with on-demand fuel and oxidant supply

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Abstract:

The size of a functioning "system" rather than the individual components determines the success of many miniaturization efforts. While most of the existing micro fuel-cell research has been focusing on the fuel-cell stack, our approach has been to systematically eliminate all the ancillary components with the goal of miniaturizing the full system. In this paper, we present a miniature fuel-cell system that combines the self-pumping of fuel and self-generation of oxidant altogether in a box-shape device of a few centimeters. Since the fuel is pumped on demand inside the system without requiring any external assistance, the device is self-sufficient and portable. Furthermore, the oxygen is generated on demand inside the system without requiring the ambient air, so that the device can be stacked in multiple. Constructed simply as liquids in a solid container, this active fuel-cell system resembles a battery to the user.

Keywords: Miniature fuel cells; On-demand oxygen supply; Stackable fuel cells; Portable fuel cells; Self-pumping fuel cells

INTRODUCTION

Long-lasting portable power sources are in great need to supply power to portable consumer electronics integrated with emerging technologies [1-3]. Today's military also needs light and compact power sources with longer life to support the soldiers in the field [4]. Furthermore, as microelectromechanical systems (MEMS) technology advanced, numerous micro sensors and devices have become available, such as remote sensors and diagnostic systems, demanding microscale power sources on chip [5-7]. The need for the miniature power sources is stronger than ever.

Being environmentally friendly, fuel cells are attractive in both macro and micro scales. Especially in microscale, the simple construction compared to internal combustion engines and high theoretical energy density compared to batteries make fuel cells a strong candidate. Miniature fuel cells, based on direct methanol fuel cell (DMFC) technology [8-10] and direct formic acid fuel cell (DFAFC) [11-13], have been actively reported using a membrane electrode assembly (MEA) [14-15] or a membraneless technique [16-19]. Moreover, the U.S. Department of Transportation has approved the use of some fuel cells in airplanes, removing what companies have called a major barrier keeping micro fuel cells out of laptops and cell phones [20].

One of the main remaining barriers against commercialization is the lack of ability to miniaturize the fuel cell as a system because of the so-called "packaging penalty". Current state-of-the-art proton exchange membrane (PEM) fuel-cell systems still consist of several ancillary components [20-21]. Although many fuel cells reported in the literature are well shrunk in size and named micro fuel cells, almost all of them are micro fuel-cell *stack*, not a micro fuel cell complete as a standalone system. To operate as a complete system, the micro fuel-cell stacks are attached to ancillary components that significantly increase the volume and lower the energy density of a system. More specifically, they require: a pump to flow the liquid fuel and to force the flow against carbon dioxide bubble clogging; a gas separator to remove the bubbles; and often a pressurized oxygen tank to deliver oxygen to the system. The schematic drawing of the components needed in a usual microfluidic fuel cell is shown in Fig. 1. Unfortunately, miniaturization and packaging of the entire system is prohibitively challenging since these supporting components take up significant portions of the total volume, posing limitation in miniaturization. When the supporting structures are miniaturized as much as possible and integrated into the system, the inactive (i.e., non-fuel) materials take up a considerable volume of

the fuel-cell system, diminishing the fuel and oxidant storage capacity. The packaging penalty becomes unacceptably high if a fuel-cell system (not a fuel-cell stack) should be below ~1 cm in size – the main reason why the flurry of activities in micro fuel cells subsided after early 2000s and failed to provide a chance to compete with batteries. With only a small amount of fuel available in the system, the advantage of high energy density is simply lost in a complete (i.e., full, standalone) fuel-cell system when miniaturized. Furthermore, the complexity of integrating the moving ancillary components in a small space would make the miniature system expensive and unreliable.

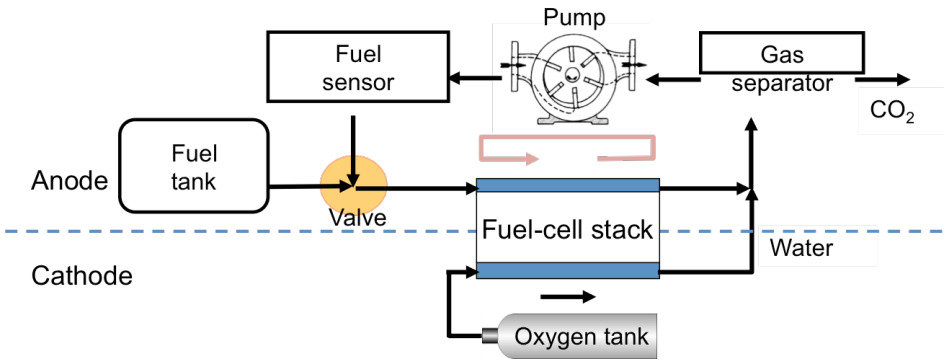


Figure 1: A fuel-cell system needs ancillary components to provide and regulate the fuel and oxidant in addition to the fuel-cell stack. In a miniaturized configuration, these supporting components take up significant portions of the total volume, posing a serious limitation against miniaturizing the system.

We have previously reported a self-pumping fuel cell that has an embedded ability to pump the liquid fuel within microfluidic channels, allowing one to miniaturize fuel cells (at least the anodic side) without the packaging penalty [22-23]. Unlike other passive fuel cells [9, 13, 24], the self-pumping fuel cell is an active fuel cell; it actively pumps to deliver fresh fuel from a reservoir, where fuel concentration is kept relatively constant. Utilizing the carbon dioxide byproduct on anode was the key idea of the self-pumping technology. By making the growing carbon dioxide bubbles to always expand from the inlet side to the outlet before being vented out, the fuel was pumped in one direction. Doing so enabled us to eliminate the mechanical pump and gas separator, as shown in Fig. 2. This method is in principle applicable and flexible to any kind of liquid fuel, as long as the fuel produces carbon dioxide as byproduct on anode. While the fuel was supplied through self-pumping system, oxygen was provided through air-breathing cathode directly from ambient air. Although the oxygen tank was eliminated, relying on oxygen

supply from air limited the application of the miniature fuel-cell system, because the system could not be stacked for higher power output.

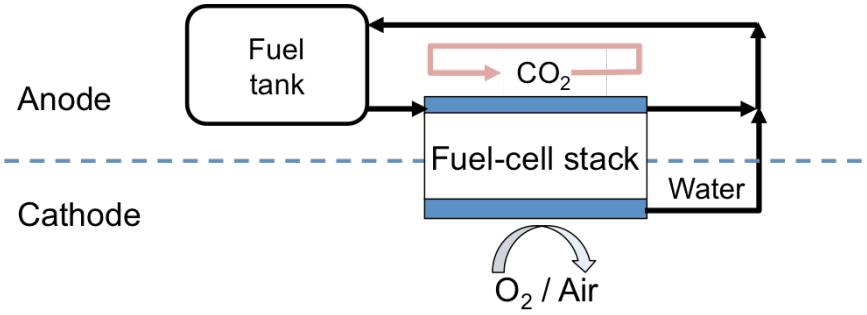


Figure 2: Simplified fuel-cell system previously developed from our group [23]. Oxygen is provided from the ambient air.

In this report, we first report the development of a O_2-generating plate that, when in contact with a hydrogen peroxide solution on one side, grows a thin layer of oxygen gas on the other side in a self-regulating manner. In pursuit of realizing a complete fuel-cell system, we then integrate the O_2-generating mechanism with our previously proven air-breathing fuel-cell system [23]. This unique oxygen supply takes up a much smaller volume than the existing designs, which would require ancillary components, such as a pressurized oxygen tank with a regulator. Elimination of the oxygen tank or the need to access the ambient air allows the fuel-cell system to be designed as a standard unit that can be easily stacked.

Mechanism:

The fuel-cell system reported in this paper, schematically illustrated in Fig. 3, was designed to integrate two main technologies—self-regulated fuel pumping and self-regulated oxygen supply—into one device. The top portion marked A, consisting of a fuel cartridge and a fuel channel, is essentially an air-breathing fuel-cell system developed in [23] and shown Fig. 2, which self-pumps the fuel in a self-regulating manner. The bottom portion marked B is an oxygen supply cartridge, which supplies oxygen directly to the gas diffusion electrode (GDE), i.e., the cathode, of the fuel channel in a self-regulating manner. The O_2-supply cartridge was developed to solve the problem of mixed potential in the O_2-generating surface in our preliminary study [25], as detailed in the Supplementary.

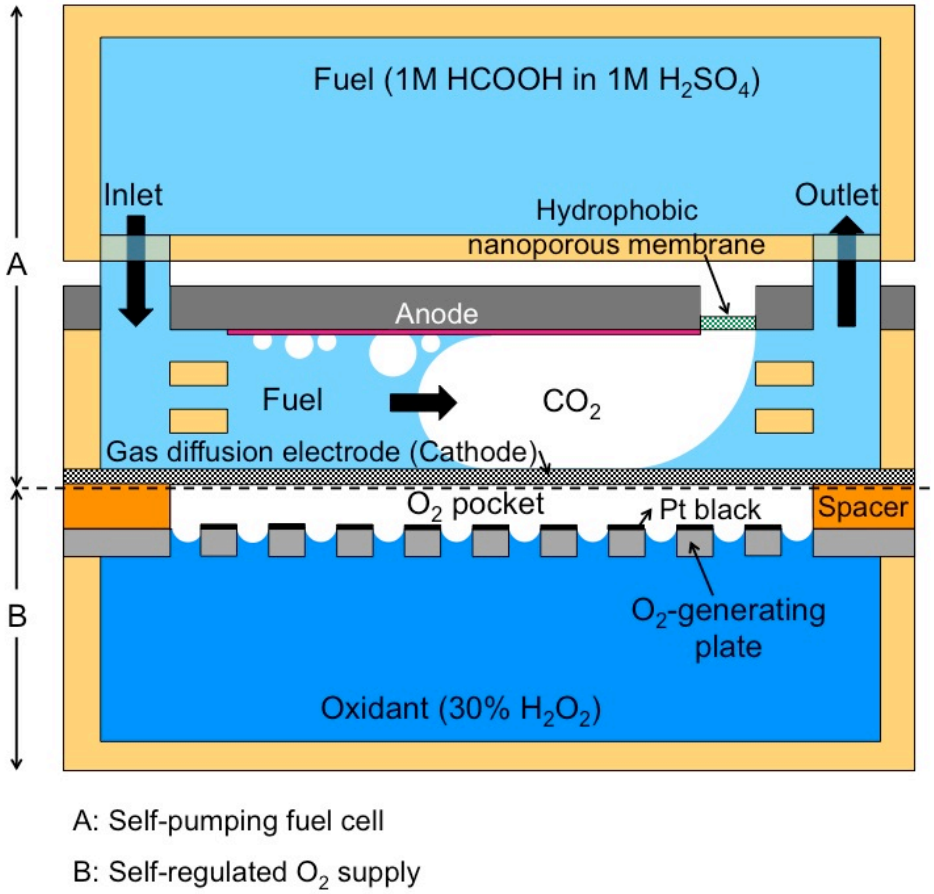


Figure 3: Schematic description of the proposed fuel-cell system, which integrates two technologies into one device: top portion marked A is the membraneless, self-pumping, air-breathing fuel-cell system [23] and the bottom portion marked B is the self-regulated, oxygen-generation mechanism inspired by [25].

Working mechanism of the fuel-cell system

In the top portion A of Fig. 3, the fuel in the fuel channel is pumped by directional growth during the fuel-cell reaction, following [22]. When the fuel-cell circuit is closed to draw the power, fuel-cell reaction begins to generate the electricity as well as carbon dioxide and water as byproduct. The bubbles cannot grow or move back to the fuel inlet because the constrictions in the channel near the inlet work as a check valve. The bubbles are only allowed to grow or move towards the outlet and vent through the hydrophobic nanoporous membrane. The resulting bubble movements actively pump the fuel in one direction while eliminating the carbon dioxide bubbles, only when the power is drawn, i.e., in a self-regulating manner.

In the bottom portion B of Fig. 3, the oxygen supply cartridge consists of a hydrophilic plate with microscale through-holes that wick the catholyte (30% hydrogen peroxide) from the

oxidant cartridge below the plate to the catalyst (Pt black) on top, where the hydrogen peroxide is decomposed into oxygen. Once the pocket between the O_2-generating plate and the cathode surface at the bottom of the fuel channel is filled with oxygen gas, the catalyst is dewetted of catholyte and ceases to generate oxygen. Once the oxygen gas is consumed and the catalyst is wet by H_2O_2 again, the oxygen decomposition resumes, i.e., the oxygen generation is self-regulated by demand.

In the proposed fuel-cell system (Fig. 3), the Pt catalyst on the O_2-generating plate and that on the gas diffusion electrode (GDE) have different roles. Unlike other fuel cells that utilize H_2O_2, in this design the cathode catalyst on GDE does not face H_2O_2 but face O_2 gas. Consider the O_2-generating plate defining the topside of the H_2O_2 cartridge. First, the H_2O_2-containing catholyte is wicked through the microscale holes in the plate to reach the catalyst on top of the plate. As the wicked H_2O_2 is decomposed to O_2 and bubbles grow to fill the space above the O_2-generating plate with an oxygen pocket, the cathode catalyst on the bottom of the GDE is covered with only O_2 gas so that the mixed potential due to H_2O_2 decomposition does not occur on the cathode. In other words, the cathode reduces O_2 to water, completing the fuel-cell reaction, while the O_2-generating plate decomposes H_2O_2 into O_2 and provides the pure gaseous O_2 to the cathode.

Fabrication:

Once established, fabrication of the proposed fuel-cell system is relatively simple compared to the existing micro fuel cells due to its simple construction without any moving part. The exploded schematic of Fig. 4 lists all the components of the fuel-cell system conceived in Fig. 3. Fabrication of the components for the fuel side of the system—the anode, cathode, and channel—was reported in [23]. For the rest, the fuel cartridge, the oxidant cartridges and the spacer plate were machined from a sheet of chemically inert plastic, polycarbonate, using a computer numerical control (CNC) milling machine and a manual mill. The O_2-generating plate was microfabricated from silicon.

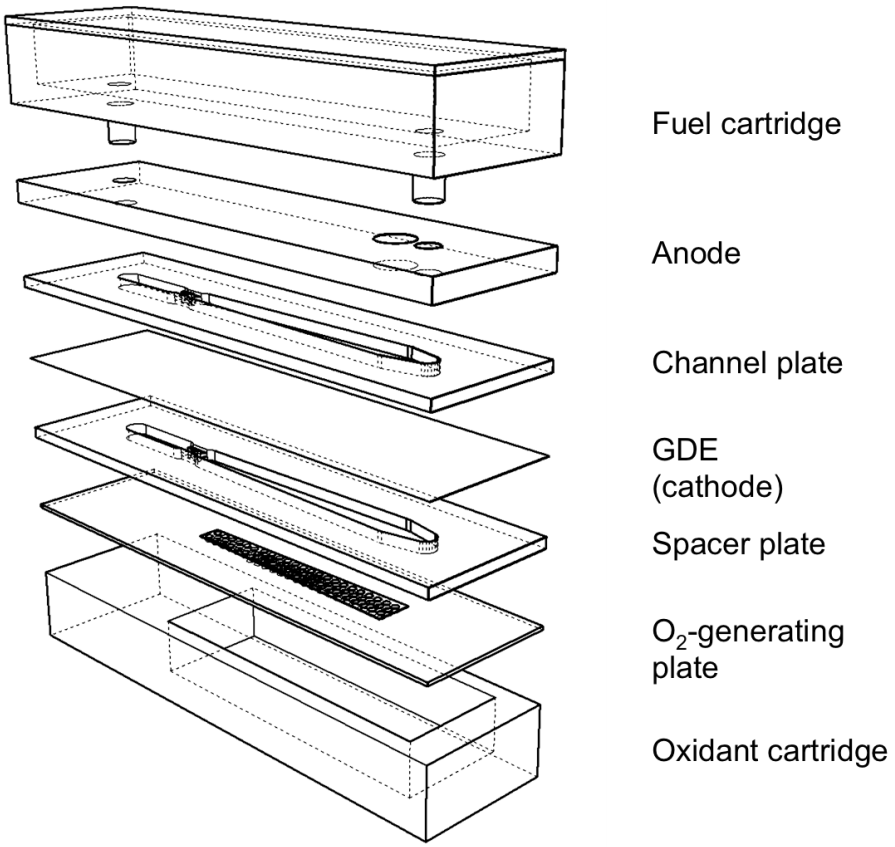


Figure 4: Drawing of the fuel-cell system in exploded view, showing all the solid components. The anode is machined from a graphite plate; the cathode is a commercially available gas diffusion electrode; and the O_2-generating plate is micromachined from silicon. Other components are machined from chemically inert polycarbonate sheets and blocks.

Fabrication of oxygen-generation plate

The top of the oxidant cartridge is an O_2-generating plate fabricated as summarized in Fig. 5. Starting with a 4" silicon wafer (500 μm thick), we first deposited a 3 μm-thick silicon dioxide by plasma-enhanced chemical vapor deposition (PECVD) and patterned an array of holes of 100 μm diameter and 200 μm pitch. After through-hole etching by deep reactive-ion-etching (DRIE) using the silicon dioxide as the masking layer, the silicon piece was removed of the remaining PECVD silicon dioxide then thermally oxidized. The oxidation made sure the through-holes were hydrophilic. After evaporating 20/200 nm Cr/Au seed layer, plating area was defined following the shape of active section in the channel. We electroplated Pt black on the defined area using 1 A/cm^2 for 10 seconds, which produced a material with large surface area for rigorous hydrogen peroxide decomposition. The plating solution was prepared by mixing 1 gram

of chloroplatinic acid (Sigma Aldrich) into 100 mL of deionized (DI) water and 30 μL of lead acetate (Sigma Aldrich). The fabricated O_2-generating plate is shown in Fig. 6. The optical pictures on the left column show the topside of the plate facing the cathode. The shape of the plated Pt black area was determined to match the shape of the fuel channel. The bottom side of the plate is the upper bound of the hydrogen peroxide (catholyte) cartridge. Successful deposition of Pt black with high surface area was confirmed under the scanning electron microscopy (SEM).

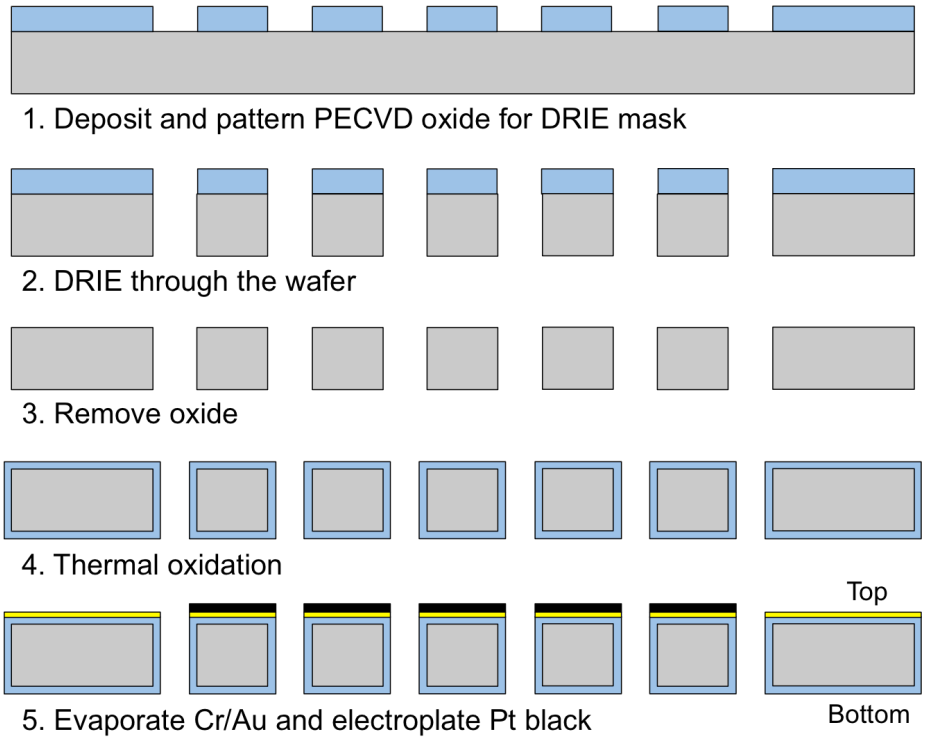


Figure 5: Process flow to fabricate the O_2-generating plate containing hydrophilic through-holes. Platinum black is electroplated only on top surface.

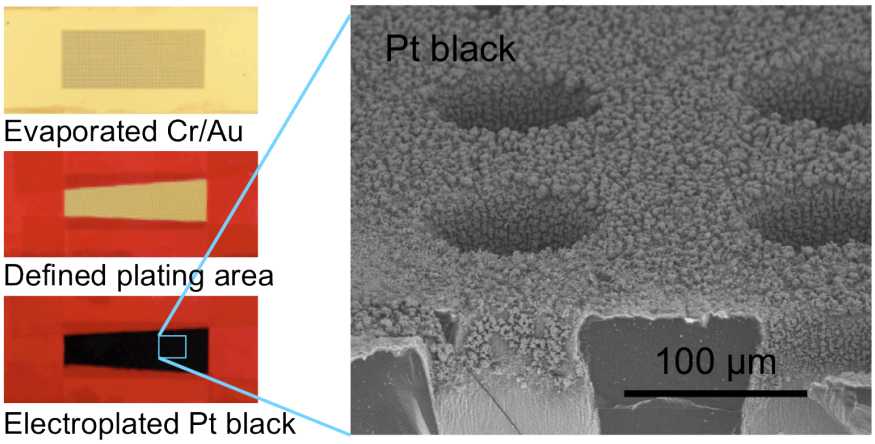


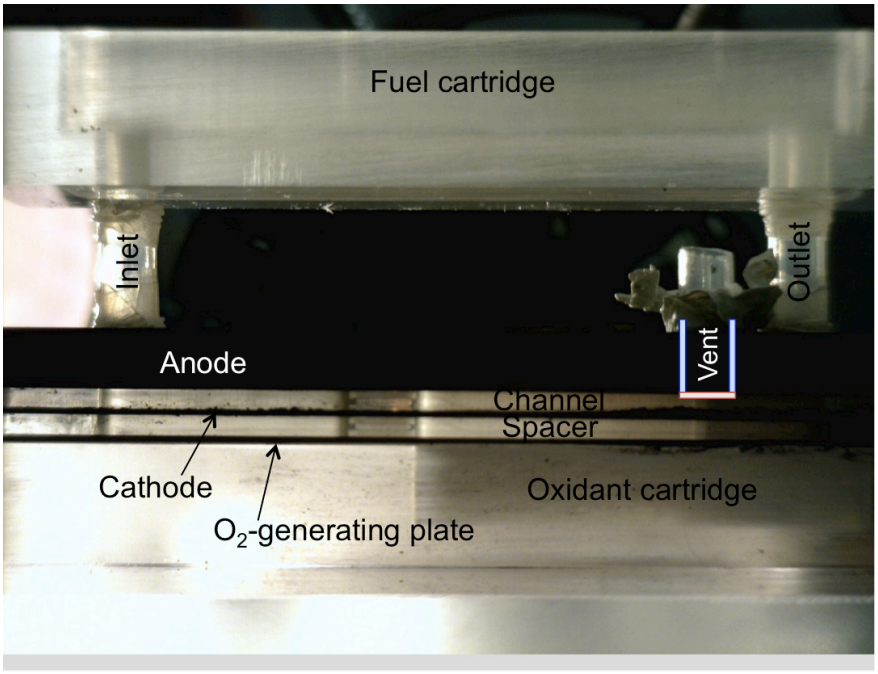
Figure 6: Optical and SEM pictures of the top surface of the O_2-generating plate fabricated in Fig. 5. The three optical pictures show the three sequential steps within the Stage 5 of Fig. 5, leading to the Pt black area in the shape of the fuel channel. After evaporating Cr/Au layer on a silicon piece of the Stage 4 of Fig. 5 (left-top picture) and manually defining the channel shape with an electrical tape (left-middle picture), a layer of Pt was electroplated on the exposed Au using high current density (1 A/cm^2) (left-bottom picture) which produces Pt of especially high surface area, as shown in the SEM image (right picture). The SEM image also shows the through-holes.

The above fabrication of the O_2-generating plate is much simpler than the preliminary version [25] because there is no need to deposit platinum black inside the micropockets shown in Fig. S1(a). Also, since the plate does not serve as a cathode anymore, the silicon wafer does not need to be highly conductive. Furthermore, for mass manufacturing in the future, the silicon plate with through-holes can be simply replaced with a porous glass plate, eliminating the photolithography and leaving only Cr/Au deposition and Pt black electro-deposition as the necessary steps.

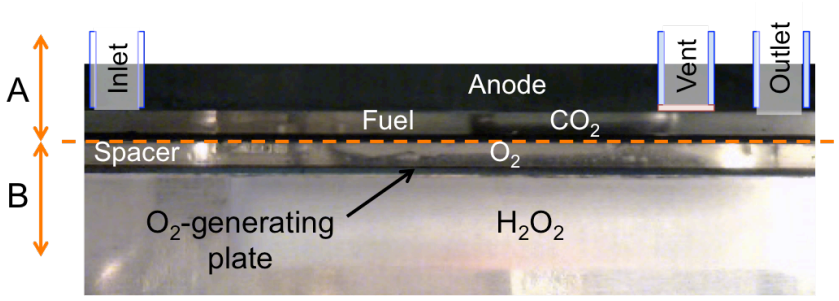
Assembly of fuel-cell system

After the components were fabricated, the three plates of anode, channel and cathode were assembled, and the venting hole was filled with a nanoporous venting plug (refer to [23] for detailed description of venting plug). Then, the fuel cartridge is mated. For the assembly, the plates were sandwiched and bonded with an adhesive gasket layer cut out from Parafilm® at 80 °C. The sealing was good enough to prevent any leakage from the assembly during the tests. However, the oxidant cartridge was not glued to the O_2-generating plate to access and refill the oxidant cartridge easily during the performance characterization. Instead, after refilling, we used

a mechanical clamp to attach the oxidant cartridge to the air-breathing fuel-cell system. The assembled device is shown in Fig. 7(a) at dry state without fuel and oxidant. The closer view of Fig. 7(b) taken during fuel-cell operation shows the role of each compartment in the fuel-cell system.



(a)



A: Self-pumping fuel cell

B: Self-regulated O_2 supply

(b)

Figure 7: Fully assembled fuel-cell system, combining the self-pumping fuel cell and the self-regulated O_2 supply in one device. (a) The picture shows the entire system including the fuel cartridge and the oxidant cartridges. (b) The picture is a snapshot of the fuel channel and oxygen pocket during fuel-cell operation. The CO_2 bubbles in the fuel channel and the O_2 bubbles in the O_2 gas pocket are visible from side of the fuel-cell system assembled of transparent plates.

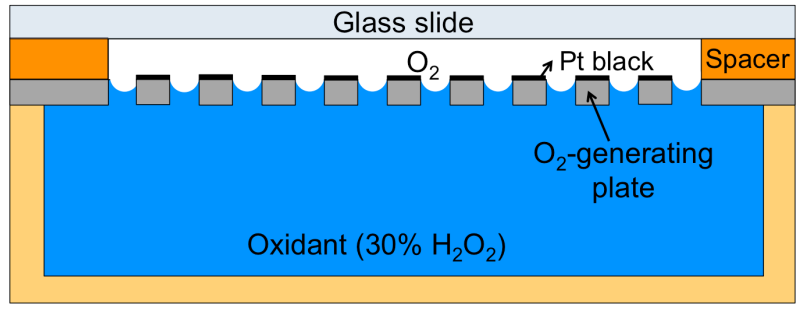
Experiments and results:

Verification of self-limiting oxygen generation

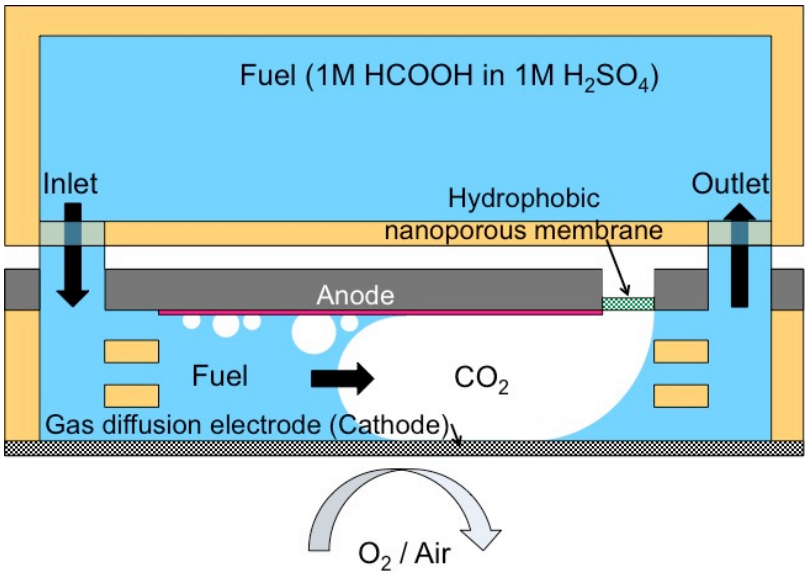
Generation of the oxygen gas was evaluated independently with the configuration shown in Fig. 8(a) before completing the fuel-cell system. After the O_2-generating plate was placed as the top plate of the oxidant cartridge, a spacer plate and a glass slide was added and fixed with a mechanical clamp. The glass slide was adopted to monitor the creation of oxygen bubbles and their gradual filling of the spacer to form an oxygen pocket. The oxidant cartridge was filled with 30% hydrogen peroxide. Rigorous oxygen generation and quick gas filling (~9 mL/min) of the pocket between the O_2-generating plate and the glass slide has been observed, as shown in Fig. 9. Oxygen generation ceased after the O_2 pocket dewetted the entire Pt surface. Once the oxygen pressure reached the clamping pressure on the assembly, oxygen was vented out, beginning the next cycle of H_2O_2 wicking and rigorous oxygen generation. A slight overpressure of the O_2 pocket would help keep the catalyst surface dry in the fully assembled fuel-cell system.

Performance of fully assembled fuel-cell system

The current and voltage output from the fuel-cell system was monitored using a power supply (Keithley 2400) connected to a computer for recording. Before fully assembling the fuel-cell system, the subsystem of an air-breathing fuel-cell system was first evaluated to independently assess the self-pumping of the fuel by exposing the GDE cathode to the ambient air, as shown in Fig. 8(b). After fully assembling the system, the stable OCP of a fully assembled fuel-cell system reached 0.6-0.7 V, as shown in Fig. 10. For the polarization curve, the fully assembled fuel-cell system showed similar performance compared with the air-breathing fuel-cell system. The maximum power density of 18.8 mW/cm^2 was obtained, which is slightly improved (by 12.5 %) from the previously reported data of air-breathing fuel cell [23]. Not only the power density slightly improved but also the OCP remained high at 0.6-0.7 V without exposing the cathode to air or using a bulky oxygen tank.



(a)



(b)

Figure 8: Evaluations of the subsystems of the fuel-cell system. (a) A glass slide was assembled on the oxidant cartridge, and generation of oxygen bubbles and gas filling of the pocket above the O_2-generating plate were observed from top through the glass slide. (b) An air-breathing fuel-cell system was tested to confirm the self-pumping in the fuel channel. A complete fuel-cell system of Fig. 3 is obtained by assembling the oxidant cartridge of (a) without glass slide and the air-breathing fuel-cell system of (b) into one.

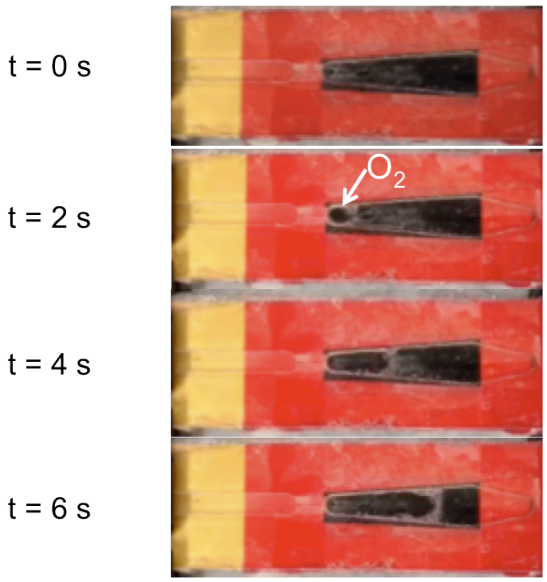


Figure 9: Snapshots of rigorous O_2 generation during testing of oxygen supply subsystem of the fuel-cell system. Rapid O_2 generation (~ 9 mL/min) was observed, followed by a pause and start of the next cycle.

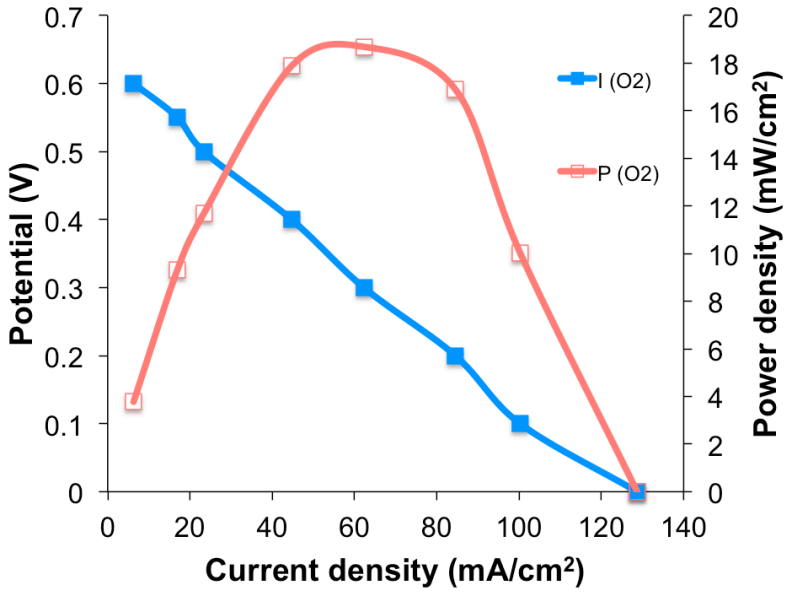


Figure 10: Polarization curve drawn from the fully assembled fuel-cell system. Blue curve corresponds to the potential axis and red curve corresponds to the power density axis. The measurements showed 0.65 V OCP and 18.8 mW cm−2 peak power density at 0.3 V.

Continuous operation of fully assembled fuel-cell system

The fully assembled fuel-cell system was tested for continuous operation with 5 mL of 1M formic acid in 1M sulfuric acid in the fuel cartridge and 1.5 mL of 30% H_2O_2 in the oxidant

cartridge. Under the external load of 0.2 V, which is close to the voltage at the peak power density, the fuel-cell system continued to operate until the oxidant was depleted of oxygen, as shown with the black curve named "Fully assembled fuel-cell system" in Fig. 11. The current-generation pattern resembled that of the air-breathing fuel-cell system [23], as expected. During the operation, the fuel was observed to self-pump in the fuel channel, and the oxygen bubbles were found growing rigorously to form the oxygen pocket, as shown in the Supplementary Video. These dynamic activities were visible from the side of the assembled system because most of the components were made from a transparent plate.

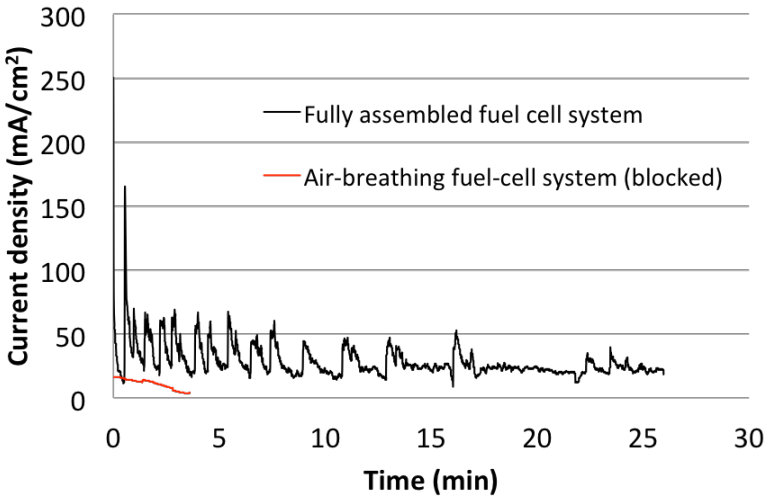


Figure 11: Operation of the fully assembled fuel-cell system with load of 0.2 V lasted over 25 minutes, as shown in black. The system generated the current by steady self-pumping until the oxidant cartridge was depleted of oxygen. The fully assembled fuel-cell system, supplied of O_2 internally, showed cyclical current generation, verifying the self-pumped operation even when blocked of the ambient air to simulate the stacked condition. Despite the current decrease after the initial couple of self-pumping cycles, the cyclical pattern of the current density indicates continuous fuel-cell operation. Note the power generation is periodic in this single-channel device but would be smoother if the system is of multiple channels. In comparison, when blocked of the ambient air to simulate the stacked condition, operation of the air-breathing fuel-cell system lost the current density quickly and lasted only 3-4 minutes, as shown in red.

To demonstrate the viability of the proposed fuel-cell system in stacked conditions, also measured was the current density of an air-breathing fuel-cell system (Fig. 8(b)) covered with a glass slide at the bottom to simulate a stacked condition. Since the cathode of the air-breathing fuel-cell system was blocked from the ambient air, the current density output was lowered significantly, as shown with the red curve named "Air-breathing fuel-cell system with air

blocked". Also, no self-pumping was observed in the fuel channel even when the load to the system was removed for maximum current flow. The slight current output was because the glass slide was placed on and not sealed to the cathode for this test.

A typical fully assembled fuel-cell system fabricated in this work operated for 15-30 mins, after which the cathode catalyst started to get deactivated. When reactivated by applying reverse potential [26], the fuel-cell system resumed working until it was deactivated again after another period of current generation. However, the repeated deactivation and reactivation deteriorated the current output gradually over time. A proper reactivation technology or a novel catalyst that remains active throughout fuel-cell operation would greatly extend the operation lifetime of the current fuel-cell system. Lastly, the current prototype device has been built with oversized solid components and generous spaces between them to ease the machining, manual assembly, and visualization. Even with the current catalyst, optimized design and professional fabrication alone are anticipated to increase the energy density and power density of the device by 2-3 orders of magnitude to the level of many batteries. Additional innovations, such as in catalyst, would be needed to realize the full capability of the current fuel-cell system and ultimately outperform Li-ion batteries.

Conclusion:

A miniature fuel-cell system free of any ancillary component and stackable for higher power output has been developed. An oxygen-generating plate effective for system integration has been newly developed to supply pure oxygen gas directly to the previously proven air-breathing fuel-cell system within the full system. The resulting system complete with the self-regulated oxygen supply showed improved power density compared with the previous air-breathing counterpart. This unique oxygen supply takes up a dramatically smaller volume than the existing designs, which require ancillary components, such as a pressurized oxygen tank with a regulator. Not using the oxygen in ambient air, this fuel-cell system can be stacked in multiple to satisfy higher power demands. Overcoming the packaging penalty of miniaturization, the reported fuel-cell system is expected to be capable of eventually outperforming the current Li-ion batteries. Despite the need for much additional advancement before harnessing the full capability in power generation, this paper nevertheless verifies the viability of the proposed fuel-cell system by

demonstrating the fuel pumping and oxygen supply all in self-regulating manners within one physical unit that is stackable and scalable.

Acknowledgments:

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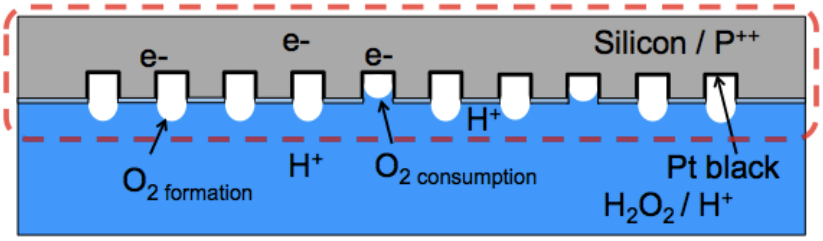
Supplementary:

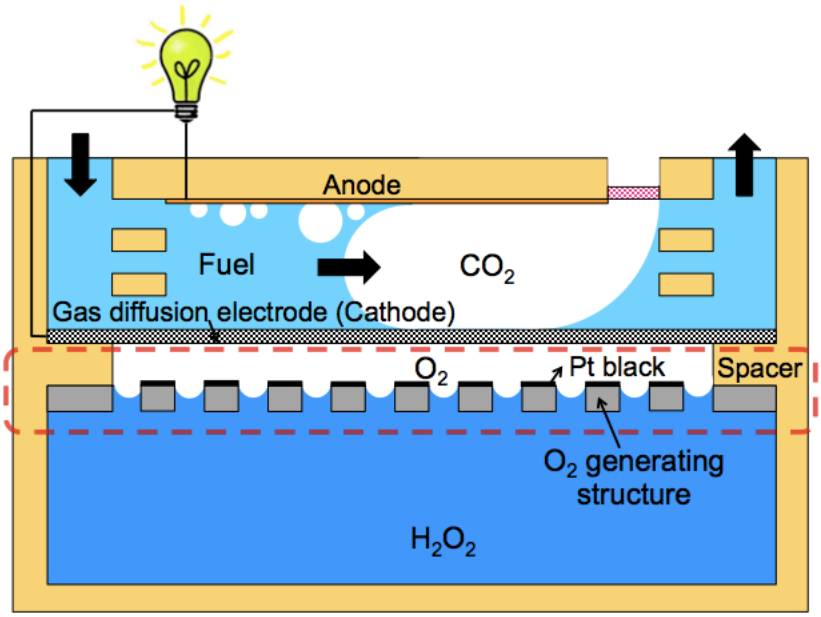
Mixed potential issue on O_2-generating plate

In order to integrate the oxygen-generating structure as a cathode in the fuel-cell system, we had to first solve the mixed potential issue in the cathode. When the oxygen supply was integrated, the cathode structure in its early configuration [25] had to serve as both oxygen generation (giving electron) and consumption (receiving electron). In this early design, the issue of mixed potential turned out to be unavoidable.

In order to address the mixed potential issue, we developed a new design that separates the oxygen generation from the oxygen consumption on the cathode. Figure S1(a) explains the mechanism of the current design, modified from the previous version (Fig. S1(b)) [25]. A silicon-based oxygen generating structure was kept at a distance away from the cathode by a spacer to blanket the backside of air-breathing cathode with a layer of oxygen. In this way, the gas diffusion electrode (i.e., cathode) was in direct contact with high concentration of oxygen for sufficient supply even at high consumption. More importantly, the mixed potential issue is solved since hydrogen peroxide decomposition (i.e., electron giving) and oxygen reduction (i.e., electron receiving) are occurring at their designated structures.



(a)



(b)

Fig. S1: Drawings describing how the mixed potential issue of (a) the earlier design, where the gaseous O_2 was generated and consumed at the same structure [25], was solved in (b) the current design, where the cathode and the O_2-generating plate are separated by a pocket filled with gaseous O_2.

Video: Miniature_fuel_cell_system.wmv

The video clip starts with a full side view of the fuel-cell system in action and continues with a cropped view focusing on the fuel channel and O_2 pocket. The fuel is seen being pumped by the CO_2 bubbles, and O_2 gas is seen generated and consumed.