SELF-CONTAINED OXYGEN SUPPLY
FOR SELF-REGULATING MINIATURE FUEL CELL

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Abstract: We report a microstructure, which if electrified in a hydrogen peroxide solution covers its top with a thin layer of oxygen gas in a self-regulating manner. In pursuit of realizing a full fuel cell with no moving part, we have successfully developed such an oxygen-generating surface and integrated it as a direct oxygen supply to the cathode of our previously developed miniature fuel cells. The resulting fuel cell showed a significant increase in current density, compared with the previous air-breathing counterpart. This unique oxygen supply takes up a much smaller volume than the existing designs, which require ancillary components, such as a pressurized oxygen tank with a regulator. In designing a fully functional (i.e., self-sustainable) miniature fuel cell, elimination of the need to access the ambient air allows a stackable configuration for higher power demands.

Keywords: Miniature fuel cell; Micro fuel cell; Self-regulating oxygen supply; Stackable fuel cell

INTRODUCTION

Although there has been a flurry of activity in developing microfluidic fuel cells for its promising future with high theoretical energy density, the difficulty in miniaturizing and packaging the ancillary components (e.g., pumps, regulators) hindered fuel cells from becoming a compact product to compete with batteries. The inactive ancillary components would occupy a significant volume in the fuel cell – the so-called "packaging penalty," reducing the volume for active fluids (e.g., fuel and oxidant). With only a small amount of active fluids in the system, the advantage of high energy density is simply lost. Furthermore, the complexity of integrating the moving ancillary components would make the miniature system expensive and unreliable.

Our approach in developing miniature fuel cells is to systematically eliminate all the ancillary components required for fuel cell operation in order to overcome the above-mentioned problems. Furthermore, a self-regulated operation, i.e., consuming the fuel only when there is an external load without a discrete unit for sensing and feedback, would be an ideal design. Previously, we have successfully eliminated major ancillary components, liquid fuel pumps and gas separators and oxygen tanks, by designing bubble pumping mechanism inside the channel and employing an air-breathing cathode [1-2]. In the bubble pumping mechanism, carbon dioxide naturally generated inside the anodic channel forms gas bubbles that fill and directionally grow inside the channel towards outlet. Bubbles grow until they reach the hydrophobic porous membrane, then vent out to the atmosphere without liquid leakage, inducing a new stream of fuel into the channel to start the new cycle of bubble pumping [1]. We have also avoided the use of oxygen tank by adopting an air-breathing cathode [2]. Although the air-breathing simplifies the design of fuel cells, it would not provide enough air if the fuel cells are to be stacked to power a larger system in the future [3-5].

Until now, performance of the miniature fuel cells without pressurized oxygen tank (e.g., the air-breathing fuel cells) suffered from limited oxygen supply. The efforts to seek for alternative oxygen sources have not been fruitful. Ideally, high concentration of oxygen should be supplied actively in a constrained structure even when the cells are stacked directly on top of each other. In pursuit of a higher concentration oxygen source, hydrogen peroxide has been considered promising because of its advantage of compact storage in a liquid state and fast decomposition into oxygen [6-8], compared with the oxygen dissolved in aqueous streams [9].

Recently, we have reported a self-contained oxygen generation and consumption cathode, which adopted hydrogen peroxide in a microfluidic fuel cell, in order to solve the oxygen deficiency problem (Fig. 1(a) [10]). Complementing the self-pumping fuel supply [1-2], the self-regulated oxygen supply decomposed hydrogen peroxide into oxygen in catalyst micropockets and utilized the oxygen directly for cathodic reaction. Oxygen bubbles were created on board spontaneously when hydrogen peroxide met the catalyst deposited inside the microstructured pockets designed on the cathode. However, when the oxygen supply was integrated with an anodic fuel cell to build a full fuel cell, a single structure served as both oxygen generation and consumption. In this design, unfortunately, the issue of mixed potential turned out unavoidable. In order to address the mixed potential issue, here we introduce a new design that

separates the oxygen generation from the oxygen consumption on the cathode.

MECHANISM

Figure 1(a) explains the mechanism of the current design, modified from the previous version (Fig. 1(b)) [10]. A silicon-based oxygen generating structure is set some distance away from the cathode by a spacer to blanket the backside of air-breathing cathode with a layer of oxygen and providing a direct contact of oxygen to gas diffusion electrode (i.e., cathode). 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.

Instead of having micropockets, the current design consists of hydrophilic through holes to wick catholyte (3% hydrogen peroxide in DI water) to the catalyst (Pt black) surface, where hydrogen peroxide is decomposed into oxygen. Once the gap between the oxygen-generating structure and cathode is filled with oxygen gas, the catalyst is covered with the gas and ceases to generate more oxygen until it is consumed to expose catalyst to hydrogen peroxide containing catholyte.
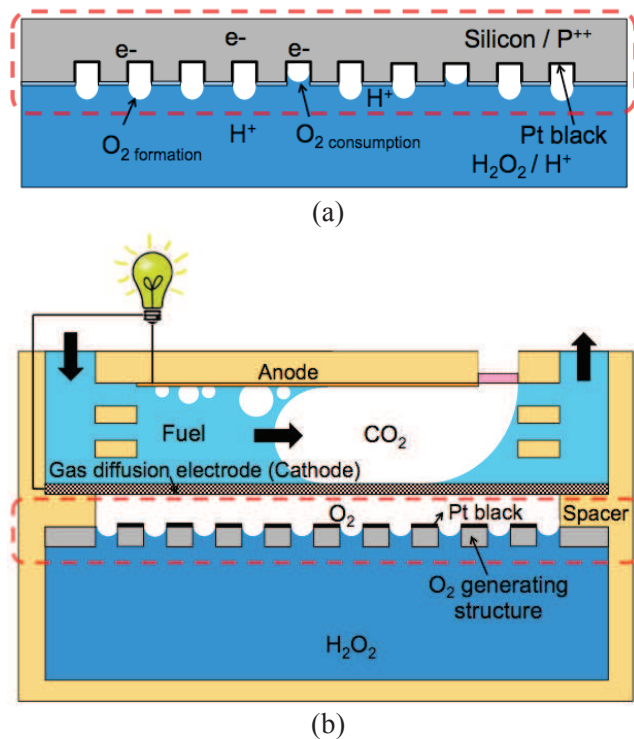

(a)

(b)

Figure 1. Schematic design of (a) previously reported design [10] compared to (b) the full fuel cell combining the self-regulated oxygen supply directly on cathode of self-pumping fuel cell.

FABRICATION

The fabrication of oxygen-generation structure has become simpler because there is no need to deposit platinum black inside the pockets anymore (Fig. 2 vs. Fig. 2 of [10]). Previously, in order to deposit Pt black inside the micropockets, uniform coating of gold seed layer was important before the platinum-plating step. Also vacuuming the structure before the electroplating was important to remove the air trapped inside the structure and to ensure that the plating solution wets the pockets for reliable plating process. In comparison, in the current design we only need platinum black on the topside of the structure, making the process muck simpler and reliable. Starting with a 4" silicon wafer (500 μm thick), we first deposit and pattern a 3 μm silicon dioxide into arrays of 100 μm holes with 200 μm pitch to mask the subsequent DRIE. After through-hole etching by DRIE, the wafer is thoroughly cleaned and thermally oxidized. The oxidation enables the through-holes of the structure to wick the hydrogen peroxide through the holes to the Pt black on the other side by its hydrophilic nature. After evaporating 20/200 nm Cr/Au seed layer, we electroplated a high surface area Pt black on a defined area at 1 A/cm^2 for 10 seconds for rigorous hydrogen peroxide decomposition. The plating solution was prepared by mixing 1 gram of chloroplatinic acid (Sigma Aldrich) into 100 mL of DI water and 30 μL of lead acetate (Sigma Aldrich).

Since the microstructures do not serve as a cathode anymore, the silicon wafer does not need to be highly conductive anymore. Furthermore, in case of mass manufacturing, the structure made by the fourth step in the process flow can be simply replaced with a porous glass slide, leaving only Cr/Au deposition and Pt black electro-deposition.

The fabricated oxygen-generating structure is shown in Fig. 3. The images on the left column show the topside of the structure facing a gap for cathode, indicated in Figs 1 and 2. The shape of the plated Pt black area is determined to match the shape of the channel for bubble pumping. The bottom side is a thermal oxide for hydrophilic structure, where it faces the catholyte with hydrogen peroxide. Successful Pt black deposition with high surface area was checked under the microscope.
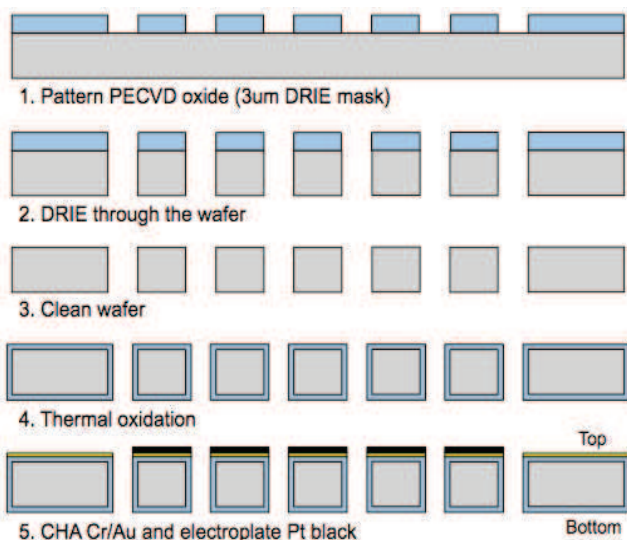
Figure 2. Process flow to fabricate oxygen generating structure with hydrophilic through holes for slow supply of hydrogen peroxide. Pt black is electroplated for hydrogen peroxide decomposition.
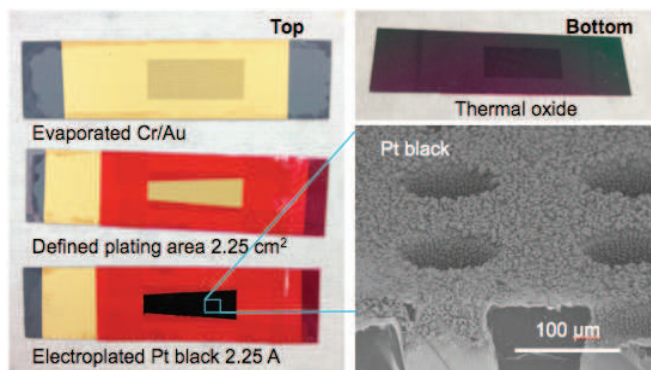

Figure 3. Images of fabricated oxygen generating structure. Top surface (indicated in Fig. 2) has Pt black in a shape corresponding to the cathode, and bottom surface has thermally grown oxide for hydrophilic wetting of hydrogen peroxide inside the holes.

EXPERIMENT

The oxygen generation from the structure has been tested by assembling the structure onto a hydrogen peroxide reservoir and placing a glass slide above the structure (Fig. 4a). Spacers placed between the substrate and the glass slide formed a gap that matched the height of the microchannel where the fuel is self-pumped for anodic action. The result has been observed from the top through the glass slide by monitoring the oxygen layer created and dewetting the spacer gap.

Furthermore, we made a preliminary testing setup of a full fuel cell by assembling the oxygen supply below the self-pumping fuel cell with air-breathing cathode [2], so that the fuel cell runs with a direct supply of oxygen generated from the structure (Fig. 4b). Fuel cell testing was performed with and without the oxygen generating structure attached on the bottom of cathode. The testing was monitored using Keithley 2400 power supply connected to a computer to record the current and voltage output from our full fuel cell.

(a)
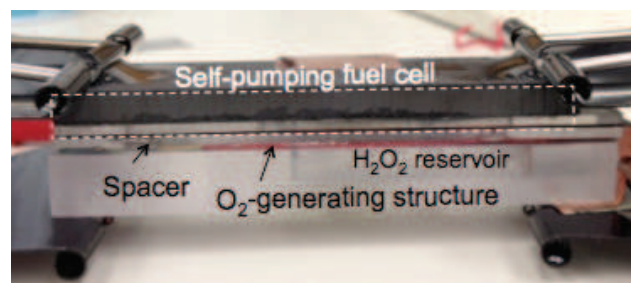
(b)

Figure 4. Picture of (a) oxygen bubble filling the gap between the oxygen generaing structure and a glass slide on top (top view), and (b) oxygen generating structure assembled with self-pumping fuel cell for direct oxygen supply to the cathode (side view).

RESULTS AND DISCUSSION

In the first preliminary testing of oxygen supply in the fabricated structure (Fig. 4a), rigorous oxygen generation and quick gas filling of the gap of ~9 mL/min have been observed using 7.5% hydrogen peroxide in DI water. Oxygen generation ceased when the gas filled the gap completely so the Pt gets fully dewetted. However, sealing of the oxygen-filled gap is of great importance. If the generated oxygen builds up enough pressure and leaks between the plates, the next cycle of hydrogen peroxide wicking would occur prematurely and the stored oxygen be wasted during the storage stage.

The second testing of the full fuel cell showed

that the miniature fuel cell integrated with the oxygen supply performs better than the fuel cell that breathed oxygen from the ambient air [2], producing a 63 % higher current density (Fig. 5).
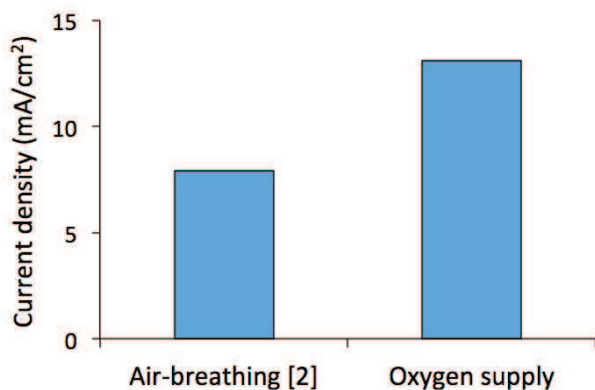

Figure 5. Preliminary data of maximum current density drawn from the integrated full fuel cell compared with the air-breathing full fuel cell [2].

CONCLUSION

We have been continuing our effort to realize a full fuel cell without any ancillary component. The recently reported self-regulated oxygen generation has been modified to integrate in a full fuel cell. The preliminary results showed the feasibility of the method. The simple yet powerful fuel cell of a solid-state (except the active fluids) construction, i.e., free of any ancillary component, makes the miniature fuel cell self-sustainable in a small volume compared with the existing design that requires a mechanical pump and a hydrogen gas tank or a reformer. Furthermore, elimination of the need to access air for oxygen breathing suggests that the miniature fuel cell may be configured stackable for higher power demands in the future.

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