Short communication

Rapid fabrication of microfluidic polymer electrolyte membrane fuel cell in PDMS by surface patterning of perfluorinated ion-exchange resin

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ABSTRACT

In this paper we demonstrate a simple and rapid fabrication method for a microfluidic polymer electrolyte membrane (PEM) fuel cell using polydimethylsiloxane (PDMS), which has become the de facto standard material in BioMEMS. Instead of integrating a Nafion sheet film between two layers of a PDMS device in a traditional "sandwich format," we pattern a perfluorinated ion-exchange resin such as a Nafion resin on a glass substrate using a reversibly bonded PDMS microchannel to generate an ion-selective membrane between the fuel-cell electrodes. After this patterning step, the assembly of the microfluidic fuel cell is accomplished by simple oxygen plasma bonding between the PDMS chip and the glass substrate. In an example implementation, the planar PEM microfluidic fuel cell generates an open circuit voltage of 600–800 mV and delivers a maximum current output of nearly 4 μA. To enhance the power output of the fuel cell we utilize self-assembled colloidal arrays as a support matrix for the Nafion resin. Such arrays allow us to increase the thickness of the ion-selective membrane to 20 μm and increase the current output by 166%. Our novel fabrication method enables rapid prototyping of microfluidic fuel cells to study various ion-exchange resins for the polymer electrolyte membrane. Our work will facilitate the development of miniature, implantable, on-chip power sources for biomedical applications.

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1. Introduction

For increasingly many applications, such as powering portable electronic devices and other miniaturized MEMS devices, polymer electrolyte membrane fuel cells (PEMFCs) in microfluidic chip format are gaining popularity as future power sources [1,2]. Although silicon is more widely used due to the robustness of the material and the standard fabrication method, polydimethylsiloxane (PDMS) is gaining wider use, especially in BioMEMS applications, due to material properties such as ease and rapidity of replication in non-cleanroom environments, biocompatibility, and flexibility. The conventional approach to building a microfluidic fuel cell is to seal an ion-selective membrane sheet between two layers of the device in either a bipolar or a planar design. However, this integration strategy has an inherent leakage problem [3] and requires permanent mechanical clamping to hold the sandwiched structure in place [4]. There have also been attempts to replace the ion-selective membrane by a laminar flow junction inside the microchannel [5,6]. However, such strategies need a high flow rate of the fuel

and oxidant in the range of few hundreds of μL min^{-1} to maintain the liquid junction, thus making it necessary to drive fluids by methods like syringe pumping. By adopting a planar fuel cell design approach [4] in more biologically relevant PDMS material, we patterned a submicron-thick Nafion membrane on a glass substrate instead of sandwiching a thin Nafion sheet. Due to the flexibility of the PDMS material, which has a Young's modulus of 360–870 kPa, Nafion membranes up to a thickness of ~400 nm can be tightly sealed between the PDMS chip and glass substrate by standard oxygen plasma bonding. From a fabrication point of the view, the surface patterning method can be seamlessly integrated into a standard microfabrication process flow and allows simple and rapid in-plane integration of the Nafion membrane into a PEM microfluidic fuel cell without cumbersome clamping. Our approach facilitates integration of microfluidic fuel cells into existing BioMEMS devices as on-chip power sources. Furthermore, it makes possible to build massively parallel arrays of microfluidic fuel cells.

2. Experimental methods

We used a standard soft lithography technique to fabricate the microfluidic fuel cell in PDMS (Sylgard 184, Dow Corning Inc., Mid-

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(a) Fabrication steps

(b) Micro flow patterning
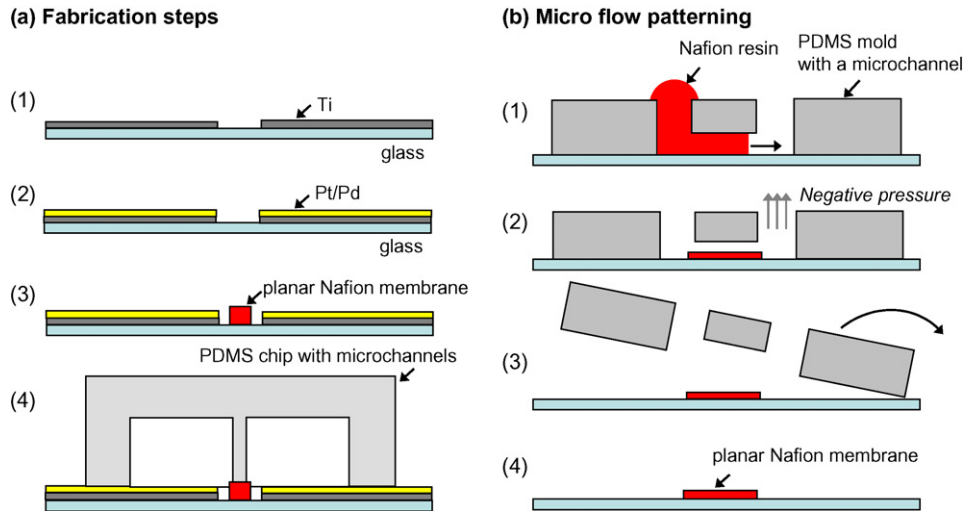
Fig. 1. (a) Fabrication scheme: (1) deposition of 20 nm Ti seed layer, (2) successive deposition of 50 nm Pt and 50 nm Pd electrodes, (3) patterning of a planar Nafion membrane between the electrodes, (4) plasma bonding of a PDMS device on top of the patterned glass substrate. (b) Principle of the microflow patterning technique: (1) filling of a reversibly bonded PDMS microchannel with Nafion resin, (2) applying negative pressure to flush the Nafion resin through the microchannel completely, (3) removal of the PDMS mold, (4) curing of the patterned resin on a hotplate at 95 °C for 5 min.

land, MI). Fabrication of the microfluidic fuel cell includes the following fabrication steps: (1) master fabrication in SU-8, (2) PDMS pouring/curing, (3) depositing electrodes on a glass substrate, (4) surface patterning of Nafion resin between the electrodes and (5) irreversible bonding of a PDMS chip with microchannels and a Nafion-patterned glass substrate via oxygen plasma bonding. Fabrication steps (3–5) are shown in Fig. 1a. As for the electrodes, we deposited a pair of Pt/Pd electrodes on the pyrex wafer using a standard e-beam lift-off process. First a 20 nm layer of Ti was deposited as an adhesion layer, then 50 nm of Pt and 50 nm of Pd were successively deposited to establish a catalyst layer on the electrode. To pattern a Nafion resin between the electrodes we used a microflow patterning technique. This technique is shown schematically in Fig. 1b. For this step we positioned a PDMS mold with a microchannel (100 µm deep, 250 µm wide, and 10 mm long) between the two electrodes and reversibly bonded it to the glass substrate. Then we filled the microfluidic channel with 1 µL of a low-viscosity Nafion resin (5 wt% in lower aliphatic alcohols and water containing 15–20% water, Sigma–Aldrich) using capillary pressure. To reduce the thickness, negative pressure was applied at the other end of the microchannel. When the Nafion resin was completely flushed out of the channel, the glass plate was heated at 95 °C for 5 min. After the Nafion resin was fully cured, the reversibly bonded PDMS mold was peeled off and a submicron-thick membrane with a thickness of 200–400 nm was obtained. Finally, a PDMS device with microchannels was bonded on top of the patterned glass substrate by standard oxygen plasma bonding. The assembled device was heated to 70 °C for 12 h to achieve higher bonding strength between the PDMS device and the patterned glass substrate. A single microfluidic fuel cell after assembly via plasma bonding is schematically shown in Fig. 2.

To characterize the performance of a single fuel cell device, we used 8.8 M formic acid (HCOOH) as the fuel and 10 mM potassium permanganate ($KMnO_4$) as the oxidant at ambient temperature. Formic acid has proven to be a good alternative fuel to methanol [7,8]. The fuel and the oxidant can be delivered from pipette tips using atmospheric pressure, or alternatively by a syringe pump via inserted tubing. To achieve constant flow rates of the fuel and oxidant, we used a syringe pump (Harvard Apparatus, Holliston, MA).
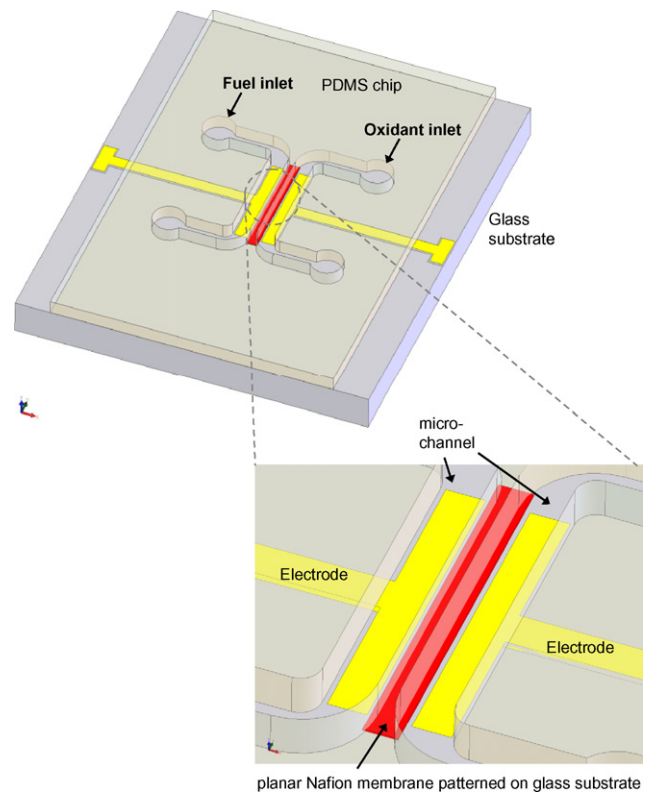
Fig. 2. Schematic of a microfluidic fuel cell with a planar ion-selective membrane between the electrodes. (Gap between the two microchannels: 100 µm; gap between the electrodes: 400 µm; width of the Nafion membrane: 250 µm; area of the electrode: 0.7 mm (width) × 9.6 mm (length) = 6.72 mm^2).

3. Results and discussion

A Nafion membrane patterned using the microflow technique, described in Section 2, is shown in the SEM image of Fig. 3a. Up to a thickness of 400 nm there was no visible gap between the planar Nafion membrane and the PDMS device sealing from the top. A single planar microfluidic fuel cell after the final assembly via
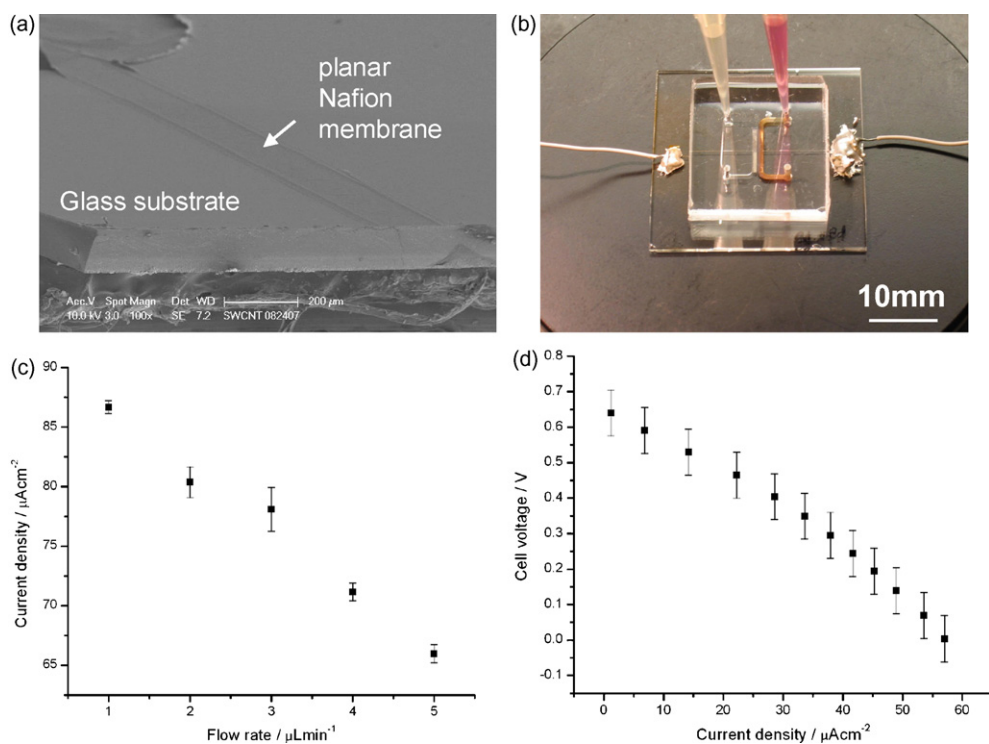
Fig. 3. (a) SEM image of a planar Nafion membrane patterned on a glass substrate. (b) Single microfluidic fuel cell in PDMS. Formic acid as the fuel was delivered to the left inlet while potassium permanganate as the oxidant was delivered to the right inlet. (c) Current density versus the flow rate of the fuel and oxidant. (d) Characteristic voltage–current density profile of a single microfluidic fuel cell.

plasma bonding is shown in Fig. 3b. Measurements of current density at different flow rates of the fuel and oxidant are plotted in Fig. 3c. As this figure indicates, the current density was a decreasing function of flow rate. The maximum current density achieved

was $86.66\,\mu A\,cm^{-2}$ (the total current output was $5.82\,\mu A$) at a flow rate of $1\,\mu L\,min^{-1}$. This result is directly related to shorter residence times of protons reaching the cathode at higher flow rates. Using a potentiostat (AMETEK Princeton Applied Research
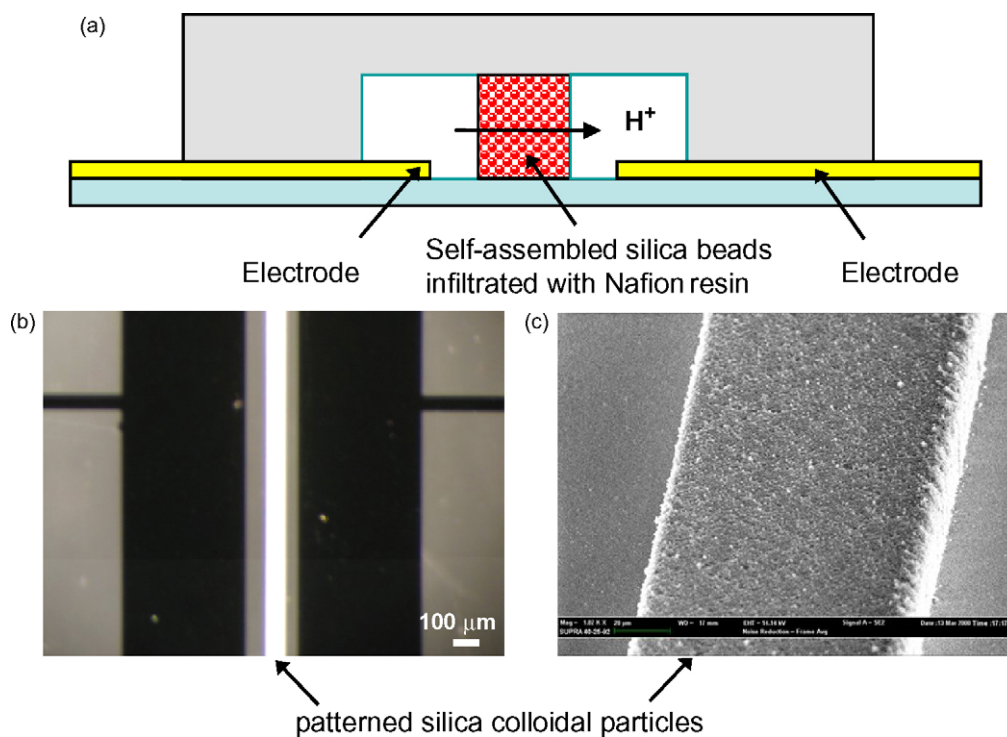
Fig. 4. (a) Increase of the fuel cell efficiency by increasing the thickness of the proton-exchange membrane via self-assembled silica colloidal array infiltrated with Nafion resin. (b) Self-assembled silica colloidal array between the electrodes. (c) SEM image of the patterned silica colloidal array (900 nm silica beads).

263A, Oak Ridge, TN), we also measured the I–V curve at a constant flow rate of 0.5 μL min^{-1}. As shown in Fig. 3d, we achieved an open circuit voltage V_{open} of 600–800 mV. The variable OCV was due to the thickness variation of the patterned Nafion membrane that can vary between 200 nm and 400 nm. Also, the device-to-device variation of the plasma bonding strength between the PDMS chip and Nafion membrane can lead to a variation of the OCV. The maximum current density achieved was 61.8 μA cm^{-2} (the total current output was 4.15 μA). Compared to the performance of a similar planar device described in [4], the current density of our planar device was approximately 16 times lower while the open circuit voltage was twice as high. One reason for these differences is that the electrode of our device (6.72×10^{-2} cm^2 compared to 1.8×10^{-2} cm^2 in [4]) was clearly oversized for the planar design. The effective area of the electrode that contributes to current generation in the planar design is probably only a small portion in close proximity to the Nafion membrane. The relatively large spacing of 400 μm between the electrodes could be another limiting factor in our device. Since this spacing defines the distance protons must travel from anode to cathode, it should be as short as possible and ideally 100–200 μm. Along with this spacing, the clearance between the microchannels should also be decreased (∼50 μm). A further limiting factor could be the thickness of the Nafion membrane. In our planar device the thickness of the patterned Nafion membrane was only 200–400 nm, significantly less than the 50 μm thick Nafion sheet used by Motokawa [4]. Our improvement strategy can be explained with the following relationship derived from the DC resistance of a nanogap junction [9]: $R_m \sim W_m/(D_m \cdot L_m)$, where R_m is the DC resistance of a membrane, W_m, D_m, L_m are the width, thickness, and length of the membrane, respectively, under the assumption that the membrane is of rectangular shape. According to this relationship, we need to reduce the width of the membrane, corresponding to the spacing between the electrodes, and increase the cross-sectional area of the membrane by increasing the thickness of the membrane and its length ($D_m \cdot L_m$). In order to increase the cross-sectional area we could pattern a significantly thicker Nafion membrane, or use a solid matrix (such as self-assembled silica colloidal arrays) to achieve the necessary height and subsequently infiltrate it with Nafion resin. The latter concept is schematically shown in Fig. 4a. We patterned an array of 900 nm silica colloidal particles (Polysciences, Warrington, PA) between the electrodes using the microflow technique, as shown in

Fig. 4b. The colloidal particle array exhibited homogeneous packing, as shown in Fig. 4c. Preliminary results with this device showed that we could increase the current density by 166% compared to the planar membrane device.

4. Conclusions

We have developed a simple and rapid method to fabricate planar PEM microfluidic fuel cells in PDMS. Instead of sandwiching a Nafion membrane, which can complicate the assembly process, we patterned a submicron thick ion-selective Nafion membrane and integrated it in-plane between the PDMS device and the glass substrate via standard plasma bonding. To improve the power output of the device we demonstrated fabrication of a thicker ion-selective membrane by using silica colloidal array as a solid matrix for Nafion resin. We note that arraying many micro fuel cells such as the one we describe here in a massively parallel architecture is another viable option for increasing the power output. Once fully developed, our approach will allow rapid fabrication of PEM microfluidic fuel cells and facilitate their integration into miniaturized devices such as implanted biomedical devices as on-chip power sources.

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