



Short communication

Monolithic micro-direct methanol fuel cell in polydimethylsiloxane with microfluidic channel-integrated Nafion strip

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ABSTRACT

We demonstrate a monolithic polymer electrolyte membrane fuel cell by integrating a narrow (200 μm) Nafion strip in a molded polydimethylsiloxane (PDMS) structure. We propose two designs, based on two 200 μm -wide and two 80 μm -wide parallel microfluidic channels, sandwiching the Nafion strip, respectively. Clamping the PDMS/Nafion assembly with a glass chip that has catalyst-covered Au electrodes, results in a leak-tight fuel cell with stable electrical output. Using 1 M CH_3OH in 0.5 M H_2SO_4 solution as fuel in the anodic channel, we compare the performance of (I) O_2 -saturated 0.5 M H_2SO_4 and (II) 0.01 M H_2O_2 in 0.5 M H_2SO_4 oxidant solutions in the cathodic channel. For the 200 μm channel width, the fuel cell has a maximum power density of 0.5 mW cm^{-2} and 1.5 mW cm^{-2} at room temperature, for oxidants I and II, respectively, with fuel and oxidant flow rates in the 50–160 $\mu\text{L min}^{-1}$ range. A maximum power density of 3.0 mW cm^{-2} is obtained, using oxidant II for the chip with 80 μm -wide channel, due to an improved design that reduces oxidant and fuel depletion effects near the electrodes.

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1. Introduction

Microfabricated liquid fuel cells are of increasing interest for high-energy density portable applications [1–3]. Fuel cells operating on liquid fuel, like methanol, allow a simple system design and low temperature operation. The overall performance of a fuel cell is a very sensitive function of parameters, like the choice of electrodes and catalysts, fuel and oxidant solutions, the use of a proton exchange membrane (PEM) or not, and the microfluidic design. Moreover, easy assembly and the use of affordable materials and system components are important issues. A high electrical output power density can be obtained in rather complex bipolar micro-direct methanol fuel cells (μ -DMFC), in which the PEM or membrane electrode assembly (MEA) is sandwiched between fuel and oxidant flow chambers [2–6]. In a monolithic fuel cell design, the anodic and cathodic channels are realized in the same substrate, which allows easy prototyping. Monolithic designs can include a proton exchange membrane [7,8], or can be membraneless [9–12]. In the former case, membrane integration and leakage can present an issue, while a membraneless strategy requires high-precision fuel and oxidant flows (a few hundreds of $\mu\text{L min}^{-1}$) to maintain the liquid junction. Using PDMS elastomeric fluidic channels can avoid leakage problems during hybrid integration of the PEM [8] or of electrodes [13]. The latter approach was shown particularly inter-

esting for high electrical power output, when porous electrodes with high catalytic surface area are used [13].

We demonstrate a monolithic microfluidic PEM fuel cell by integrating a narrow Nafion strip in a molded PDMS structure. Clamping the PDMS/Nafion assembly with a glass chip that has catalyst-covered Au electrodes, results in a rapid prototypable and leak-tight fuel cell. We use methanol as fuel, and, as oxidant solutions, we compare O_2 -saturated sulphuric acid and hydrogen peroxide in sulphuric acid. We investigate the role of flow velocity of fuel and oxidant on the fuel cell performance.

2. Design and experimental methods

PDMS is chosen as material for our μ -DMFC, because of its easy application and its good chemical resistance [14]. Fig. 1a and b are schematic oblique and side views of the planar μ -DMFC, respectively. The device is based on three components: a PDMS chip with patterned microchannels, a narrow Nafion strip and a float glass substrate with catalytic electrodes. This planar structure allows the protons generated at the anode to be transferred to the cathode, without requiring a complex MEA. As illustrated in Fig. 1c, the individual microfluidic channels of fuel and oxidant are simply formed by placing the rigid 200 μm -wide Nafion strip using a dedicated guiding channel in the PDMS chip.

The fabrication of the planar μ -DMFC includes the following steps, shown in Fig. 2: (1) a 170 μm thick SU8 structure for definition of the microchannel is patterned on a Si wafer; (2) PDMS (Sylgard 184, Dow Corning Inc. Midland, MI) is poured onto this

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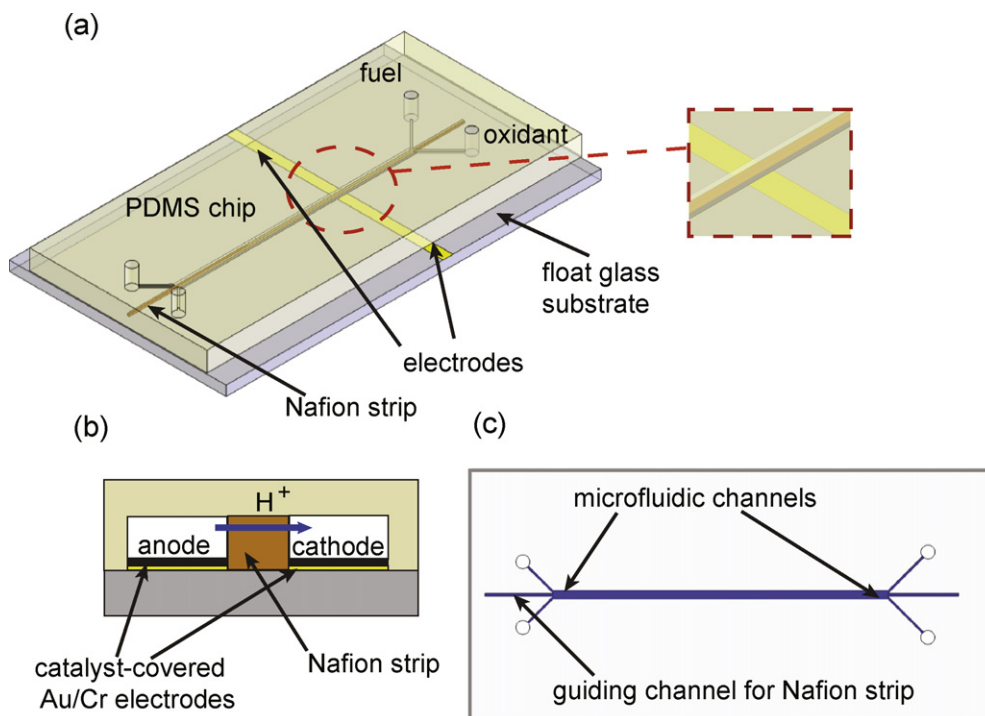


Fig. 1. (a) Oblique schematic view of the μ -DMFC. (b) Schematic cross-section of the μ -DMFC with integrated Nafion strip. (c) Top view of the PDMS chip design.

master structure and it is cured at 75 °C for 2 h, after which the PDMS chip with integrated guiding channel is peeled off from the mold. (3) Using a metallic shadow mask, we deposit a 100 nm thick Au electrode using a 5 nm chromium adhesion layer (Auto 306 Resistance evaporation system, Edwards, Crawley, UK) on a piranha-cleaned glass slide (Menzel GmbH, Braunschweig, Germany). (4) Pt/Ru (Pt:Ru = 1:1) catalyst, supported on carbon black with metal content 60% (BASF fuel cell Inc., Somerset, US), is mixed with Nafion solution (5 wt% Nafion 5112, DuPont) and isopropanol, giving a final catalyst concentration of 5 mg mL⁻¹ and a catalyst/Nafion ratio of 7:3 [12]; this mixture is wet-sprayed using an airbrush (Evolution Two in One, Harder & Steenbeck, Norderstedt, Germany) onto the Au electrode, forming the anode of the μ -DMFC. A similar procedure is applied for depositing Pt/C catalyst on the cathode. The catalyst loading on the electrode is ~ 2 mg cm⁻². (5) A Nafion strip is cut from a larger Nafion 117 membrane (thickness 175 μ m, DuPont) by in house-made adjustable razor blades

and is conditioned by a series of steps: subsequently, we use 10% H₂O₂, deionized water (DI) H₂O, 1 M H₂SO₄ and DI H₂O baths during 2 h each at 80 °C. (6) The Nafion strip is placed precisely in between the fuel and oxidant microfluidic channels by means of a guiding channel. (7) The assembly of the planar μ -DMFC is completed by placing the Nafion strip-integrated PDMS chip on top of the catalyst-covered glass chip and mechanically clamping the device using two thick poly(methyl methacrylate) (PMMA) sheets with fluidic access holes and aluminium foil as current collectors.

The performance of the planar μ -DMFC is assessed at room temperature and ambient pressure. The fuel (1 M CH₃OH/0.5 M H₂SO₄) is fed to the anodic microfluidic channel and the oxidant (type I: 0.5 M H₂SO₄/O₂-saturated, type II: 0.5 M H₂SO₄/0.01 M H₂O₂) to the cathodic microfluidic channel, respectively. Peristaltic pumps (ISM 831, ISMATEC, Glattbrugg, Switzerland) are connected to the chip for fuel and oxidant refreshment.

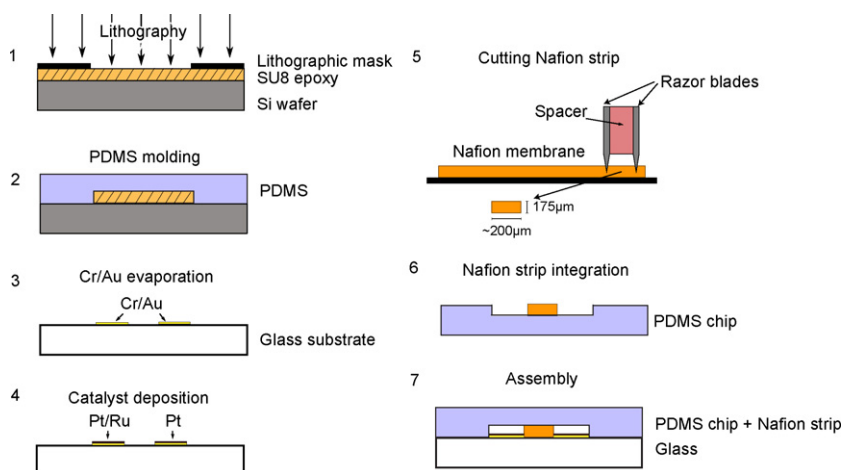


Fig. 2. Schematic of the μ -DMFC fabrication process.

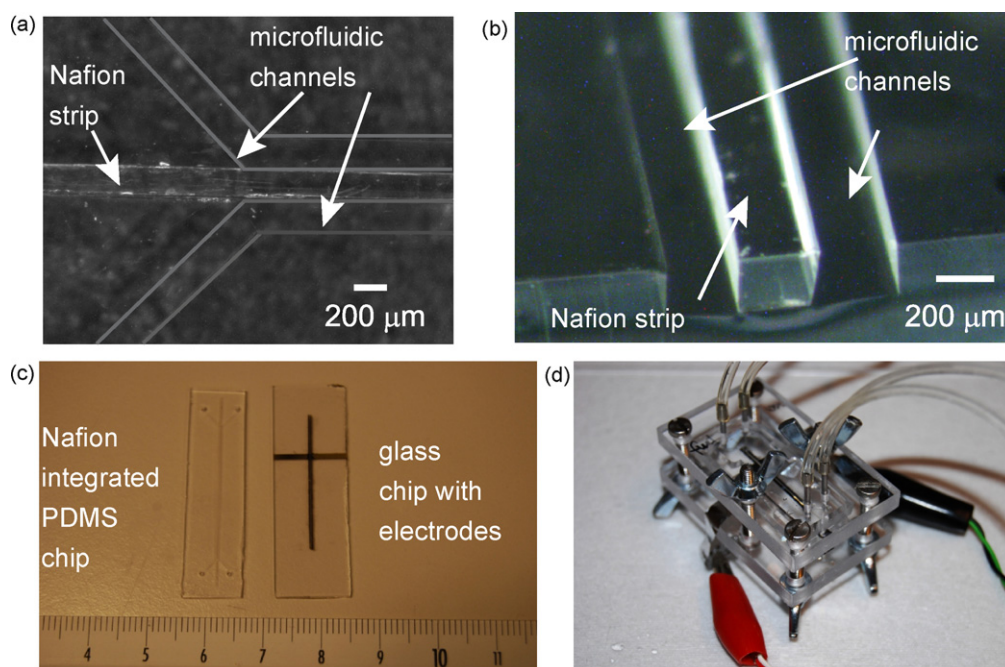


Fig. 3. Photographs of (a) top view and (b) cross-sectional view of the PDMS microfluidic channels with 200 μm Nafion strip-integrated in the guiding channel. (c) Finalized PDMS and glass chips, and (d) the μ -DMFC mounted in its experimental setup.

3. Results and discussion

The top and cross-sectional views of the Nafion strip-integrated PDMS chip are depicted in Fig. 3a and b, respectively. The guiding channel (200 μm) in the PDMS results in accurate positioning of the Nafion strip. The PDMS chip with integrated Nafion strip and the glass chip with catalyst-covered electrodes are shown in Fig. 3c. A single planar μ -DMFC mounted in its experimental setup is shown in Fig. 3d. Two types of chips with different microfluidic channel width and length are studied: Chip A has a channel width of 200 μm and a length of 24 mm, while Chip B has a width of 80 μm and a length of 11 mm. A potentiostat/galvanostat (AMETEK Princeton Applied Research 263A, Oak Ridge, TN, US) is used to evaluate the performance of the μ -DMFCs. We use 30–80 $\mu\text{L min}^{-1}$ flow rates for the fuel and 80–160 $\mu\text{L min}^{-1}$ flow rates for the oxidant. For Chip B, the smaller microfluidic channel leads to a higher average flow velocity. A higher velocity is in favor of reduced fuel and oxidant depletion effects near the catalytic electrodes (see further) [10].

As Fig. 4a indicates, when using oxidant I into Chip A, a limiting current density of 2.6 mA cm^{-2} is obtained with fuel and oxidant flow rate of 50 $\mu\text{L min}^{-1}$ and 160 $\mu\text{L min}^{-1}$, respectively. A higher flow rate of oxidant results in a better refreshment of the oxidant solution and, thus, a higher limiting current and power density. This is related to the low solubility of oxygen in the oxidant solution (1.2 mmol kg^{-1} at ambient pressure and temperature) [15]. Using oxidant II considerably enhances the maximum power density to 1.5 mW cm^{-2} , which is nearly three times higher than when using oxidant I at identical fuel and oxidant flow rates. The open circuit potential (OCP) of 0.5 V using oxidant II is lower than the 0.55 V obtained using oxidant I, a small difference that can be explained by oxygen bubbles evolving from the H_2O_2 reaction on the catalyst at the cathode [12]. Fig. 4a allows to conclude that oxidant II is the most promising for achieving a high power density.

Fig. 4b shows the performance of Chip B by feeding fuel and oxidant II at different flow rates. A higher limiting current and power density is obtained for a higher oxidant flow rate, while the fuel flow rate is not critical for the performance. This points to

the oxidant reaction being performance-limiting for the μ -DMFC [16]. Crossover of methanol through the Nafion strip from the anodic microfluidic channel can reduce the oxidant concentration near the cathode [17], an effect which can be reduced by having a better refreshment of oxidant using a higher flow rate. Compared to the highest power density of 1.5 mW cm^{-2} using oxidant II in Chip A (see Fig. 4a), Chip B generates a power density up to 3 mW cm^{-2} when operated under identical experimental conditions. The main physico-chemical difference between Chips A and B is the cross-sectional velocity of oxidant and fuel (in case of 80 $\mu\text{L min}^{-1}$, the average flow velocity for Chip A is 39 mm s^{-1} , while it is 98 mm s^{-1} for Chip B). A higher velocity clearly reduces oxidant depletion effects near the electrodes and is in favor of a higher reaction rate. We note that the ratio of the concentration boundary layer thickness $4\sqrt{(Dl)/v}$ [10,18], calculated at $l=11$ mm downstream the fluidic channel for both chips, to the channel depth d is equal to 0.55 and 0.35 for Chips A and B, respectively, with $D=1.98 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ the oxygen diffusion coefficient in the water-based oxidant solution [19], and v the average velocity of the oxidant solution. This means that for Chip B, oxidant depletion effects near the electrode surface are less important. Furthermore, as indicated in the numerical work of Chen et al. [20], since the depletion zone along the electrode surface gradually grows downstreamwards, a longer microchannel should result in a lower average current density. This could also be an explanation for the better performance of Chip B, which has a shorter length of the microfluidic channel. Fig. 4c shows the cell potential as a function of time for Chip B for a fuel flow rate of 50 $\mu\text{L min}^{-1}$ and an oxidant II flow rate of 160 $\mu\text{L min}^{-1}$, first without current load and second with a current of 5.7 mA cm^{-2} . In both cases, the potential nearly stays constant indicating the high stability of our μ -DMFC.

When comparing with literature, the power density of a PDMS-based planar μ -DMFC with patterned Nafion resin [8] is, despite the use of different fuel and oxidant, two magnitudes smaller than our device. The reported power density of 0.8 mW cm^{-2} generated from a silicon-based μ -DMFC [7] is a factor 1.5 smaller than our Chip B (results not shown), when operating with the same oxidant I, but for

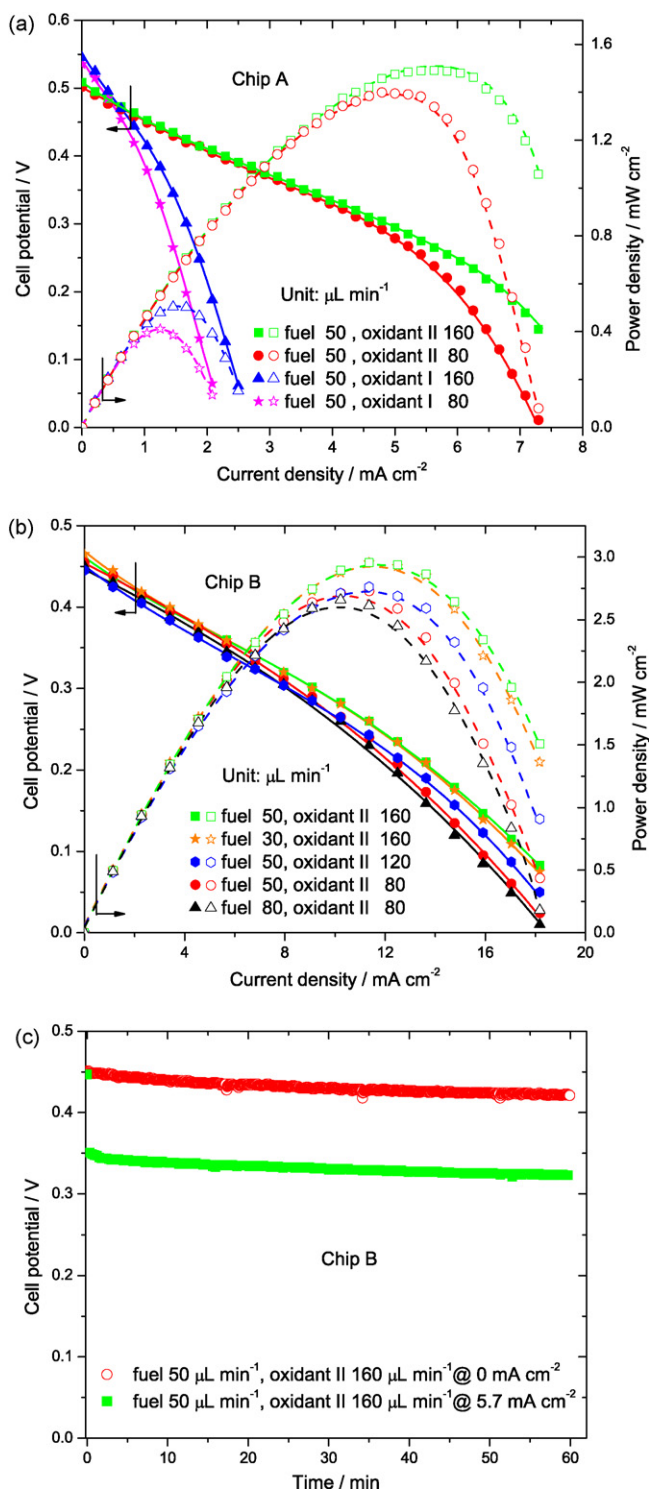


Fig. 4. (a) Polarization and power density curves of a μ -DMFC using oxidants I and II for Chip A. Each electrode area in contact with fuel or oxidant is 0.048 cm^2 . (b) Polarization and power density curves of a μ -DMFC using oxidant II in Chip B for different fuel/oxidant flow rates. Each electrode area in contact with fuel or oxidant is 0.0088 cm^2 . The lines in (a) and (b) are guides to the eye. (c) Time dependence of cell potential of Chip B using oxidant II and under a 0 mA cm^{-2} and 5.7 mA cm^{-2} current load, respectively.

higher fuel concentration ($2 \text{ M CH}_3\text{OH}/0.5 \text{ M H}_2\text{SO}_4$). We checked that, by increasing the concentration of H_2O_2 in 0.5 M sulfuric acid to 0.1 mol L^{-1} , an even higher output power density of 5 mW cm^{-2} and a limiting current density of 43 mA cm^{-2} is achieved for our Chip B. In this experiment, fuel ($1 \text{ M CH}_3\text{OH}/0.5 \text{ M H}_2\text{SO}_4$)

and oxidant ($0.5 \text{ M H}_2\text{SO}_4/0.1 \text{ M H}_2\text{O}_2$) are fed at $50 \mu\text{L min}^{-1}$ and $160 \mu\text{L min}^{-1}$, respectively. This performance again indicates the important role of the oxidant concentration in the cathodic microfluidic channel.

4. Conclusion and outlook

We have compared two μ -DMFC designs, in which two $200 \mu\text{m}$ -wide and two $80 \mu\text{m}$ -wide parallel microfluidic channels, are sandwiching a Nafion PEM strip, respectively. Using $1 \text{ M CH}_3\text{OH}$ in $0.5 \text{ M H}_2\text{SO}_4$ solution as fuel in the anodic channel, we compare the performance of (I) O_2 -saturated $0.5 \text{ M H}_2\text{SO}_4$ and (II) $0.01 \text{ M H}_2\text{O}_2$ in $0.5 \text{ M H}_2\text{SO}_4$ oxidant solutions in the cathodic channel. For the chip of $200 \mu\text{m}$ channel width, the fuel cell reaches a maximum power density of 0.5 mW cm^{-2} and 1.5 mW cm^{-2} at room temperature, for oxidants I and II, respectively, for fuel and oxidant flow rates in the 50 – $160 \mu\text{L min}^{-1}$ range. A maximum power density of 3.0 mW cm^{-2} is obtained for the chip of $80 \mu\text{m}$ -wide channel, using oxidant II with higher oxidizing power. Our results indicate the important role of the oxidant concentration in the cathodic microfluidic channel, and the advantage a higher velocity has in reducing oxidant depletion effects near the electrodes. In future, we intend to explore an alternative PDMS stamping technology to bond the Nafion-integrated PDMS chip to the glass chip using a liquid PDMS bonding layer [21], leading to a more compact μ -DMFC. Also the influence of channel geometry and fuel and oxidant flow effects will be further studied.

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