AIR-BREATHING LAMINAR FLOW BASED MICROFLUIDIC FUEL CELL

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Supporting Information

Chemicals. All chemicals and solvents were purchased from the vendors indicated below. In addition, formic acid was obtained from Acros (Morris Plains, NJ) and sulfuric acid from GFS Chemicals (Powell, OH).

Fabrication and assembly of the laminar flow-based microfluidic fuel cell. A 5-mm thick graphite plate (anode, fuel cell grade graphite bipolar plate purchased from Fuel Cell Stores.com) was cleaned by sonication in large portions of Milli-Q water (Barnstead E-pure water, 18 M Ω) and dried using a heat lamp. A 2-mm (=H) thick PMMA sheet with a window of length 3 cm and width 3 mm (=W) was glued to the graphite sheet using 5 min epoxy (Devcon, MA). Three holes were drilled into the graphite sheet: two inlets, and one outlet. The first inlet (0.5 M sulfuric acid inlet) was smaller in diameter compared to the second inlet (fuel stream inlet). This ensured the multistream laminar flow of the two streams on top of each other, rather than the electrolyte stream partly encapsulating the fuel stream. Polyethylene tubing (Intramedic) was glued to the inlet and outlet holes. Figure S1 shows the top view of the LFFC with a GDE as the cathode.



Figure S1. Schematic showing the top view of the LFFC with integrated, air-breathing gas diffusion electrode as the cathode.

The catalyst ink for the anode side was prepared by sonicating the required amounts of Pd black nanoparticles (Alfa Aesar, MA) and Nafion (Dupont, 5 wt% solution,) in water (200 μ l) for at least 30 min. The catalyst ink was added drop wise onto the exposed area of the graphite plate, between the second inlet and the outlet, and allowed to dry. The total geometric surface area over which the anode catalyst is applied equals 0.62 cm²; L = 2.05 cm (See Fig. S1) multiplied by W = 0.3 cm. The resulting anode catalyst layer had a catalyst loading of 10 mg/cm² of Pd and 1.5 mg/cm² of Nafion.

A sheet of Toray carbon paper with a platinum loading of $0.35 \text{ mg/cm}^2 \text{ using } 10\% \text{ Pt}$ on Vulcan XC 72 (E-TEK, NJ) was used as the gas diffusion cathode. This gas diffusion electrode was treated with isopropyl alcohol and dried under a lamp. A mixture of Pt black nanoparticles and Nafion suspended in water: isopropyl alcohol = 5:1 was painted onto the gas diffusion electrode. The addition of Nafion provides good proton conductivity in the gas diffusion layer. The composition of cathode catalyst layer was 2 mg/cm² of Pt and 0.1 mg/cm² of Nafion. The gas diffusion electrode was positioned on top of the PMMA to close the channel. This assembly was held together using paper binder clips (Highmark).

Fuel cell testing. The fuel cell assembly was mounted on a clamp, and the fuel and the electrolyte streams were supplied into the microfluidic fuel cell using a syringe pump (PHD 2000, Harvard Apparatus) at flowrates of 0.3 ml/min per channel (pressure driven flow). The open cell potential was recorded after allowing the system to reach a steady value. The polarization curves were obtained using an in-house built active electronic load interfaced to the PC using a LabJack USB U12 interface (LabJack, Lakewood CO). A constant cell potential was applied, and the current in the circuit was measured after waiting for the cell to reach steady state, which takes anywhere from 20 seconds to 2 min.

Anode and cathode potential measurements. The fuel and the electrolyte streams pass over the anode and cathode respectively, and leave the microfluidic channel through the outlet, which drains into a beaker. A Ag/AgCl reference electrode (in 3 M NaCl, BAS,West-Lafayette, IN) is placed into this beaker to enable recording of the performance of the cathode and anode independently (see reference 10 for more details). For this work, the total cell potential as well as the cathode potential was measured at each of the cell potentials. The anode potential was obtained by deducting the cell potential from the cathode potential. For clarity, the anode and cathode polarization curves for the LFFC without GDE are replotted in Figure S2, since the detailed shape of this data is hard to discern in Figure 2c of the manuscript.



Figure S2. Anodic and cathodic potentials vs. Ag/AgCl using 1 M HCOOH in 0.5 M H_2SO_4 acid as the fuel stream for an LFFC *without* a GDE (same but re-plotted data as shown in Fig. 2c of the manuscript).