Supporting Information

Membrane-less electrolyzer for hydrogen production across the pH scale

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METHODS

Fabrication. Electrodes are patterned on a Borofloat glass wafer. First, a 10 nm film of titanium is sputtered on top of the wafer to promote adhesion of 175 nm thick platinum or 150 nm thick nickel-iron top layer (81% Ni, 19% Fe). The shape of electrodes is patterned on top of platinum/Ni-Fe layer by photolithography and Ion Beam Etching (IBE) is used to etch the non-covered areas. Each electrode is 70 µm wide and 1 cm long with and edge to edge distance of 105 µm. The microchannels are etched in a photolithographically patterned silicon wafer using Deep Reactive Ion Etching (DRIE) technique. The wafer is rendered non-conductive by growing a 100 nm thick oxide layer using Low Pressure Chemical Vapor Deposition (LPCVD) before photolithography step. The depth as measured by a mechanical profilemeter is 61 µm and the width of the main channel is 275 µm. The width of each branch in the T-junction is 100 µm. Fluidic and electric access holes are devised by a diamond scriber after this step. Four set of electrodes and fluidic networks are patterned on each wafer. After plasma cleaning, the two wafers are aligned together in a Back Side Aligner (BSA) tool and bonded using standard anodic bonding technique. Distance between electrode's edge to the microchannel side wall is 15 µm. Finally, the four devices on the bonded platform are separated using a dicing machine. Small Polydimethylsiloxane (PDMS) pieces are plasma bonded on top of fluidic ports to provide a flexible bed for connections. Short wires are soldered to the electrodes ends in order to facilitate electrical connections to the potentiostat. The fabrication process flow is shown in Figure S1.

Measurements. The chip is mounted on a motorized stage and the electrolyte is provided into the chip using a syringe pump. Two tubes carry gas and electrolyte mixtures from the outlets into inverted glass tubes filled with water. The gases go up in the tubes and get trapped beneath their closed end. For volumetric measurement of the produced gases, the glass tubes are replaced by inverted 10 ml glass burettes with 20 µL graduation scale. To measure the crossover, 500 µA of current is provided to the electrodes using a potentiostat (BioLogic) for 90 minutes and then the collected gas in each tube is mixed with 10 mL of air and collected in gas tight syringes. The gases are then injected into a gas chromatographer (Bruker) for analysis. By definition, the gas crossover is the relative amount of O_2 in H_2 tube to the total amount of gas in H_2 tube. However, for practical reasons, the amount reported in this paper is the relative amount of H_2 in O_2 tube to the total amount of H_2 in both tubes. Due to higher relative pressure of H_2 and its higher diffusion coefficient, this quantity is always larger than the classic definition and, therefore, it is a conservative measurement. A simple reflection microscope is set up next to the motorized stage which enables imaging of the chip's inside. All other electrochemical measurements are done in the same setup and the same potentiostat. Impedance spectroscopy is done in the frequency range of 10 kHz to 3 MHz. Scan rate and range for voltammetry measurements are 10 mV/s and 0 to 2.6 V, respectively. Figure S2 shows the experimental setup.

Calculations. For calculation of solution resistance, the following formula is utilized:

$$R = \frac{L}{\kappa A}$$

Where κ is the specific conductivity of 1 M sulfuric acid at 25 °C (0.4 S/cm[1]), L is the distance between furthest edges of the electrodes (245 μm) and A is the area where ionic transport happens (61 μm by 1 cm).

The pressure drop can be found for a rectangular channel with aspect ratio – width to height – less than one and Reynolds number less than 1000 within 0.26% accuracy using the following formula:

$$\Delta p = QR$$

Where Q is the volumetric flow rate and $R = \frac{a\mu L}{WH^3}$, is the fluidic resistance. a is a dimensionless parameter depending on the width (W) to height (H) ratio of the channel[2], W/H:

$$a = 12\left[1 - \frac{192H}{\pi^5 W}\tanh\left(\frac{\pi W}{2H}\right)\right]^{-1}$$

In the fabricated electrolyzer, aspect ratio is 0.22 and Reynolds number is 19.8 for 12 ml/h flow rate. Therefore, the pressure drop equals 7.4 kPa at this flow rate assuming viscosity and density for water at 20 °C i.e. 1 mPa.s and 1000 kg/m^3. It is worth noting that this value is for single phase flow and may differ slightly from the pressure drop for bubbly flow. Assuming a pump efficiency of 75%, the input power, P_i delivered to the pump will be 0.033 mW. In other words, pumping power is 2.5 or 5% of the produced hydrogen power if the device runs at 143 or 71.5 mA/cm^2, respectively. The overall efficiency, η, at 12 ml/h is:

$$\eta = \frac{1.23V\, I - P_i}{V_{cell} I}$$

Where I is the electric current passing through the device and V_{cell} is the operational cell voltage. For instance, the efficiency is 51% for 71.5 mA/cm^2 of current and 12 ml/h of flow rate.

Peclet number:

$$Pe = \frac{UL}{D}$$

Where U is the average fluidic velocity, L is the characteristic length over which the diffusion occurs, and D is diffusion coefficient for Hydrogen. This number is the lowest possible ratio of convective to diffusive transport in the device since most of the gases are carried away in the gas phase and not in the dissolved form.

Ratio between H_2 generation rate to diffusive transport across the channel:

$$\frac{J_{gen}}{J_{diff}} = \frac{\frac{I}{zF}}{\frac{DC}{L} L_c H_c} = \frac{LI}{zFDCL_c H_c}$$

Where I is the current, z is the valency number of ions, F is the Faraday constant, L_c and H_c are the length and height of the channel, respectively.

For comparison with the volumetric gas measurements, ideal gas law is used to calculate the volume of the gases produced, assuming all of the current is spent on generating gaseous products, i.e. H_2 and O_2. With 0.5 mA current, the rate of hydrogen gas generation should be 2.59 nM/s or 18.65 µmol in two hours run of volumetric measurement. Using this value together with the standard conditions of 101.325 kPa and 293.15 K into ideal gas equation of state, PV = nRT, leads to a volume of 449 µL for Hydrogen gas. Ideally, the volume of Oxygen should be 224.5 µL. The experimental values obtained here show up to 410 µL of H_2 and 210 µL of O_2 with reading resolution of 10 µL. These amounts show collection efficiencies above 90%.

Tables

Electrolyte	0.5 M H_2SO_4	1 M H_2SO_4	1.5 M H_2SO_4	2 M H_2SO_4	1 M K_2CO_3	1M Na_3PO_4 Buffer
pH	1.1	1	0.8	0.6	8.9	6.6

Table S1. Measured pH values of various electrolytes utilized in the electrolyzer

Figures

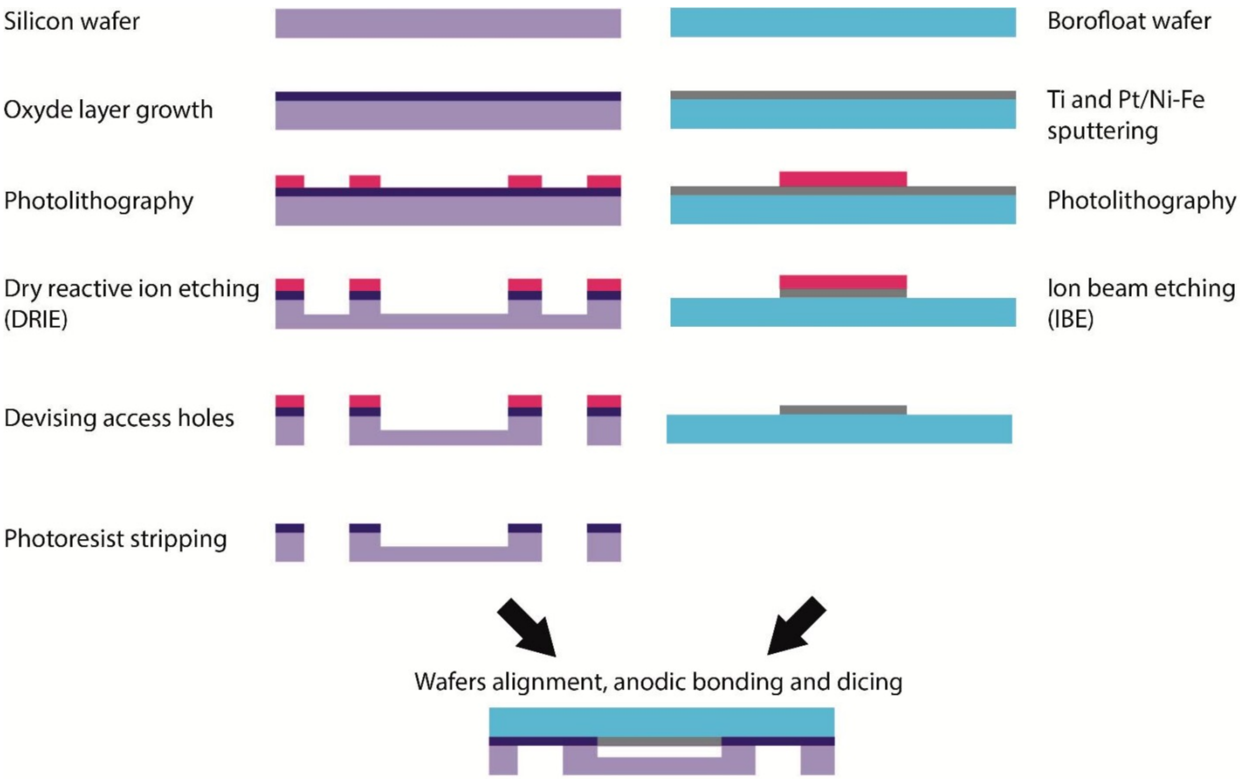

Figure S1. Fabrication procedure of the electrolyzer

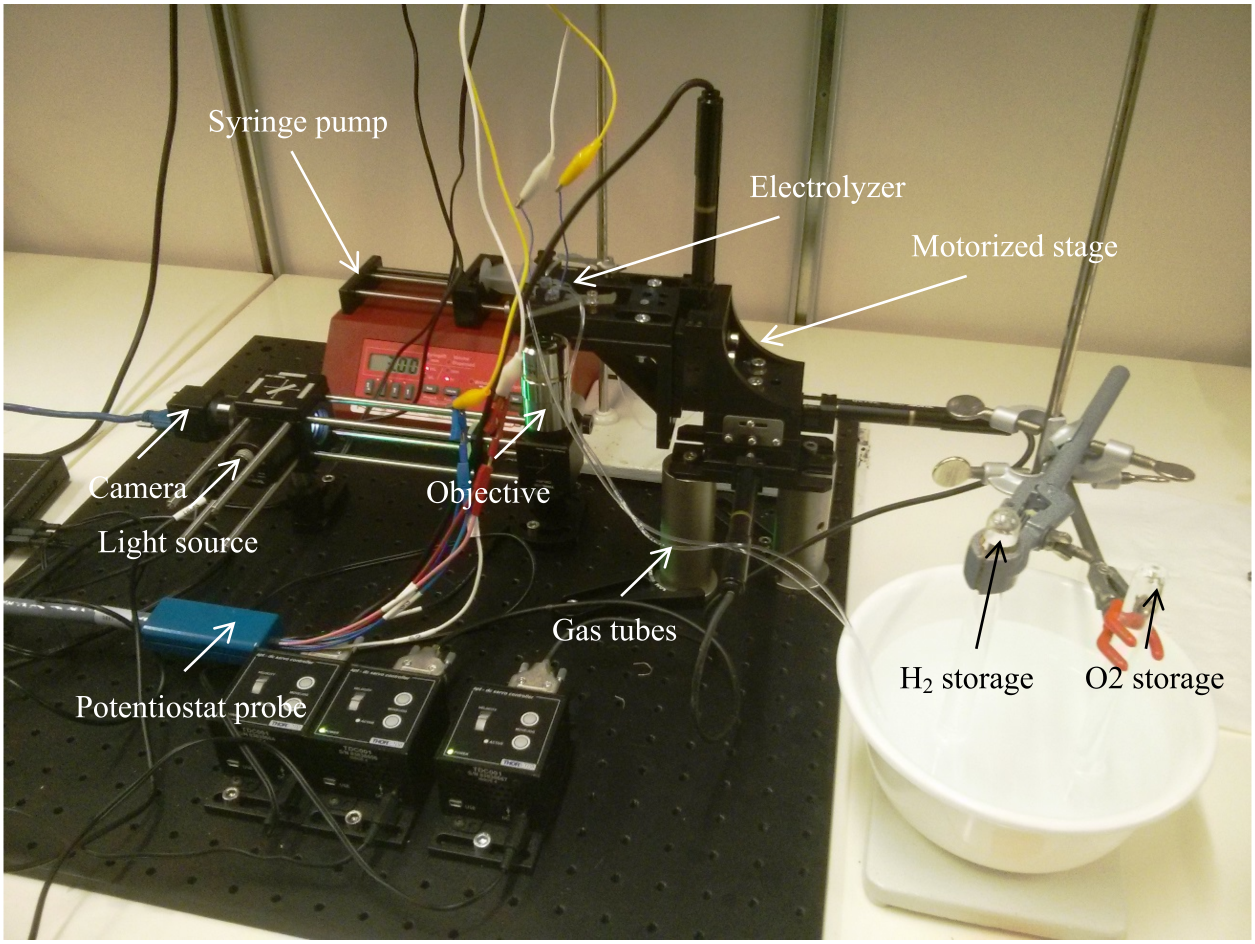

Figure S2. Experimental setup for electrochemical characterization and gas analysis

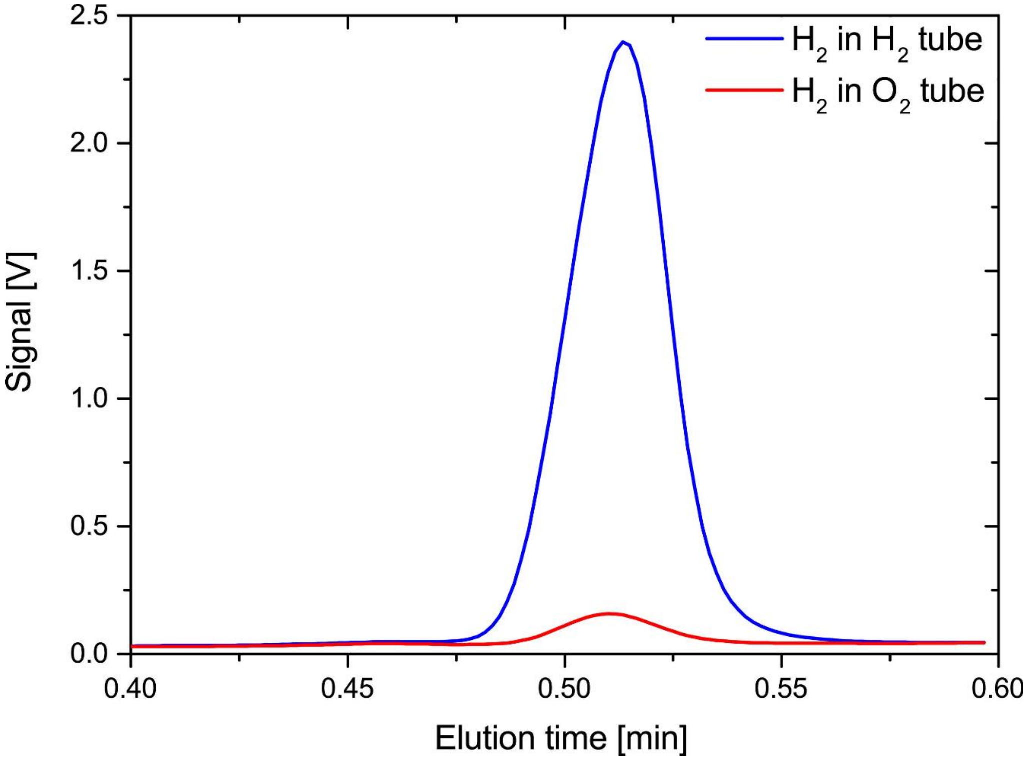

Figure S3. Chromatogram of the stored gases for 10 ml/h flow rate and 71.5 mA/cm^2

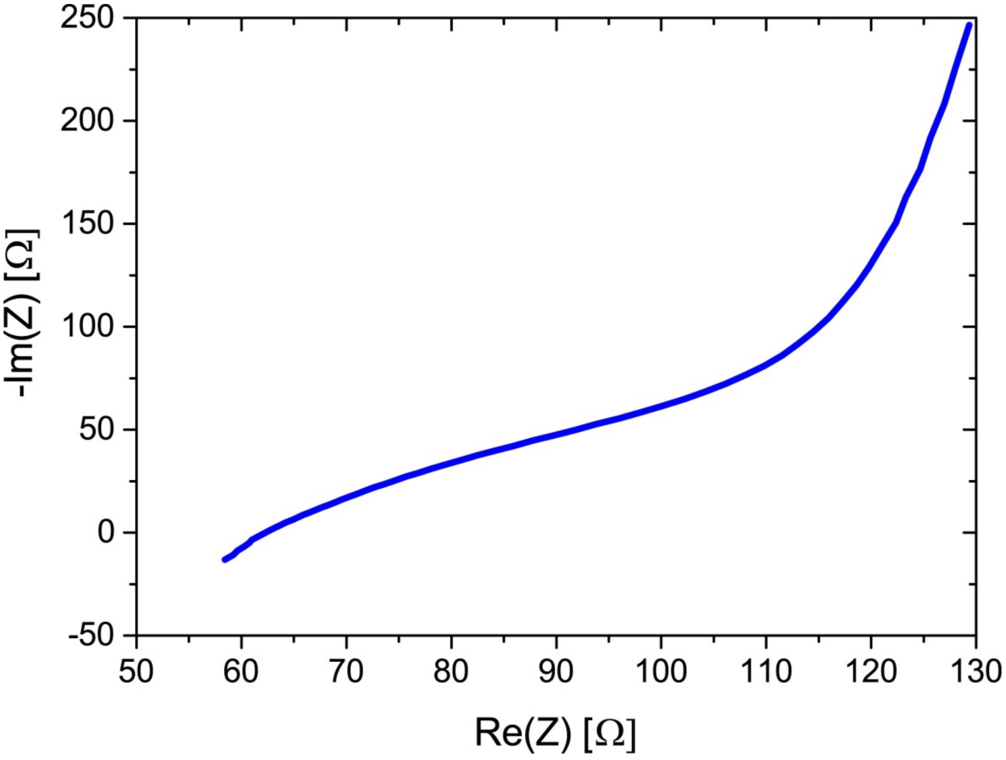

Figure S4. Nyquist plot of Electrochemical Impedance Spectroscopy (EIS) measurement for 1 M acidic electrolyte and flow rate of 12 ml/h.

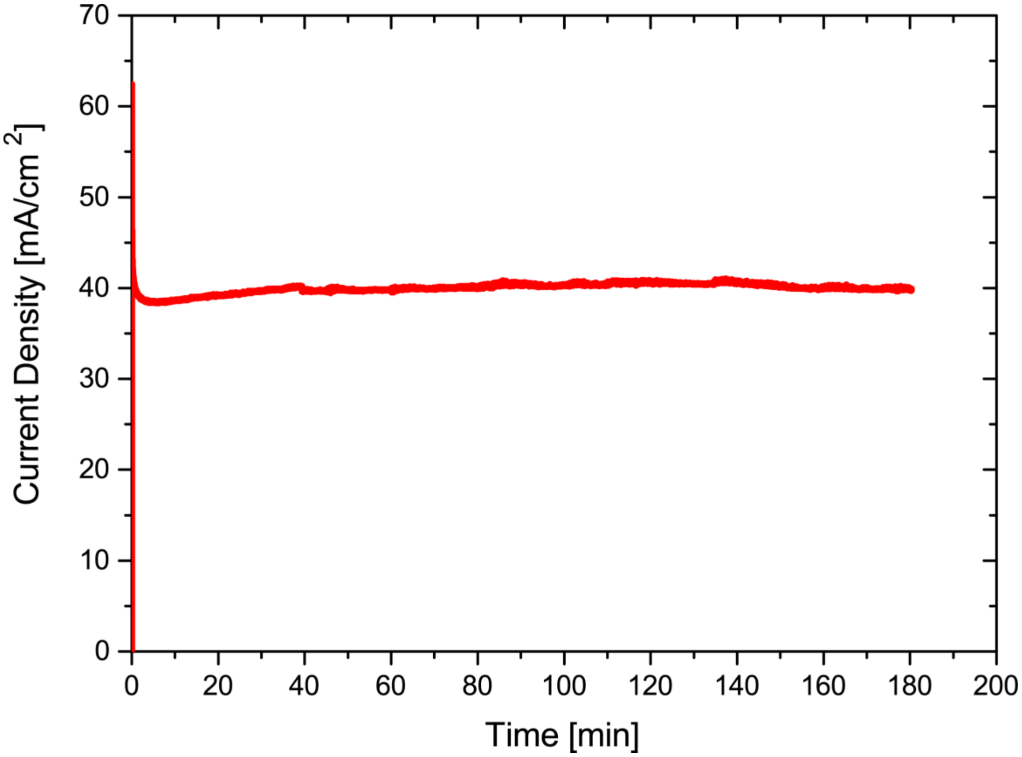

Figure S5. Potentiostatic measurement shows stable operation of the device over time with NiFe catalyst and 1M K_2CO_3 as electrolyte. Due to exponential dependence of current density on potential, this measurement highlights minor changes in the catalyst activity.

Movies

Movie S1. Video of T-junction at 1 ml/h and 143 mA/cm^2 in 1 M sulfuric acid over platinum electrodes.

Movie S2. Video of T-junction at 4 ml/h and 143 mA/cm^2 in 1 M sulfuric acid over platinum electrodes.

Movie S3. Video of T-junction at 10 ml/h and 143 mA/cm^2 in 1 M sulfuric acid over platinum electrodes.

References

1 Darling, H. E. Conductivity of Sulfuric Acid Solutions. *Journal of Chemical & Engineering Data* **9**, 421-426, doi:10.1021/je60022a041 (1964).

2 Fuerstman, M. J. *et al.* The pressure drop along rectangular microchannels containing bubbles. *Lab Chip* **7**, 1479-1489, doi:Doi 10.1039/B706549c (2007).