Electrolysis in Nanochannels for *In Situ* Reagent Generation in Confined Geometries

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Electronic Supplemental Information

I. pH Calibration

Figure S1 shows the calibration plot of fluorescence intensity *vs.* pH for fluorescein in the nanochannel device. Fluorescein solutions (10 μM) were prepared in 0.1 M phosphate buffer, which was titrated to the desired pH value. The nanochannels were then filled with solution at a particular pH, and the fluorescence intensity was recorded over timeframes of at least 30 s. The data points in Fig. S1 represent the average fluorescence intensity per pixel while the error bars are the standard deviation. A fresh set of nanochannels was used at the next pH value. The buffer concentration was increased relative to that in the H_2 generation experiments described in the main body of the manuscript (18 mM) to ensure accurate control of solution pH. A sigmoidal fit to the data (dashed line) was used to convert between observed fluorescence intensity and pH in H_2 generation experiments.

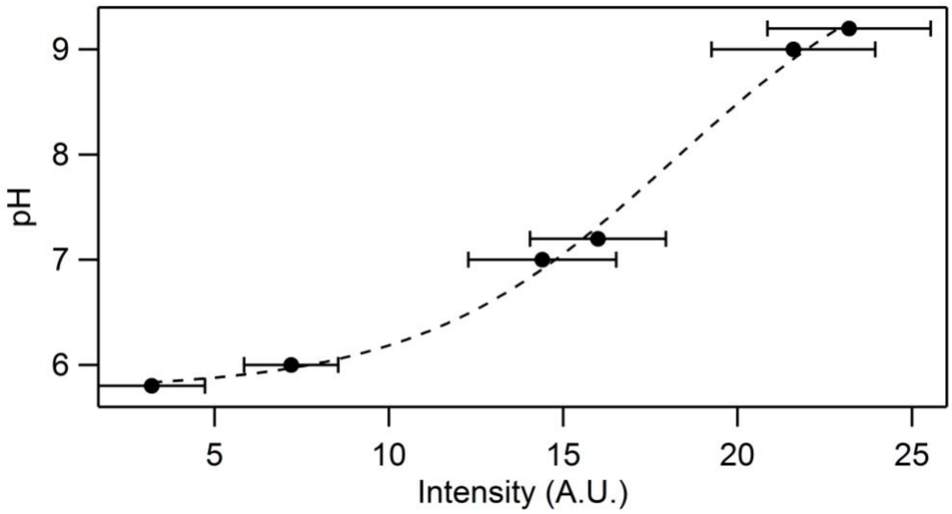

Figure S1. Calibration of pH *vs.* fluorescence intensity for buffered 10 µM fluorescein solution in nanochannels. Data represented by circles are average fluorescence intensities in nanochannels. All error bars are ±1 standard deviation.

II. Measurement of E_{eq} for the H_2 evolution reaction

A gold QRE rather than a traditional reference electrode was used in these experiments. In addition, E_{eq} for H_2 evolution on Au is not well established in the literature. In order to develop a thermodynamic relationship, potential step experiments were repeated in several nanochannel devices to determine the location of the equilibrium potential, E_{eq}, for cathodic H_2 evolution. Fig. S2 shows an extended Tafel plot from a typical device response to a broader range of applied potentials than those considered in the paper. The equilibrium potential lies approximately at the asymptote in Fig. S2 - around ~ -1.2 V *vs.* QRE. This E_{eq} value was consistent to within ~100 mV among all the devices constructed and studied.

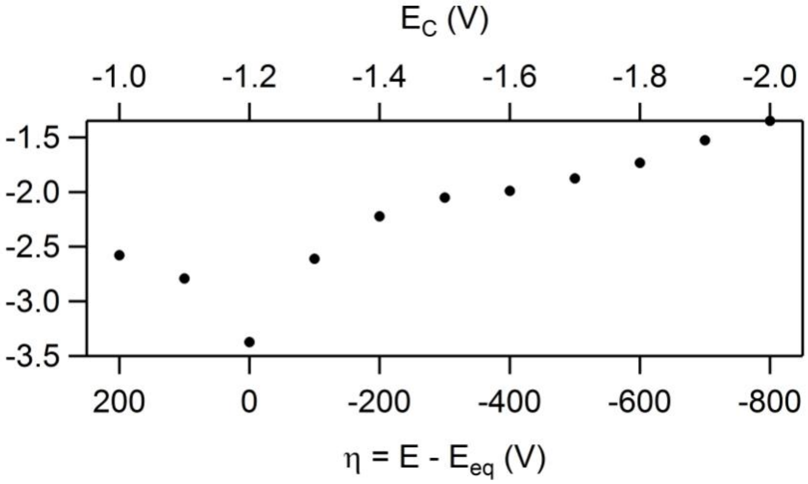

Figure S2. Typical Tafel plot for a NERA device.

III. Finite Element Simulations

A 2-D simulation geometry was created in COMSOL v.3.5a, encompassing four physical models: Incompressible Navier-Stokes flow, Convection-Diffusion of OH, Convection-Diffusion of H_2 (aq), and Conductive Media (DC). Geometry and boundary labels are shown in Fig. S3, with corresponding descriptions of the boundary conditions for each physical model in Table 1. The total simulated extent of the PDMS layer (not shown) was 50 μm.

The time dependent simulation encompassed a single cycle (3 s at $E = E_C$, 5 s at $E = E_R$) as shown by the inset to Fig. 3 (see text). The simulation was repeated for each value of E_C, for a total of 7 simulations. The discretized model included 15,119 elements and 307,780 DOF. Simulations were solved on a Dell Latitude E6410 laptop with a quad-core Intel i7 processor and 6 GB of memory, running Windows 7 Professional 64-bit. Solution time was ~ 3,000 s for each cycle.

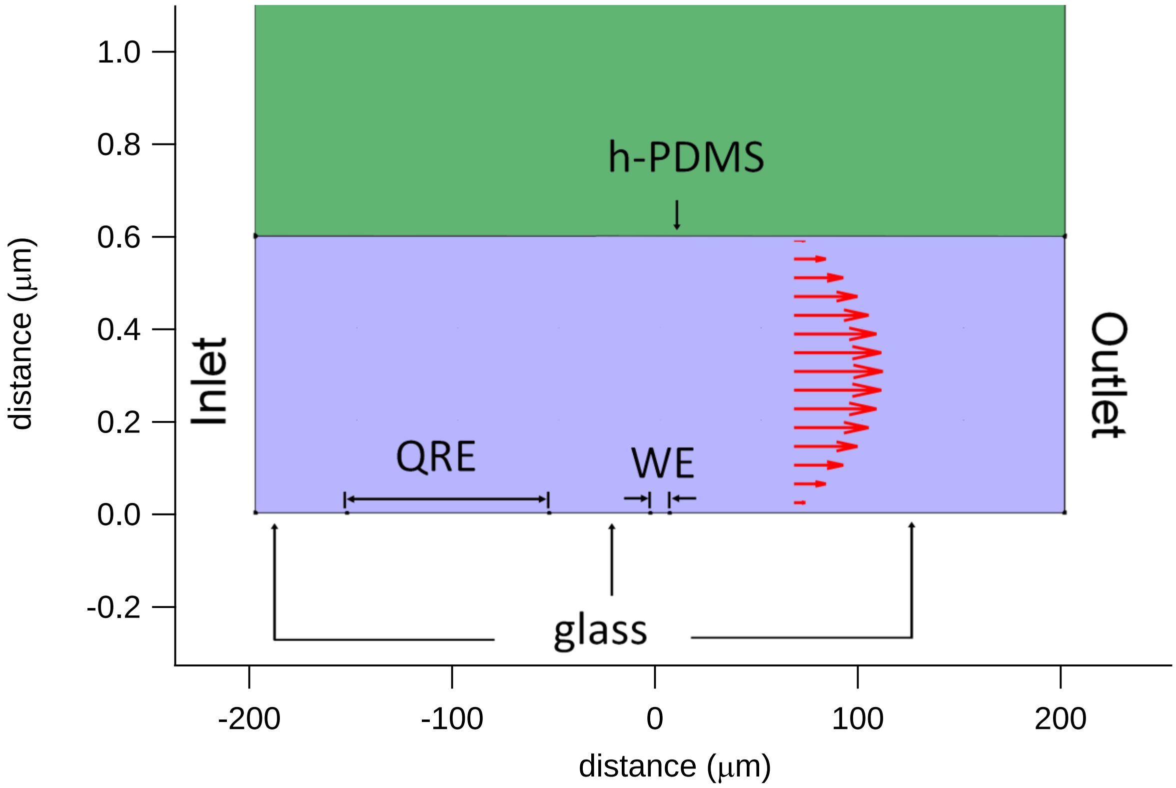

Figure S3. Simulation geometry and boundary descriptions.

Table 1. Description of the boundary conditions used for computational simulations in COMSOL.

Boundary type:	Navier- Stokes	Convection/diffusion (OH^-)	Convection/diffusion (H_2)	Conductive Media (DC)
Inlet	Laminar inflow 500 µm s^{-1}	$C = C_0$	C = 0	float
Outlet	no viscous stress	convective flux	convective flux	float
h-PDMS	no slip	insulation	Sim. I: insulation Sim. II: continuity	insulation
Glass boundary	no slip	insulation	insulation	insulation
Working electrode	no slip	Flux; determined by Butler-Volmer model in Eq. (4) (see text)	Flux; determined by stoichiometry of Rxn. 1 (see text)	$E = E_C$, $(0 < t \leq 3$ s) $E = E_R$, $(3 < t \leq 8$ s)
Reference electrode	no slip	insulation	insulation	$E = E_R$