

Supporting information

**Current Oscillations from Bipolar Nanopore for Statistical
Monitoring of Hydrogen Evolution on Confined Electrochemical
Catalyst**

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Experimental Section

Chemicals and Materials

All agents were of analytical grade. Acetone and absolute ethanol, hydrochloride acid, sulfuric acid, sodium chloride, and potassium ferrocyanide ($K_4Fe(CN)_6$) were purchased from Sinopharm Chemical Reagent Co., Ltd. The Nafion (5 wt. %) solution and Palladium on Carbon (C/Pd, 10 wt. %) catalyst were purchased from Sigma. All the solutions were prepared by using ultrapure water ($18.2\text{ M}\Omega\cdot\text{cm}$ at $25\text{ }^\circ\text{C}$) from a Milli-Q system (Billerica, MA). Borosilicate capillary glass with 1.2 mm outer diameter and 1.0 mm inner diameter were obtained from West China Medical Center (Sichuan, China).

Preparation of Bipolar Glass Nanopore.

The glass capillary was thoroughly washed by acetone, ethanol and ultrapure water. The central section of the capillary was softened in the flame of the alcohol lamp, and then the glass was pulled from both ends to form a symmetric tapering shape in the middle. A ceramic tile was used to cut the glass into two pieces from the thinnest point. The obtained pipettes were polished under an optical microscope to create a pore of about 500 nm diameter. The diameter of the obtained opening orifices was examined by SEM (Hitachi, SU8010), only pipettes with diameter of 500 ± 50 nm were selected for further experiments.

The purchased 5 wt. % Nafion solution was diluted to 0.5 wt. % with water. Then 0.5 mg C/Pd catalyst was dispersed in 10 ul of the diluted 0.5 wt. % Nafion solution to obtain C/Pd catalyst ink of 0.05 mg/ul. In general 0.5ul C/Pd catalysts ink was injected in the pipette with a syringe. The pipette was kept in a centrifugation tube and centrifuged at 8000 rpm for 20 minutes. The injected catalysts would descend in the tip zone of the pipette. The supernatant in the pipette was taken out with a syringe. Similar way to the catalyst ink, graphite powder was filled behind the catalyst ink in the pipette to control the thickness of the total bipolar electrode in the pipette to get good repeatability of the experiments. The concentration of the graphite powder in 0.5 wt. % Nafion solution is 0.05 mg/ul too. The drying of the glass pipette was done in a

vacuum drying oven at 40 °C overnight. After drying, the tip of the pipette was gently polished on a flat glass plate. The glass pipette was filled a solution of 25 mM $K_4Fe(CN)_6$ in 0.5 M H_2SO_4 with a syringe and centrifuged at 5000 rpm for 5 minutes to remove any air bubbles in the pipette.

Current Recording

The catalysts loaded glass pipette was hold on a home-made scaffold and dipped into a 0.5 M H_2SO_4 solution. The angle between the glass pipette and the glass plate base of the scaffold is maintained at 30°. The driving electrodes were a pair of Ag/AgCl electrodes. A CHI 660D electrochemical working station was used to record the amperometric i-t curves in three-electrodes mode. The Ag/AgCl electrode in trans-side of the glass pipette was the working electrode and the electrode in cis side served as the reference and counter electrode. The potential was controlled by the working station.

A microscope (SK 200, Motic China Group Co., LTD) with a CCD camera (Dino-Lite, AM-423X) was used to take the optical micrographs and the videos.

Analysis of relation of the current- τ_2

We assumed H_2 bubble situated on the electrode as a semi-sphere during the growing process, the partial pressure of a gas within the bubble, P , can be estimated by Laplace-Young equation:

$$P = \frac{2\gamma}{r_{nb}} + P_{out} \quad (1)$$

γ is the surface tension of gas liquid interface, r_{nb} is the radius of the gas bubble and P_{out} is the ambient pressure. Then the number of gas molecules can be approximately obtained from the ideal gas law.

$$\left(\frac{2\gamma}{r_{nb}} + P_{out}\right) \left(\frac{1}{2} * \frac{4}{3} \pi r_{nb}^3\right) = nRT \quad (2)$$

n is the amount of the gas, R is the gas constant and T is the temperature.

It is reasonable to assume that under a certain potential, the rate of gas generated per unit electrode surface per second is constant (v , $mol \cdot m^{-2} \cdot s^{-1}$). S is the active

surface area of the catalysts. The generation of H₂ molecule on the electrode can be expressed as:

$$dn = vSdt \quad (3)$$

From these two equations, we can derive the change of the electrode area changes over time.

$$d\left(\frac{4\pi\gamma r_{nb}^2}{3RT}\right) = v\pi(r_{pore}^2 - r_{nb}^2)dt \quad (4)$$

r_{pore} is the radius of the pore on trans side of the glass pipette. Solving this differential equation gives:

$$1 - \frac{r_{nb}^2}{r_{pore}^2} = e^{-\frac{3vRT}{4\gamma}t} = \frac{I}{I_0} \quad (5)$$

FEM simulation process for glass nanopore

The COMSOL Multiphysics software is employed for the FEM simulation. The geometry of the model glass nanopore is set according to the microscopic images shown in Figure 1, which are $r = 500$ nm, $l_{nanopore} = 250$ μm, and $l_{catalyst} = 50$ μm. The system is regarded to be steady-state and all of the processes happen in a 2D non-axisymmetric geometry.

The equation Nernst-Planck is used to compute the ionic flow.

$$J_i = -D_i\nabla c_i - \frac{FZ_i}{RT}D_i c_i \nabla \Phi + c_i u \quad (6)$$

In equation 6, J_i is the ionic flow vector, F is the Faraday's constant, T is the absolute temperature, Φ is the potential, u is the position-dependent fluid velocity, respectively. D_i , C_i , and Z_i represent the diffusion coefficient, the concentration, and the charge of species i in solution, respectively.

Due to the presence of Nafion, the catalyst loaded in the glass tube can be viewed as a bipolar electrode composed of porous materials. The experimental results also showed the total current flowing through the pore was mainly carried by the ion migration. So for the simplicity, the primary current distribution interface was chosen for the simulation. The equation (2) can be simplified to only include the migration term.

$$i = -\sigma \nabla \Phi \quad (7)$$

Here σ is the ion conductivity of the electrolyte (0.5 M H₂SO₄, 198 mS/cm)¹ and the bipolar electrode (90 mS/cm, estimated through i-V measurements in Figure 1) in the glass nanopipette.

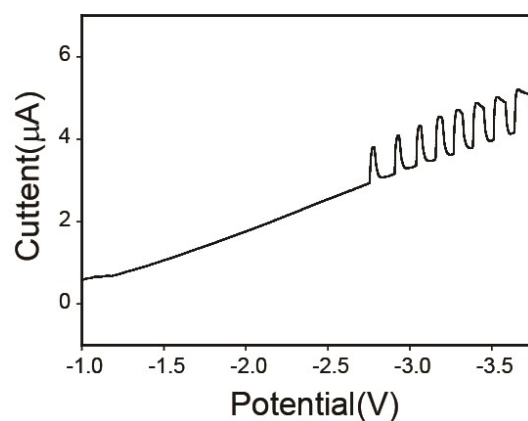


Fig. S1 Current response of the bipolar C/Pd electrode when the potential was linearly scanned from -1.0V to -3.75V in 0.5M H₂SO₄. The potential is applied across the glass pipette through a pair of Ag/AgCl electrode. The scan rate is 100 mV/s.

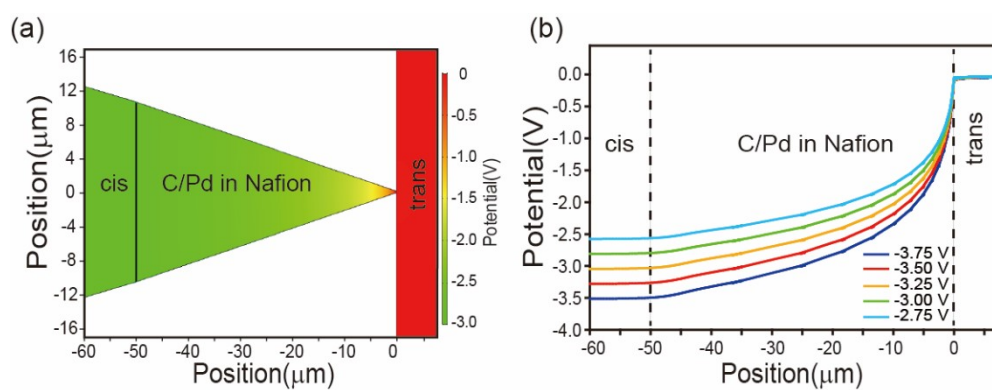


Fig. S2 (a) The simulated distribution of the biased potential along the position of the glass nanopore under a bias potential of -3.0 V. (b) The potential distribution profiles under different potentials (depicted as figure legends).

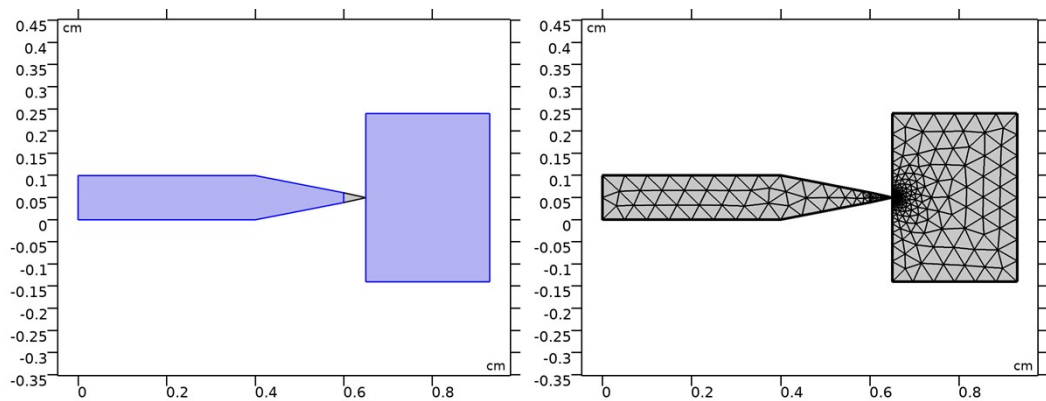


Figure S3. (a) The geometry setting of the glass nanopipette and (b) the mesh in the FEM simulation. The gray area in (a) represents the loaded catalysts as bipolar electrode and the purple are represents the electrolyte solution at the cis and trans side of the bipolar electrode.

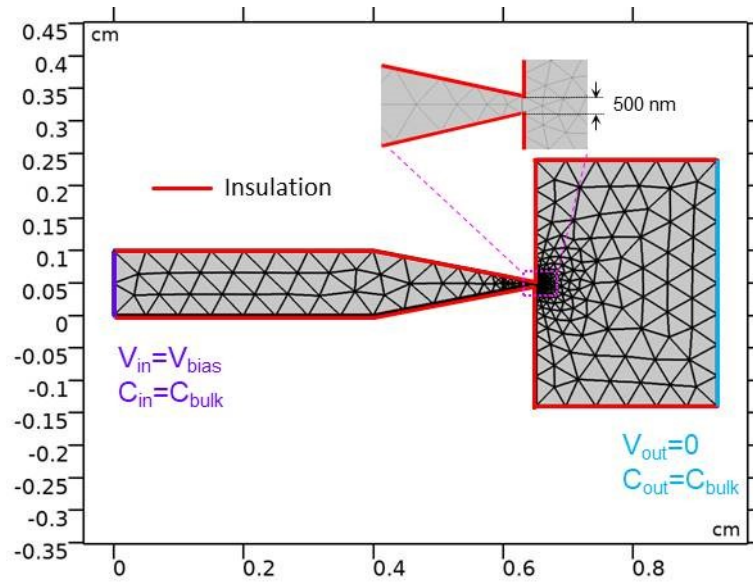


Figure S4. Boundary conditions for the FEM simulations of potential distribution through the nanopipette.

Reference

1. Y. Liu, W. P. Gates, A. Bouazza and R. K. Rowe, *Can. Geotech. J.*, 2014, **51**, 158–163.