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Electrochemical neutralization energy-assisted membrane-less microfluidic reactor for water electrolysis

SUPPLEMENTARY INFORMATION

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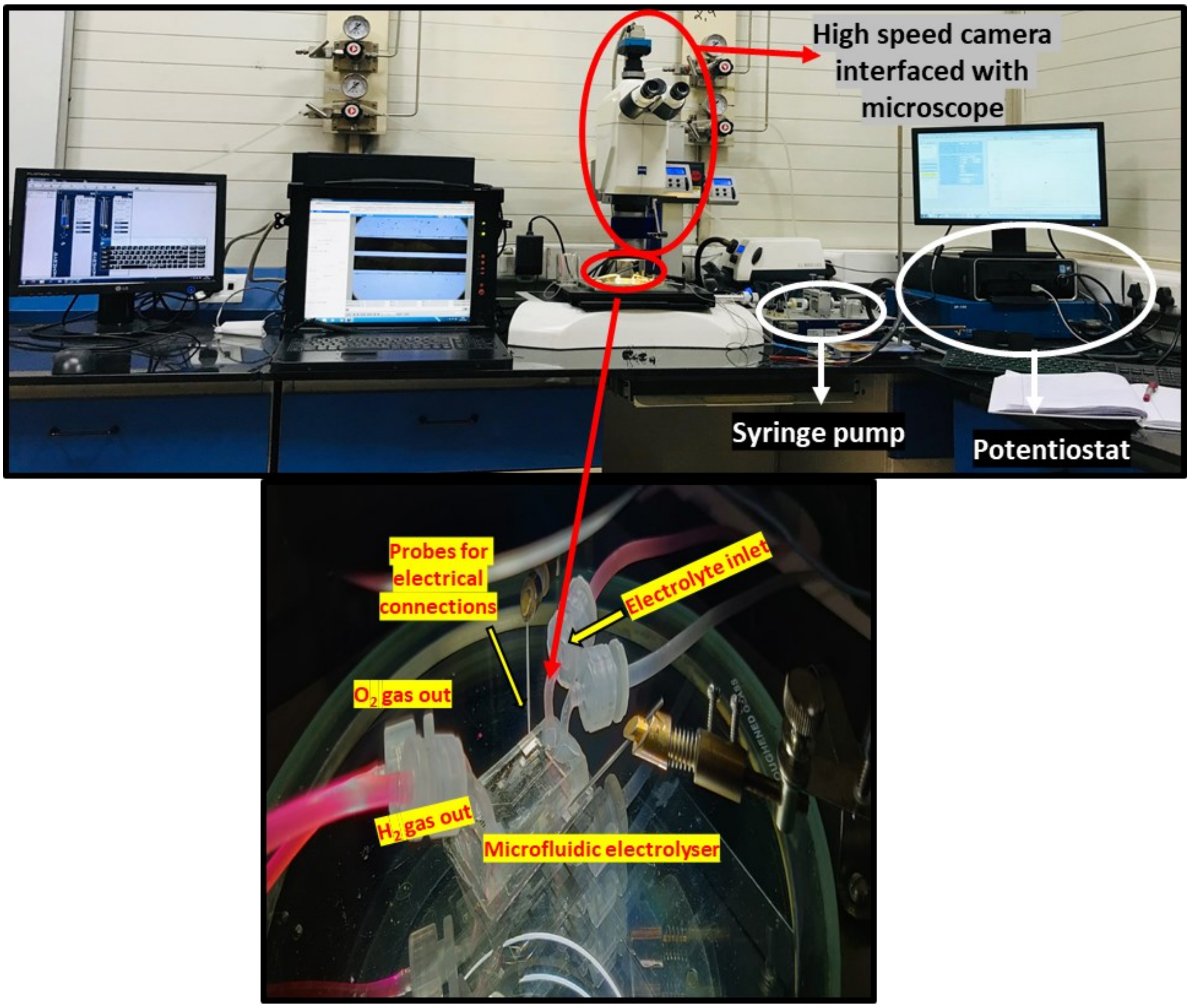

Figure S1: Setup for visual and electrochemical inspection of the microfluidic device.

Table S1: Values of the dimensionless number estimated for flow characterization in microchannel

Flow rate		At cathode (acidic electrolyte)		At anode (alkaline electrolyte)	
	Fr	Re	Pe (for H_2)	Re	Pe (for O_2)
1.4 ml min^{-1}	6.9	43.94	7.29 X 10^3	48.45	1.75 X 10^4
1.2 ml min^{-1}	5.9	37.66	6.25 X 10^3	41.53	1.50 X 10^4
1.0 ml min^{-1}	4.9	31.38	5.21 X 10^3	34.61	1.25 X 10^4
0.8 ml min^{-1}	3.9	25.10	4.17 X 10^3	27.69	1.00 X 10^4

Froude's number:

$$Fr = \frac{U^2/D_h}{g} = \frac{Inertia\ force}{Gravity\ force} \tag{S1}$$

D_h: Hydraulic diameter based on channel dimensions, (m)

U: Average velocity, (m s^{-1})

g: Gravitational acceleration constant, (9.81 m s^{-2})

Reynolds number:

$$Re = \frac{D_h U}{\vartheta} = \frac{Inertial\ force}{Viscous\ force} \tag{S2}$$

ϑ: Kinematic viscosity, (m^2 s-^{1})[1,2]

Peclet number:

$$Pe = \frac{UL}{D} = \frac{Convective\ transport}{Diffusive\ transport} \tag{S3}$$

L: Interelectrode distance (m)

D: Diffusivity (m^2 s^{-1}) [3]

Dependence of OER and HER half-cell potential based on pH following the Nernst equation [4]

At the cathode (HER):

$$4H^{+} + 4e^{-} \rightarrow 2H_2 \qquad (E^{0}_{H^{+}/H_2} = 0\ V\ vs\ RHE) \tag{S4}$$

$$E_{HER} = E^{0}_{H^{+}/H_2} - 2.303\frac{RT}{2F}log\left[\frac{\alpha_{H_2}}{\left(\alpha_{H^{+}}\right)^{4}}\right] = 0\ V - 0.059 \times (pH)_{cathode} \tag{S5}$$

At the anode (OER):

$$4OH^{-} \rightarrow 2H_2O + O_2 + 4e^{-} \qquad (E^{0}_{O_2/OH^{-}} = 1.23\ V\ vs\ RHE) \tag{S6}$$

$$E_{OER} = E^{0}_{O_2/OH^{-}} - 2.303\frac{RT}{4F}log\left[\frac{\left(\alpha_{O_2}\right)\left(\alpha_{H_2O}\right)^{2}}{\left(\alpha_{OH^{-}}\right)^{4}}\right] = 1.23 - 0.059 \times (pH)_{anode} \tag{S7}$$

Overall water splitting reaction:

$$4H^{+} + 4OH^{-} \rightarrow 2H_2O + O_2 + 2H_2 \tag{S8}$$

$$E_{theoretical} = E_{OER} - E_{HER} = 1.23 - 0.059\left[(pH)_{anode} - (pH)_{cathode}\right]$$

$$E_{theoretical} = 1.23 - 0.059\,\Delta(pH) \tag{S9}$$

where E is the half-cell potential, E^0 is the standard half-cell potential, $E_{theoretical}$ is the theoretical potential for water electrolysis, α is the chemical activity of the species, T is absolute temperature for the reactor operation, R is the universal gas constant, F is the Faraday constant, n is the number of electrons transferred per H_2.

Estimation of electrochemical neutralization energy utilization efficiency for the membrane-less microfluidic reactor for water electrolysis

The higher current density and a drastic reduction in overpotential obtained for asymmetric electrolyte as compared to the acidic or alkaline electrolyte for water electrolysis are contributed by additional energy from electrochemical neutralization. The neutralization reaction is associated with the release of heat [5]:

$$H^{+}_{(aq)} + OH^{-}_{(aq)} \rightarrow H_2O_{(l)} \qquad \Delta H^0 = -56.2 \text{ kJ mol}^{-1} \tag{S10}$$

Consider the flow of 1 M NaOH for 1 hour at 1.4 ml min^{-1}, total moles of NaOH is 0.084 moles. The total electrochemical neutralization energy associated with 0.084 moles of NaOH is -4720.8 J (-56.2 kJ mol^{-1} × 0.084 moles) or 1311 mWh.

Now the power density is calculated for the electrolyzer operating at 10 mA cm^{-2} in acidic, alkaline, and asymmetric electrolytes:

Acidic electrolyte: 2.24 V × 10 mA cm^{-2} × 0.042 cm^2 = 940.8 mWh

Alkaline electrolyte: 2.22 V × 10 mA cm^{-2} × 0.042 cm^2 = 932.4 mWh

Asymmetric electrolyte: 1.58 V × 10 mA cm^{-2} × 0.042 cm^2 = 663.6 mWh

If we consider 936.6 mWh as the average power density for electrolyzer operating under acidic or alkaline electrolyte, the difference in power density between the asymmetric electrolyte and acid/alkaline electrolyte is the contribution from electrochemical neutralization realized on the surface of the electrodes, i.e., 273 mWh (936.6 mWh – 663.6 mWh). So, the electrochemical neutralization energy utilization efficiency for water electrolysis in the microfluidic reactor is 20.8% (273 mWh/1311 mWh × 100).

Cost comparison of the typical state – of – art electrolyzer with the microfluidic electrolyzer based on the number of components

The cost of the typical state – of – art electrolyzer and the microfluidic electrolyzer are subjected to variation based on the raw materials and varying fabrication cost. However, the percent contribution of each components to the overall cost will remain the same as they comprise the vital elements involved in the fabrication of each device.

Table S2a: Typical state – of – art electrolyzer with components and system cost

Components	**System Cost**	
	USD	**%**
Membrane Electrode Assembly (MEA) [1]	203	39.96
Liquid Diffusion Layer [2]	116	22.83
Gasket [3]	114	22.44
Bipolar Flow Plates [4]	75	14.76
Total	508	

[1] Electrolyzer MEA – 3 Layer, [2] Titanium Frit, [3] Silicone Gasketing, [4] Flex-Stark Bipolar Graphite Plate. The price of the components are adopted from FuelCellStore (https://www.fuelcellstore.com/) accessed on 22-08-2020.

Table S2b[1]: Asymmetric microfluidic electrolyzer with components and system cost

Components	**System Cost**	
	USD	**%**
PDMS Microchannel	6.5	20.40
Patterned Electrodes	23.4	73.46
Tube Fittings	1.95	6.122
Total	31.85	

[1]The fabrication cost is based on the rate provided by Nanoscale Research Facility, IIT Delhi, where the device was fabricated for research purpose

Volumetric H_2 and O_2 collection efficiency

The number of moles of the product obtained theoretically is calculated by estimating the charge, Q (Coulombs) [6]:

$$Q = \int_0^t I.dt = nFN \tag{S11}$$

where F is the Faraday's constant (96485 C mol^{-1}), N is the moles, and n is the number of electrons involved in the reaction (n = 2 for HER, and n = 4 for OER). The integration is evaluated by calculating the area under the curve of Fig 7a, which is 11.14 C. Therefore, the theoretical moles of hydrogen and oxygen is calculated as:

$$N_{H_2} = \frac{Q\ (area\ under\ the\ curve\ of\ Fig\ 7a)}{nF} = \frac{11.14}{2\ \times 96485} = 5.77 \times 10^{-5} moles$$

$$N_{O_2} = \frac{Q\ (area\ under\ the\ curve\ of\ Fig\ 7a)}{nF} = \frac{11.14}{4\ \times 96485} = 2.88 \times 10^{-5} moles$$

Now, using the above values to the ideal gas law at NTP, the theoretical volume of gas generated is estimated to be: $V_{H_2} =$ 1.38 ml, and $V_{O_2} =$ 0.70 ml for hydrogen and oxygen respectively. Comparing the theoretical volume of gas with the volume obtained by water displacement technique to collect gas products after electrolysis, we evaluate the volumetric collection efficiency as:

$$Volumetric\ collection\ efficiency\ of\ H_2 = \frac{Experimental\ V_{H_2}}{Theoretical\ V_{H_2}} \times 100\% = \frac{1.3\ ml}{1.38\ ml} \times 100 = 93.14\%$$

$$Volumetric\ collection\ efficiency\ of\ O_2 = \frac{Experimental\ V_{O_2}}{Theoretical\ V_{O_2}} \times 100\% = \frac{0.64\ ml}{0.70\ ml} \times 100 = 91.43\%$$

Energy conversion efficiency based on the interelectrode distance

The energy conversion efficiency based on a simple electrosynthetic model proposed by Modestino et al. [7] is estimated to rationalize the interelectrode distance of 150 μm for the membrane-less electrolyzer. The fractional device efficiency is calculated as a function of power loss from ionic resistance (P_{ion}) and power loss from fluidic resistance (P_{fluid}) compared to the chemical energy stored in the products ($P_{storage}$) as [7]:

$$\eta = \frac{P_{storage}}{P_{storage} + P_{ion} + P_{fluid}} \quad \text{(S12)}$$

$$P_{storage} = jE^0 \quad \text{(S13)}$$

$$P_{ion} = \frac{j^2 dL}{\sigma}\text{, and} \quad \text{(S14)}$$

$$P_{fluid} = \frac{12\, \mu Q^2 L}{d^3} \quad \text{(S15)}$$

where d is the interelectrode distance, L is the length of reactor, μ is the viscosity of liquid electrolyte, and Q is the areal flow rate based on the dimension of the channel. The energy conversion efficiency is estimated to be 96.5% for the microfluidic reactor in asymmetric electrolyte operating at a current density of 23.3 mA cm^{-2} corresponding to 1.8 V (from Fig 4a) and 1.4 ml min^{-1} flow rate.

Calculation of conductivity for 0.5M H_2SO_4 and 1M NaOH based on the mobility of ions:

The conductivity is estimated based on the ionic mobilities using the following equation [6]:

$$\sigma_i = (|z_i|F)c_i u_i \tag{S16}$$

where σ_i is the conductivity, z_i is the charge number, c_i is the concentration, and u_i is the mobility of i^{th} species.

For 0.5M H_2SO_4

The mobility of the ions[8] are u_{H^+} = 36.23 × 10^{-4} cm^2/V s, and $u_{SO_4^{2-}}$ = 8.29 × 10^{-4} cm^2/V s, and c_{H+} = 10^{-3} mol cm^{-3}, and $c_{SO_4^{2-}}$ = 0.5 × 10^{-3} mol cm^{-3}, and z_{H+} = +1, and $z_{SO_4^{2-}}$ = -2. Substituting the values in Equation S16:

σ_{H^+} = 0.17 Ω^{-1} cm^{-1}, and $\sigma_{SO_4^{2-}}$ = 0.08 Ω^{-1} cm^{-1}

$$\sigma_{H_2SO_4} = \sigma_{H^+} + \sigma_{SO_4^{2-}} = 0.25\,\Omega^{-1}cm^{-1}$$

For 1M NaOH

The mobility of the ions[8] are u_{Na^+} = 5.19 × 10^{-4} cm^2/V s, and u_{OH^-} = 2.05 × 10^{-3} cm^2/V s, c_{Na+} = 10^{-3} mol cm^{-3} and c_{OH-} = 10^{-3} mol cm^{-3}, and z_{Na+} = +1 , and z_{OH-} = -1 Substituting the values in Equation S16:

σ_{Na^+} = 0.05 Ω^{-1} cm^{-1}, and σ_{OH^-} = 0.19 Ω^{-1} cm^{-1}

$$\sigma_{NaOH} = \sigma_{Na^+} + \sigma_{OH^-} = 0.24\,\Omega^{-1}cm^{-1}$$

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