

Supplementary Information For:

Hierarchically Conductive Electrodes Unlock Stable and Scalable CO₂ Electrolysis

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§1. Carbon paper and ePTFE Ohmic Loss Scaling

From the main text:

$$\Delta V_{ePTFE} = \frac{i\rho_{cat}L^2}{t_{cat}}$$

$$\Delta V_{carbon} = i\rho_{carbon}t_{carbon}$$

The ratio between the two yields:

$$\frac{\Delta V_{ePTFE}}{\Delta V_{carbon}} = \left(\frac{\rho_{cat}}{\rho_{carbon}} \right) \left(\frac{L^2}{t_{cat}t_{carbon}} \right)$$

For a commercially relevant electrode, we assume $L \sim 0.1$ m (100 cm² electrode area). t_{cat} is assumed to be of the order of 1 μm , while t_{carbon} is of the order 100 μm . The resistivity of copper (1.68 E-08 $\Omega \cdot \text{m}$) is used for ρ_{cat} and an approximate, conservative resistivity of carbon fibers (2E-06 $\Omega \cdot \text{m}$) is used for ρ_{carbon} . This gives:

$$\frac{\Delta V_{ePTFE}}{\Delta V_{carbon}} = \left(\frac{10^{-8}}{10^{-6}} \right) \left(\frac{10^{-2}}{10^{-6} \cdot 10^{-4}} \right) = \mathbf{10^6}$$

Naturally, the porosity of the catalyst layer and of the carbon paper affects conductivity substantially. This effect is not considered here, but is considered in the determining an appropriate *effective* catalyst layer thickness for the simulation model.

§2. Electrochemical Test Setups

The operating conditions of the cell were specifically selected to isolate the electrode ohmic effects with increasing electrode size. The 100 SCCM CO₂ flowrate for small cell testing was intended to keep CO₂ utilization rates low as shown in Supplementary Fig. S10 to minimize Nernstian effects at larger electrode sizes.

When testing ePTFE electrodes, the catalyst has an electrical connection to the current collector on one edge of ~2.4 mm width for ease of assembly (Supplementary Fig. S5 and S13). The connectivity of the electrode could be improved by connecting around the entire outer edge of the electrode. In our experiments, we elected to connect to only one edge to amplify the ohmic effects, such that they could be well-studied in a more tractable smaller scale cell (< 5 cm²). However, connecting the entire outer edge of the electrode does not fundamentally resolve the poor scaling of ePTFE electrodes, and would only slightly delay the scaling issues. All modeled ePTFE performance at 50 cm² and 100 cm² electrode sizes which we use for final comparison in Figure 4 assumes a well-connected electrode which is connected on all four sides, along the entire length of each side.

We note that the C₂₊ Faradaic Efficiencies of the 14.0 cm² and 50.0 cm² HCGDE electrodes are slightly lower than those observed for the 0.5 cm² and 4.2cm² HCGDE electrodes despite their adequate conductivity. Such slight variations are not unexpected due to the vastly different CO₂ utilization (Supplementary Fig. S10) conditions, residence time, and stack compression characteristics between the small cell and large cell.

§3. Electric Current Modelling

§3.1. Governing Equations

To model the spatial potential distribution, we developed a finite element model only considering ohmic sheet resistances and a pointwise current. The model was constructed using the COMSOL Multiphysics 6.0 electric currents interface of the AC/DC module, which conserves electric charge and models potential drops using the following governing equations:

$$\nabla \cdot \mathbf{J} = Q_{j,v} \quad (\text{S.1})$$

$$\mathbf{J} = \sigma \mathbf{E} \quad (\text{S.2})$$

$$\mathbf{E} = -\nabla V \quad (\text{S.3})$$

Here, $\mathbf{J}$ denotes the flux of charge, $Q_{j,v}$ represents a pointwise current source, σ denotes electrical conductivity, and V and $\mathbf{E}$ denote the potential and its gradient respectively. The model was constructed in 2 dimensions, with a constant uniform out-of-plane thickness corresponding to the thickness of the copper catalyst layer.

§3.2. Physical Properties and Assumed Inputs

To approximate the relationship between potential and pointwise current, potentials were measured over local current densities ranging from 100 A/m² to 5000 A/m² for a 0.5 cm² cell. The small cell size is chosen to ensure that ohmic losses are insignificant, thus meaning that the entire surface is equipotential. A lookup table can thus be formed which relates local potential to local current density, as shown in Table S1. Corresponding cell potentials and ethylene faradaic efficiencies were determined with a Biologic SP-150 Potentiostat and Gas Chromatography respectively.

Local Potential (V)	Total Current Density (A/m ²)	Ethylene Faradaic Efficiency
2.6	100	0
2.92	500	0.04
3.16	1000	0.1
3.37	1500	0.24
3.58	2000	0.47
3.76	2500	0.36
3.92	3000	0.21
4.09	3500	0.14
4.29	4000	0.1
4.5	4500	0.08
4.68	5000	0.07

Table S1: Lookup table relating local cathode potential to the total faradaic current density and ethylene faradaic efficiency employed in the model. These values were obtained from performance data for an 0.5cm² cell featuring a with copper catalyst and PTFE GDE cathode against an IrOx carbon paper anode.

Linearly interpolating the above table to yield current as a function of voltage ($i=i(V)$) and denoting thickness as t , a pointwise volumetric current sink was defined as:

$$Q_{j,v} = -\frac{i(V)}{t} \quad (\text{S.4})$$

To replicate the appropriate in-plane conductivity of the electrode, the copper layer is modeled as 250nm thick, matching the deposition thickness measured via Quartz Crystal Monitor (QCM) during sputter deposition. To account for the effects of porosity and 3D membrane structure, the effective in-plane conductivity of the copper was determined experimentally by applying Ohm's law to the data in Supplementary Figure S15. The resultant value of 31,761 S/cm is substantially lower than the conductivity of pure copper (~600,000 S/cm) as a result of the porosity of the ePTFE membrane, which causes longer path lengths and likely thinner depositions.

§3.3. Boundary Conditions

In this work, the above bulk mathematical formulation was employed in three different kinds of simulated geometries:

- A. To model experimental cell performance, voltage was applied from a fixed lead width at the side of the cell, with all other sides insulated. Cell performance was found to be nontrivially affected by the width of the connecting lead – this was matched to the experimental setup (2.4 mm) to improve correlation accuracy.
- B. To predict cell performance at scale under a more effective connection strategy, voltage was applied at all sides of the cell to replicate full connection. This improved performance relative to the singly connected case, reducing the characteristic resistance length scale by a factor between $\sqrt{2}$ and 2.
- C. To model the impacts of woven copper wire spacing. Here, the voltage is applied on two sides, representing the wired connections. The other two sides have periodic boundary conditions. While this could be readily simplified to a 1D model, the 2D model was retained for better visualization without a significant increase in computational time.

These geometries are depicted graphically below:

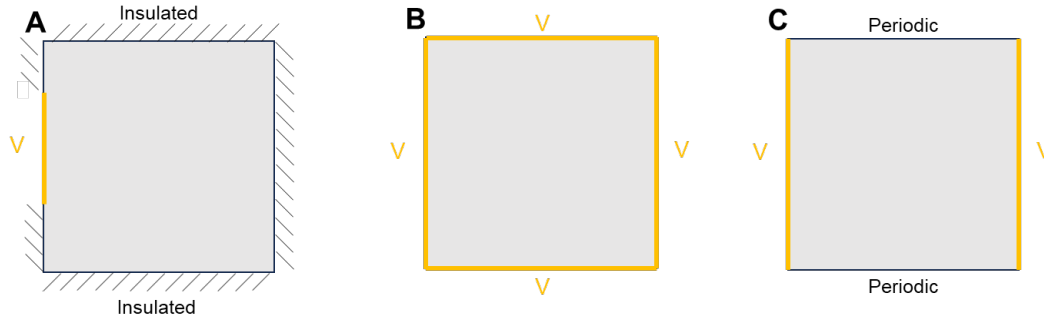


Figure S1: Depiction of simulation geometry for A) predicting experimental cell performance with a standard ePTFE GDE B) predicting cell performance at scale with a standard ePTFE GDE C) predicting performance of a HCGDE cell

Mathematically, these boundary conditions are implemented as the following:

Constant Potential	$V = V_{Applied}$	(S. 5)
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Insulation	$\mathbf{J} \cdot \mathbf{n} = 0$	(S. 6)
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Periodicity	$V_{x,y=y_1} = V_{x,y=y_2}$	(S. 7)
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§3.4. Full Cell Voltage as a Proxy For Cathode-Electrolyte Potential Drop

The model utilizes the full cell voltage to predict activity and faradaic efficiency of the cathode. In reality, the difference in potential between the cathode and the electrolyte phase is the key driving force of the reaction. We denote this $V_c - V_e$ in Supplementary Fig. S2. In a membrane-electrode assembly, measuring spatial gradients in this potential would be impractically difficult, thus why $V_c - V_a$ is used for experimental anchoring of the simulations. The full cell voltage is shown as $V_c - V_a$. In Supplementary Fig. S2, the voltage of the anode (V_a) must be constant because it is a conductive material (carbon paper) conducting electrons through its thickness. We calculate that ohmic losses through the anode are on the order of single millivolts (see supplementary info section 1). The voltage of the cathode is schematically shown to decrease with the x coordinate (which here represents the distance from the electrical contact point) due to the ohmic losses described in great detail in our work. The dashed line indicates the unknown electrolyte potential as a function of x .

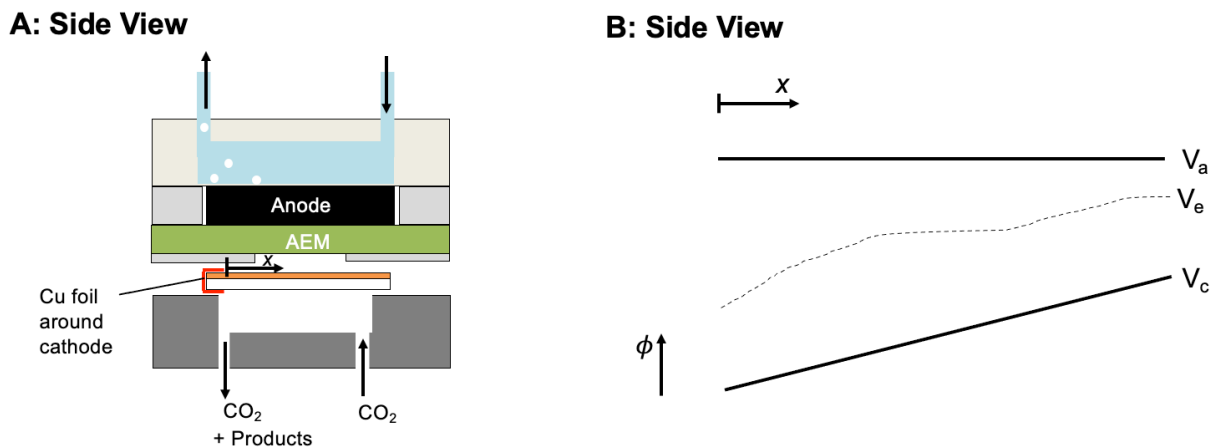


Figure S2: A) Side cross-sectional view of the cell, with the coordinate x defined as the in-plane distance from the electrical connection point. B) Schematic representations of theoretical potential (ϕ) profiles in the cell of the anode (a) electrolyte (e, unknown) and cathode (c). x

denotes the distance from the closest point of electrical connection within the plane of the catalyst/membrane.

In order to assess the profile of the electrolyte potential, we need to determine whether significant gradients in electrolyte potential are possible in the x direction. If the conductivity of the electrolyte in the x direction were to be high, then the electrolyte potential will be a flat line, for the same reasons as the anode potential. If the conductivity of the electrolyte is low relative to that of the anode and cathode, then significant variations in electrolyte potential are possible at different x positions.

$$R_{membrane,in-plane} = \frac{\rho_{membrane} L_{sidelength}}{t_{membrane} L_{sidelength}} = \frac{(10^{-1})(10^{-2})}{(10^{-4})(10^{-2})} \sim \mathbf{10^3 \Omega}$$

$$R_{cathode,in-plane} = \frac{\rho_{Cu} L_{sidelength}}{t_{Cu} L_{sidelength}} = \frac{(10^{-8})(10^{-2})}{(10^{-7})(10^{-2})} \sim \mathbf{10^{-1} \Omega}$$

$$R_{anode,through-plane} = \frac{\rho_C t_C}{t_C L_{sidelength}} = \frac{(10^{-4})(10^{-4})}{(10^{-4})(10^{-2})} \sim \mathbf{10^{-2} \Omega}$$

The in-plane membrane resistivity ($10^{-1} \text{ Ohm}\cdot\text{m}$) is calculated given the through-plane area resistivity of $0.045 \text{ Ohm}\cdot\text{cm}^2$ (Dioxide Materials) and a membrane thickness of 50 μm . This means that significant variations in the electrolyte potential are possible in the x direction. Moreover, it means that the potential of the electrolyte at any point x will be dictated by the potentials of anode and cathode at that same coordinate x, rather than the neighboring conditions at $x+dx$ or $x-dx$. This scaling analysis enables the *local* treatment of the reaction, in that the reaction at any point x is influenced *only* by the potential applied at the anode and cathode *at that x position*.

Given that this local treatment is possible, we posit that the electrolyte potential V_e will be solely a function of the difference in cathode and anode potential, $V_c - V_a$. Therefore we expect a one-to-one mapping between $V_c - V_a$ and $V_c - V_e$. This enables the use of $V_c - V_a$ (i.e. the cell voltage) as a proxy variable for $V_c - V_e$.

§4. Product Measurement, Faradaic Efficiency, and Electrical Efficiency

Faradaic Efficiency (FE) is calculated as:

$$FE = \frac{I_{product}}{I_{total}} = \frac{z\dot{n}F}{I_{total}}$$

where z is the moles of electrons required per mole of product, $\dot{n}$ is the molar production rate, and F is Faraday's constant. Product production rates are measured in three streams (cathode gas, cathode cold trap, anolyte) as shown in Supplementary Figure S5. Gaseous products were measured for each experiment. The gas chromatograph was linearly calibrated with a custom gas mix including all reported gasses (hydrogen, methane, carbon monoxide, ethylene). ^1H NMR was linearly calibrated with relevant concentrations of acetaldehyde, formate, acetate, n-propanol, and ethanol. All liquid and gas products totaled together should reach approximately 100% FE. Gaseous and liquid products were simultaneously interrogated for the 4.2 cm² ePTFE GDE and the 50.0 cm² HCGDE to validate complete measurement of products. As shown in Supplementary Fig. S19, nearly 100% FE is obtained for all current densities. Experimental repeatability is demonstrated in Supplementary Fig. S9 for the 4.2 cm² ePTFE GDE, wherein the voltage varies by less than 2% between experiments and the product FE varies by less than 4% between experiments using electrodes and membranes fabricated in different batches.

Electrical Efficiency (EE) is calculated using the FE, the cell voltage V , and the thermodynamic voltage of product formation V_{thermo} (1.15-1.2 V for C_{2+} products):

$$EE = \sum_i FE_i \cdot \frac{V_{thermo,i}}{V}$$

Figure 4B Faradaic Efficiencies

C_{2+} FE in Figure 4B for the 50 cm² HCGDE is directly experimentally interrogated as shown in Supplementary Figure S19.

C_{2+} FE in Figure 4B for the 4.2 cm² and 14 cm² HCGDE are estimated by assuming 100% FE (validated in Supplementary Fig. S19) and calculating the liquid product FE as $FE_{liquids} = 100\% - FE_{gases}$. Because all substantial liquid products are C_{2+} products (as validated in Supplementary Fig. S19), the C_{2+} FE is estimated as $FE_{C_{2+}} = FE_{C_2H_4} + FE_{liquids}$. The full accounting of FE to 100% +/- 5% is also validated in Supplementary Fig S19.

§5. HCGDE design considerations

Ohmic losses through the wire

The introduction of micrometric conductors into the GDE reduces the ohmic loss through the catalyst layer. At the same time, it is also important to ensure that there are not significant ohmic losses through the micrometric conductors themselves. Given a wire spacing s and wire diameter d shown in Supplementary Figure S20, we can calculate the limiting length l of the micrometric wire to keep ohmic losses below a certain limit:

$$l_{limit} \sim \frac{\Delta V_{limit} \pi d^2}{4 i s^2}$$

For a current density i of 400 mA/cm², a spacing of 4 mm, a wire diameter of 75 μm, and a desired voltage limit of 10 mV, we find a limiting length of 7.0 cm. This matches the length of the wires in the 50.0 cm² electrode. This equation is a conservative estimate, as it assumes a constant current through the wire while practically the current should decrease along the wire as current passes from the wire into the catalyst layer.

This consideration would become increasingly relevant at larger electrode sizes. Several approaches can be employed at significantly larger electrode sizes in order to maintain low ohmic losses. We note that l_{limit} does not set a limit on the actual electrode size possible, rather, it sets a limit on the length of wire exposed along the catalyst as shown in Supplementary Figure S20. For example, in the case of a 10,000 cm² electrode (100 x 100 cm²), a single wire can be sewn into the GDE such that it runs along the catalyst for 7 cm a total of 15 times, resurfacing to the back of the GDE after each 7 cm stretch. Connection to the current collector at the backside of the GDE “resets” the ohmic loss and keeps each wire segment in parallel. Alternatively, l_{limit} can be increased by using larger wire diameters or reducing the spacing of the wires.

HCDGE wire footprint calculations

For the wire configuration, the wire area fraction can easily be calculated:

$$\frac{A_{wire}}{A_{catalyst}} \sim \frac{d}{s}$$

For the experimentally used parameters, this area fraction is negligible at $< 2\%$.

Image analysis software was used to estimate the area of the holes required for passing the wire through the electrode. This area is less than 1% of the total catalyst area, again negligible.

§6. Literature ePTFE Electrode Size: Supplementary Figure S28

Data

We searched the literature to catalog the performance of all (to the best of our knowledge) electrochemical CO₂ conversion GDEs which use ePTFE gas diffusion layers and target C₂₊ products. Electrodes producing predominantly CO and formate were neglected.

Ref	Electrode size (cm ²)	C ₂₊ FE (%)	Total Current Density (mA/cm ²)	Full Cell Voltage (V)
1	5	70	255	3.8
2	10	70	~200	-1.6V vs Ag/AgCl
3	1	~68	300	~-0.9V vs RHE
4	1	77	240	4.3
5	1	84	230	3.65
6	5	65	200	4.2
7	5	55	200	4.4
8	1	80	250	-0.7V vs RHE
9	1	80	200	2.5
10	1	90	300	2.85
11	5	75	200	4.2
12	4.5	91	150	3.7
13	5	80	200	3.9
14	2	75	100	2.7
15	1	42	173	~-0.7V vs RHE
16	1	88	400	~-2V vs RHE
17	5	90	200	3.4
18	1	80	200	3.7
19	5	92	160	3.67
20	1	48	1200	4.2
21	1.1	76	1700	-1.1V vs RHE
22	2.0	47	200	-1.85V vs RHE
23	4	47	~30	-1.49 V vs RHE
24	5	~77	200	~-0.8V vs RHE
25	2.25	~40	100	-2.2V vs Ag/AgCl
26	1	84	900	3.90
27	1	85	800	-1.15V vs RHE

28	1	80	100	3.3
29	1	75	200	3.5
<i>This Work</i>	50.0	74	200	3.52

Table S2: Literature ePTFE electrode size, maximum C₂₊ Faradaic Efficiency, and full cell voltage as could best be determined. A single most representative data point was taken from each paper. Cell voltages are full cell voltages unless otherwise specified. For works which did not fully characterize all products, only the measured C₂₊ products are counted.

§7. Flooding and other Instability and Degradation Modes

Fig. 5 and Supplementary Fig. S23 compile the long-term stability testing results performed in this work, along with further post-mortem characterization in Supplementary Fig. S24-25.

Supplementary Fig. S23 shows the stability tests on carbon paper substrates at different current densities. We identified that there are two potentially independent instability mechanisms at play in carbon paper electrodes:

The first is a discrete flooding event on the order of ~30 minutes as shown in Supplementary Figure 1B. This instability mode has been observed before, and has been rationalized as an intrusion of liquid which prevents CO₂R, resulting in hydroxide generation and thus a decrease in membrane resistance, lowering cell voltages and CO₂R FE³⁰. We observe that this instability mode is not always present under all conditions, appearing only in Supplementary Fig S23B.

The second mechanism is a continuous and gradual decay in CO₂R FE. We observe this to occur in both the 100mA/cm² and 170mA/cm² carbon paper experiments, but not the

100mA/cm² ePTFE HCGDE stability experiment. This effect occurs over the course of ~40 hours for both the 100 and 170mA/cm² experiments, resulting in negligible CO₂R FE by the end of the experiment. Due to the gradual nature of this instability, we hypothesize that it is due to gradual restriction of CO₂ gas diffusion to the catalyst due to degradation of GDL hydrophobicity and build-up of water and low-surface tension alcohol products. Supplementary Figure S24A reinforces this notion, as the backside of the carbon paper GDL is noticeably wetted upon disassembly.

With regards to this second mechanism, which drives the most relevant losses in efficiency, we have performed post-mortem analysis on the wetting properties of carbon paper electrodes after these extended stability runs. This data can be found in Supplementary Figure S24 and considers the advancing and receding contact angles of water on the backside of the GDL. The data, in aggregate, clearly demonstrate a remarkable loss of hydrophobicity of carbon paper electrodes, with a receding contact angle of water which is practically zero. This means that if any liquid, whether water or liquid alcohol products, enters the GDL, it will remain pinned within the micropores of the GDL and be impossible to reasonably remove. This effect is visible in Supplementary Fig. S24A and S25A. This liquid will block CO₂ access to the catalyst, leading to the decreased FE we observe in our experiments. We also find that electrolysis at -3.5V on a carbon paper substrate results in rapidly decreasing contact angles and pinning of water droplets (Supplementary Figure S25).

In comparison, the same characterization for the back-side of the ePTFE HCGDE GDL used in the 70-hour stability experiment shows a minor, if any, change in receding water contact angle as shown in Supplementary Figure S24B. Thus, water and liquid products are significantly easier to remove from the ePTFE GDL. We conjecture that this characteristic is why this second

mechanism does not appear to be present in our long-term stability results for ePTFE HCGDE. The ePTFE substrate is not free from all instability modes, however, and still faces issues with catalyst morphology changes and salt precipitation. In order to maintain consistent flow to the ePTFE HCGDE long-term experiments (Figure 5), small amounts of DI were flown through the cathode chamber to dissolve and dislodge any blocking salts. This operational freedom is only possible due to the sustained hydrophobicity ePTFE. The same DI water flow did not beneficially impact the performance for the carbon paper stability experiments.

We also investigated other aspects of our systems, including imaging our microwire conductors to verify no obvious corrosion (Supplementary Fig. S26), measuring resistance of the microwires before and after operation (Supplementary Fig. S27), and have included data verifying the inlet and outlet gas flow rates (Supplementary Fig. S11).

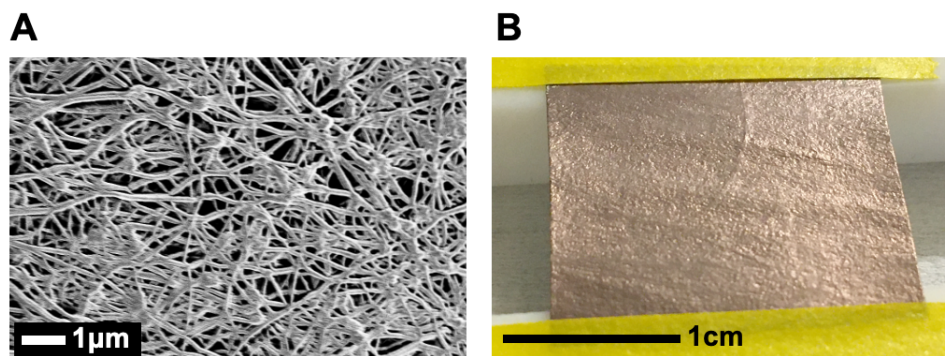


Figure S3: A) Scanning Electron Microscope (SEM) image of 250 nm copper sputtered atop a 450 nm pore size ePTFE membrane. B) Image of the catalyst side of a 4.2 cm² ePTFE electrode.

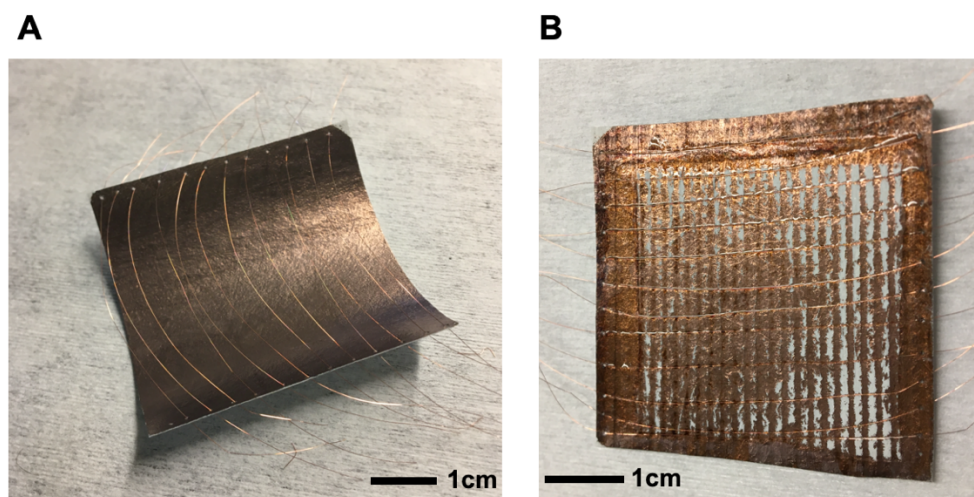


Figure S4: A) 14 cm² wire HCGDE before assembly into the electrochemical cell. B) 14 cm² wire HCGDE after assembly and disassembly. The wires maintain their regular spacing and do not damage the ePTFE membrane or ion exchange membrane. The areas where the copper has been removed occur due to adherence to the ion exchange membrane, independent of the presence of the wires.

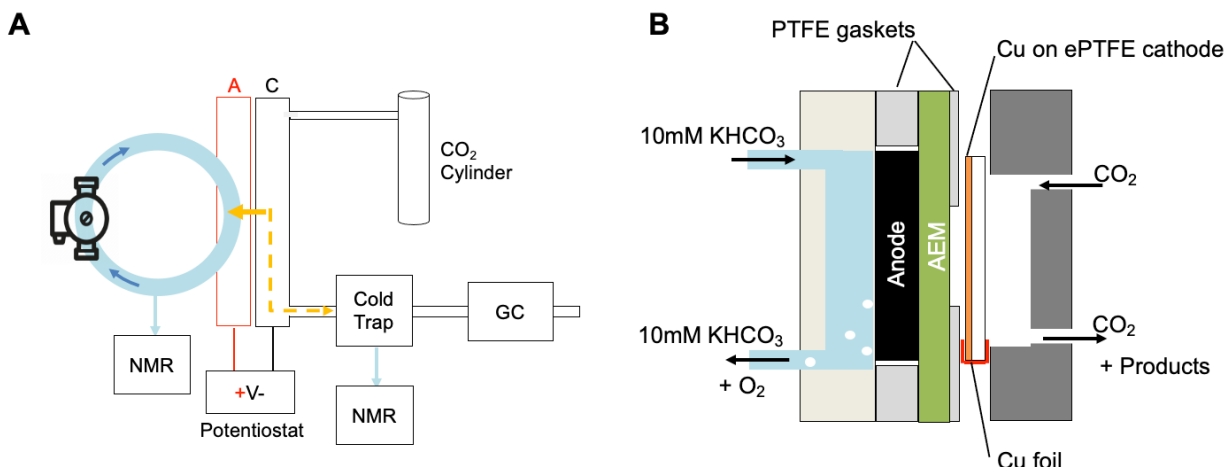


Figure S5: A) Flow schematic of the electrochemical test setup. 10mM KHCO₃ is recirculated through the anode with a peristaltic pump. A potentiostat controls the current density and measures the voltage. CO₂ (99.995%) enters the cathode, the remaining CO₂ and products exit the cathode and proceed through a cold trap to condense conversion product vapors, before reaching the Gas Chromatograph (GC). Yellow arrows delineate the path of liquid products, with some crossing over the membrane to the anolyte and some ending up in the cold trap. Both the anolyte and cold trap liquid are sampled and characterized with NMR to reach ~100% Faradaic Efficiency. B) General schematic of the MEA electrochemical test cells used in this work. An Anion Exchange Membrane (AEM) separates the anode and cathode, each surrounded by PTFE gaskets. A piece of copper foil is wrapped around one edge of the cathode to electrically connect the catalyst to the flowfield/current collector.

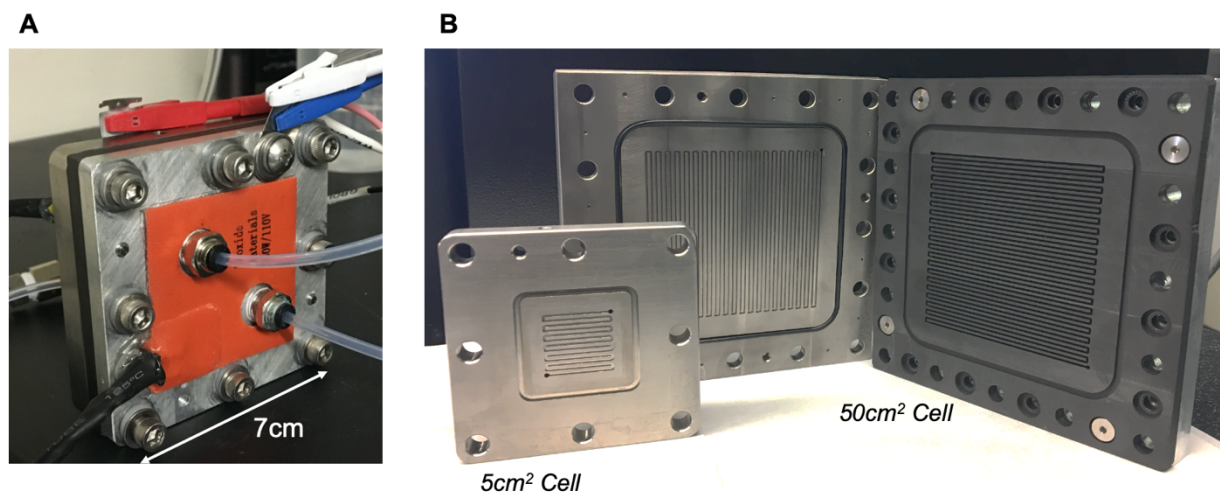


Figure S6: A) Assembled MEA testbed for testing electrodes of sizes less than 5 cm². Potentiostat leads are connected at the top. The graphite cathodic flowfield has an additional aluminum current collector plate to ensure mechanical integrity. Pictured joule heater was not used in any experiments. B) 5 cm² and custom-made 50 cm² flowfields. The materials, flowfield pattern, flowfield gap widths, and flowfield gap spacings are the same for both electrolyzers.

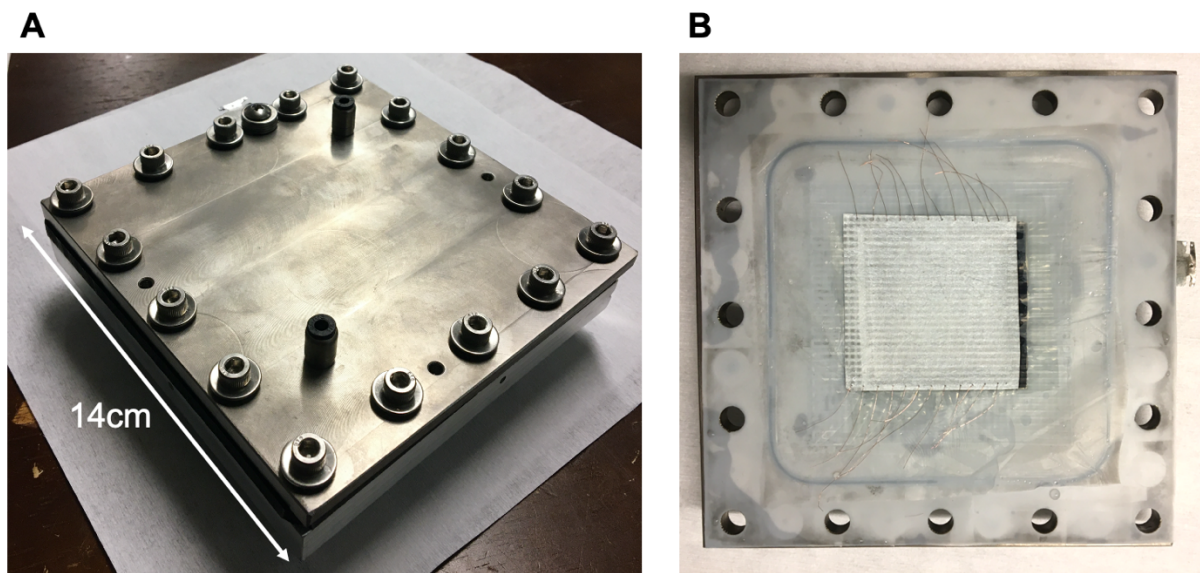


Figure S7: A) Fully assembled custom-made 50 cm² cell. B) Backside view of the cathode after disassembly showing the HCGDE wires.

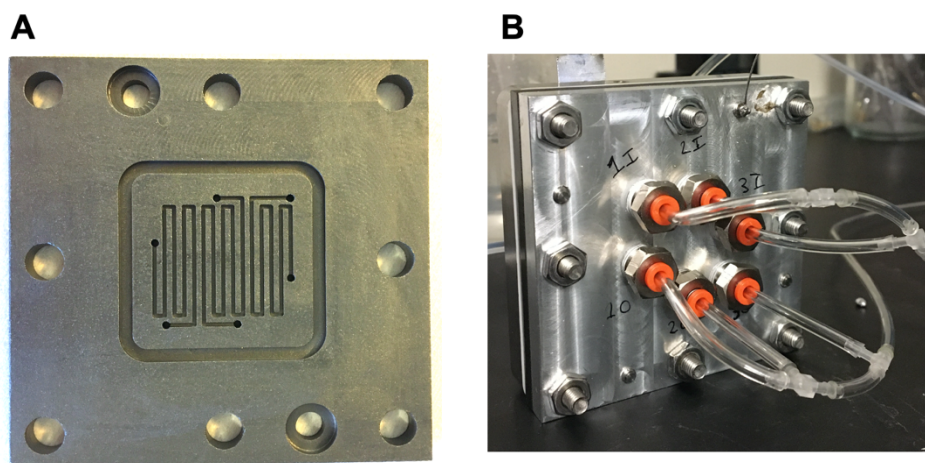


Figure S8: A) Three-part cell cathodic graphite flowfield, featuring three isolated serpentine paths. The total flowfield area is 5.0 cm². B) Electrochemical cell with three inlets and three outlets. During experiments, one of the outlets is redirected to the gas chromatograph while the two others are exhausted. The exhaust outlets use identical tubing to that which goes to the gas chromatograph to ensure equal resistance and thus equal flow through the channels.

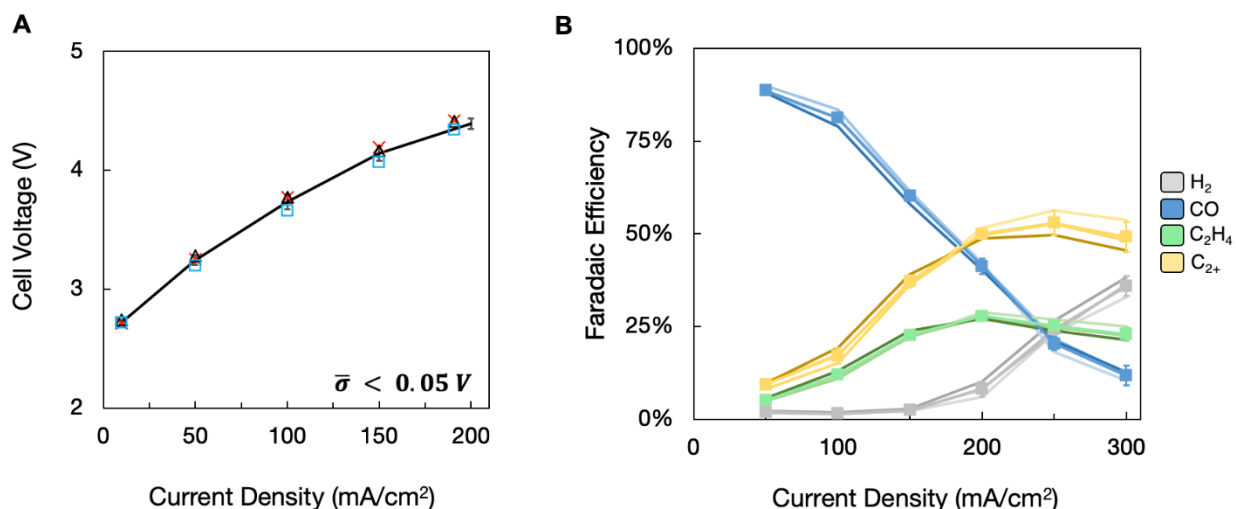


Figure S10: Repeatability data for three trials of three unique 4.2 cm² ePTFE electrodes with three separate anodes and anion exchange membranes from different production batches. A) Cell voltage as a function of current density, with black markers showing the average and error bars. B) Faradaic Efficiency as a function of current density, with individual trials shown in varying shades, with the symbols representing the average of the three trials. Error bars for many of the points are small enough to be hidden by the symbols. C₂₊ refers to liquid products, excluding C₂H₄.

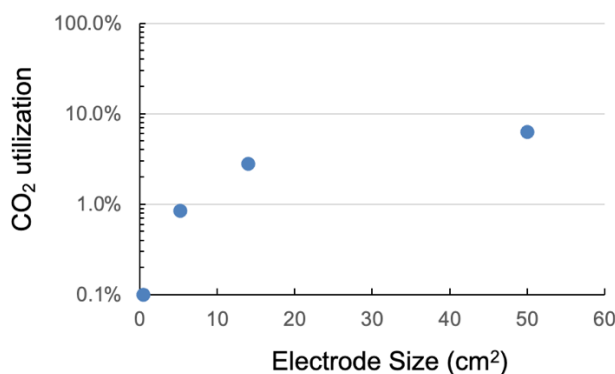


Figure S10: CO₂ utilization increases with increasing electrode size, as the CO₂ flowrate is held roughly constant (100 SCCM for <50 cm², 200 SCCM for 50 cm²).

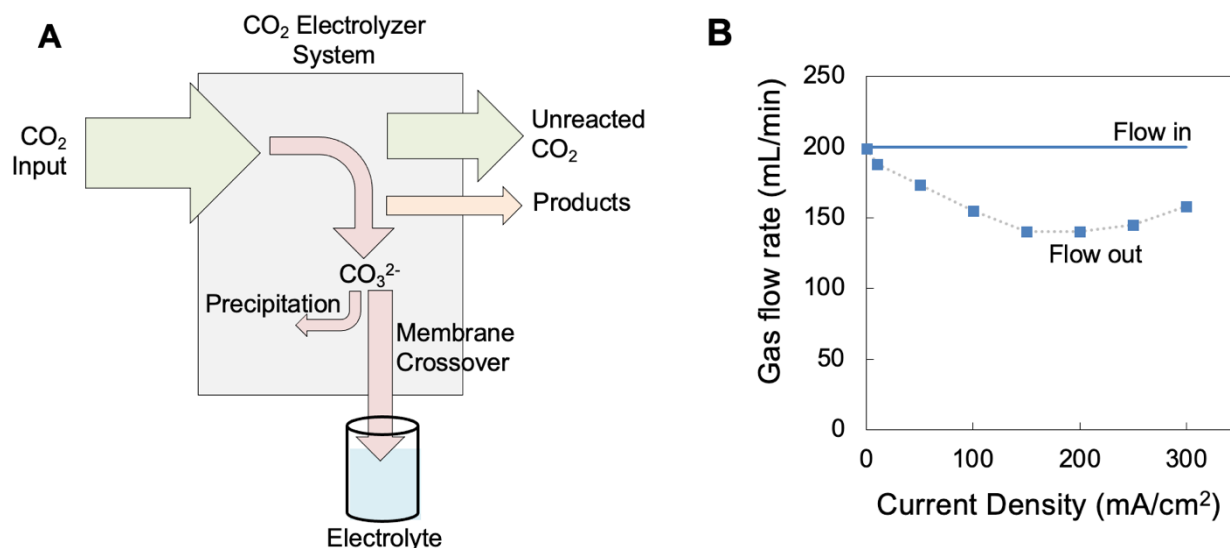


Figure S11: A) Schematic depicting mass flows in a CO₂ Electrolyzer System. Of the CO₂ flowing in, some is absorbed into the liquid phase and reacts with OH⁻ to form carbonate, which can precipitate in the cathode or cross over the membrane and into the anolyte. Some CO₂ is transformed to products, and the rest is unreacted. B) these mass flows result in unequal gas inflow and outflow rates, which is a function of the current density due to the rate of CO₂-capturing OH⁻ production, here shown for the 50 cm² reactor. The outflow must be measured to adequately characterize products rates.

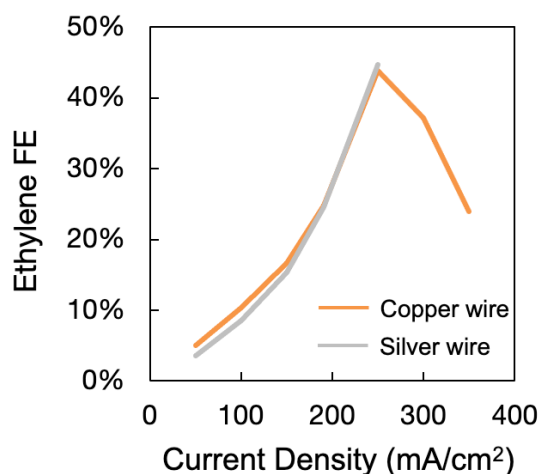


Figure S12: Performance of 4.2 cm² HCGDEs prepared with copper and silver wires (both of 75 μm diameter). The similar performance indicates that the wires do not participate significantly, as expected given their small area.

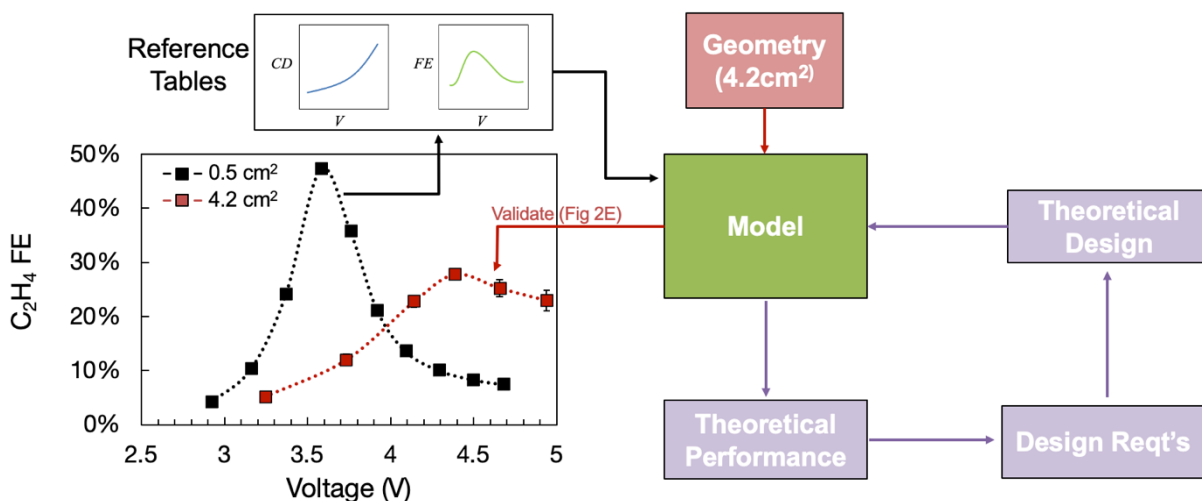


Figure S13: Flowchart of model uses. Reference performance tables are formed from the performance at 0.5 cm², where we assume ohmic losses are negligible. The model takes the 4.2 cm² geometry, solves for the electrode voltage field using the reference table and current laws, and generates a prediction for the performance of a 4.2 cm² electrode. This prediction is validated against the experimental performance. Thereafter, the model can be used to evaluate theoretical designs and establish design requirements for the HCGDE.

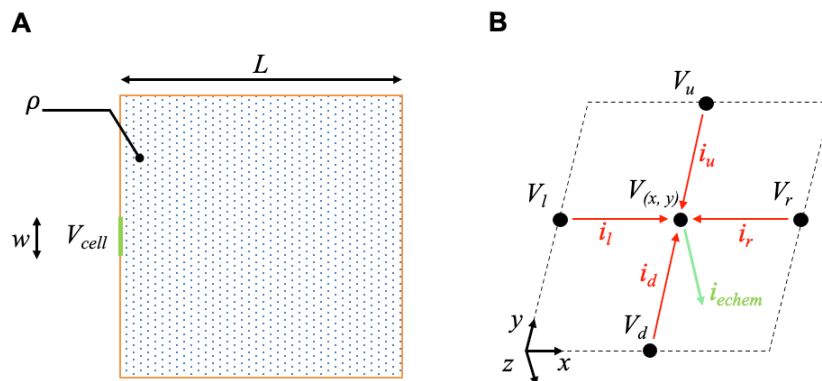


Figure S14: A) Model geometries are square with a length of L and a voltage boundary condition of width w . This width is that of the copper foil used to connect the catalyst to the current collector (~ 4 mm). B) Unit cell of the model, with currents between nodes described by Ohm's law. Each node has also an electrochemical current which leaves the electrode perpendicular to the electrode plane. This electrochemical current is determined with a look-up table to the reference performance at 0.5 cm².

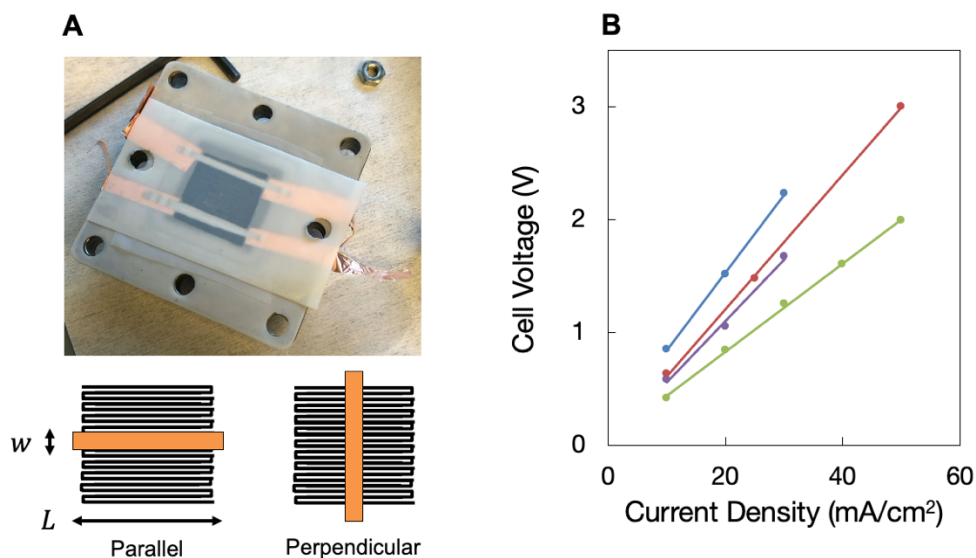


Figure S15: Experimental determination of catalyst layer effective thickness. A) Thin strips of ePTFE electrodes with a copper catalyst are assembled into the electrochemical cell with a membrane and gasketing to replicate compression effects. Experiments are performed both parallel and perpendicular to the flowfield direction to control for variable compression. B) i-V curves for the ePTFE strips show linear resistive behaviour. Blue and purple traces are aligned perpendicular, while green and red are aligned parallel to the flowfields. Both alignment directions appear to behave similarly, and the effective layer thickness is calculated using the average values of all four trials.

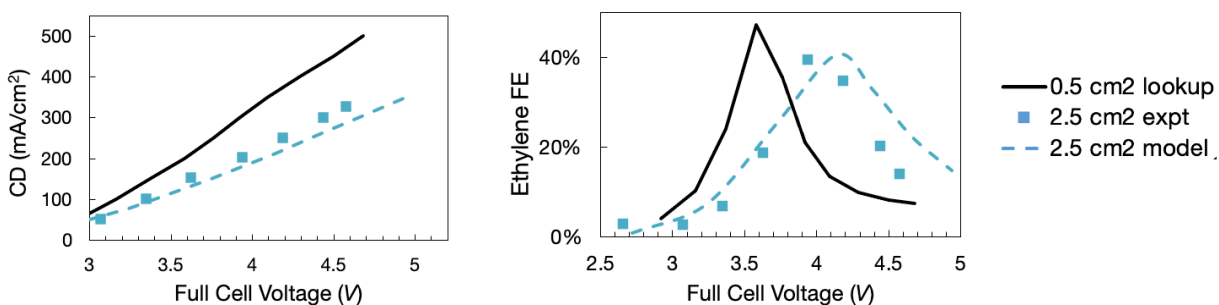


Figure S16: Model predictions for a 2.5 cm² ePTFE electrode also closely match experimental data.

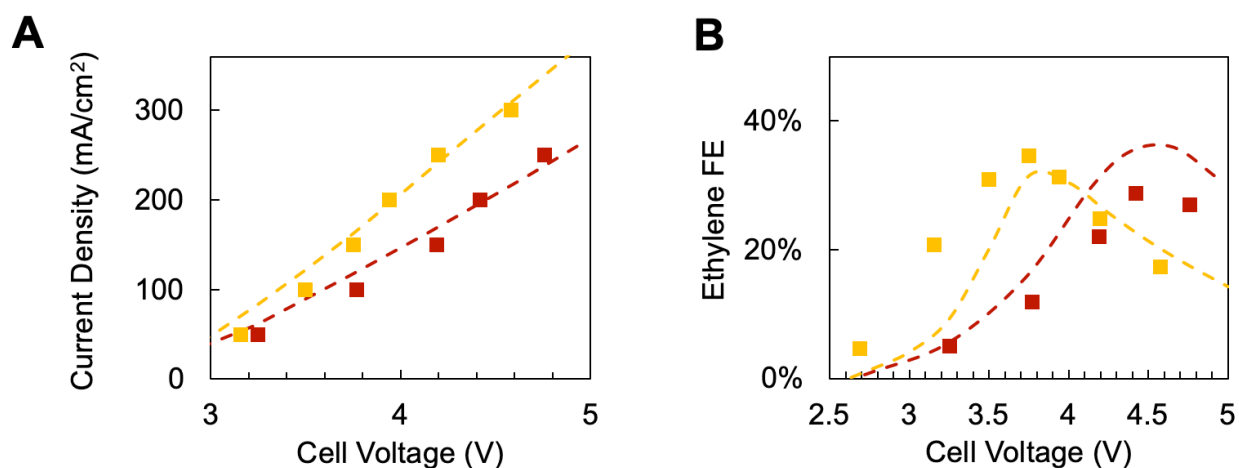
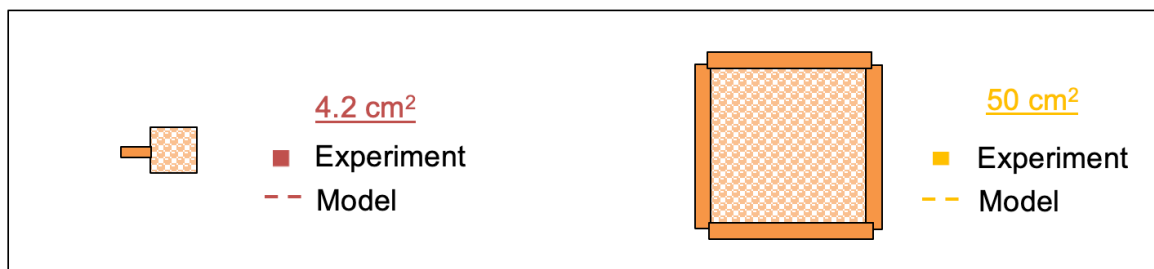


Figure S17: Further comparison of model simulations and experiments, here for different cell connection schemes. The 4.2 cm² experiments in Figure 2 are performed with a single side connection to exacerbate ohmic losses, while the 50 cm² unmodified ePTFE experiments in Figure 4 were performed with all sides connected to make a fair comparison. A) i-V curves show a strong match between model predictions and experiments. B) General trends of ethylene FE as a function of voltage hold between model predictions and experiments.

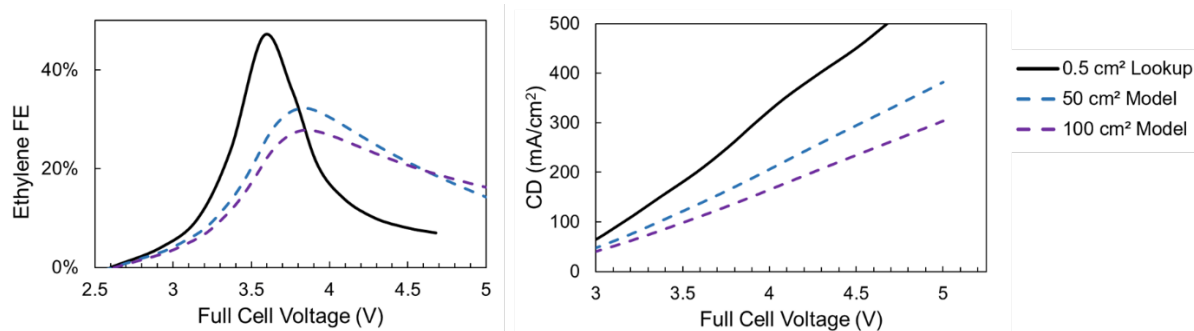


Figure S18: 50 cm² and 100 cm² predicted performance from the model.

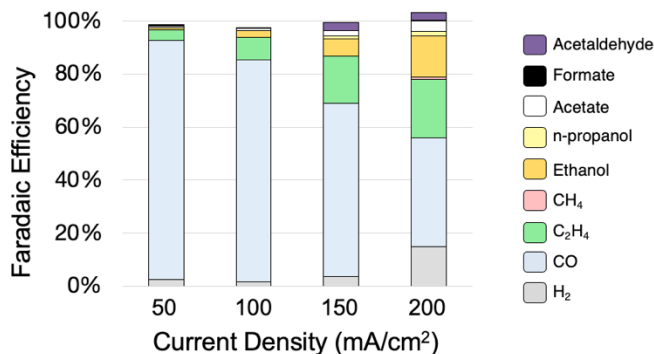
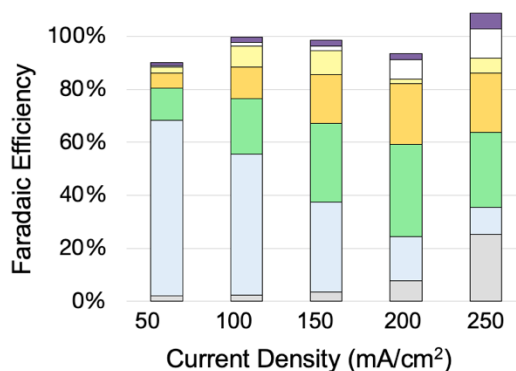
A: 4.2cm² ePTFE GDE**B: 50.0cm² HCGDE**

Figure S19: Complete gaseous and liquid product distributions from GC and NMR, totaling to approximately 100%. A) Faradaic accounting for the 4.2 cm² ePTFE GDE. B) Faradaic accounting for the 50.0 cm² wire HCGDE.

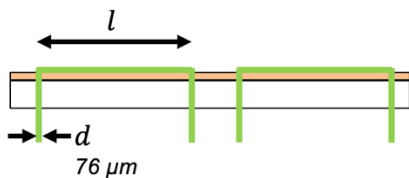
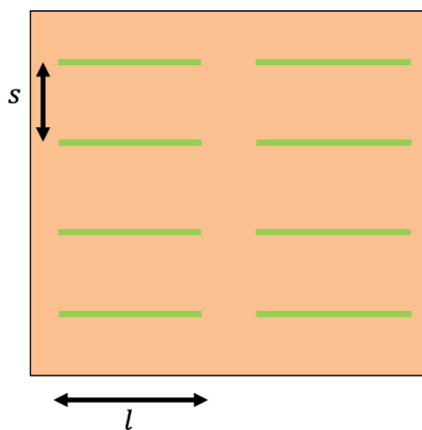
A: Side view**B: Front view**

Figure S20: A) Schematic side view and B) schematic front view of the wire HCGDE architecture for an embodiment which includes multiple columns of wire segments. Such a configuration is necessary when the side length of the electrode exceeds the critical wire length above which voltage losses through the wire itself are non-negligible.

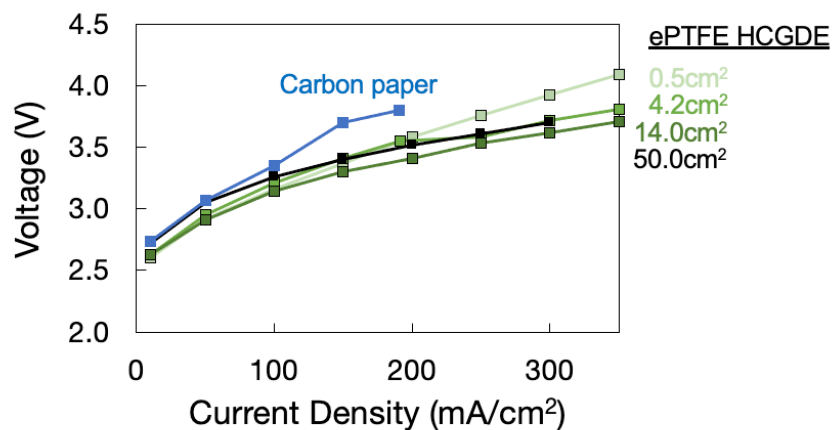


Figure S21: Comparison of cell voltage between ePTFE HCGDE cathodes and 4.2cm² carbon paper cathodes, both with 250nm Cu sputtered layers. All represented data uses the standard cell (non-stability trials) composition: IrOx anode on carbon paper substrate (Dioxide Materials) and a Sustainion X37-50 AEM (Dioxide Materials)

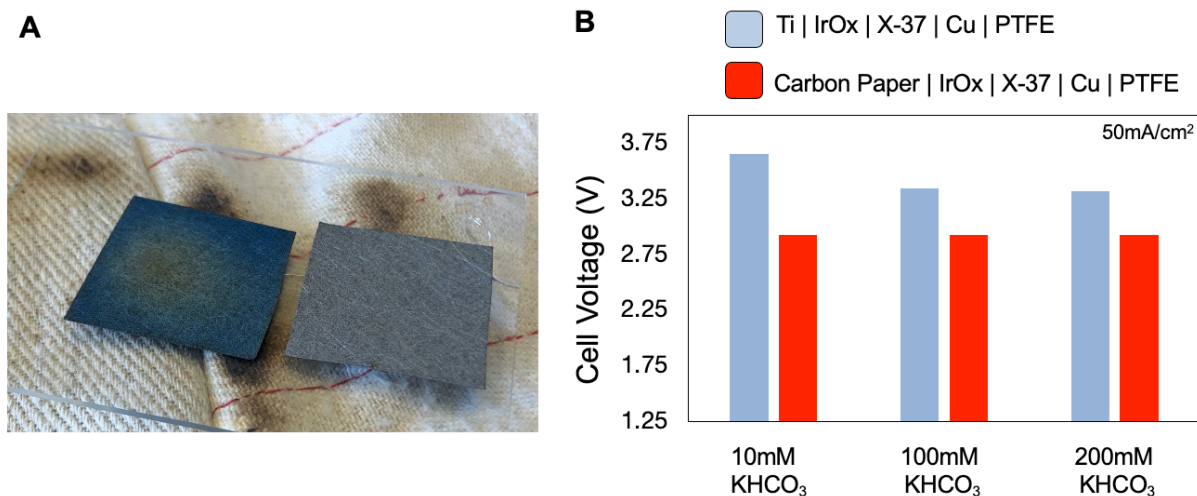


Figure S22: A) Right: 2.5x2.5 cm² titanium felt before IrOx deposition. Left: 2.5x2.5 cm² titanium felt after IrOx deposition. B) Full cell voltage at various analyte concentrations for both synthesized titanium felt IrOx anodes and purchased Dioxide materials carbon paper anodes.

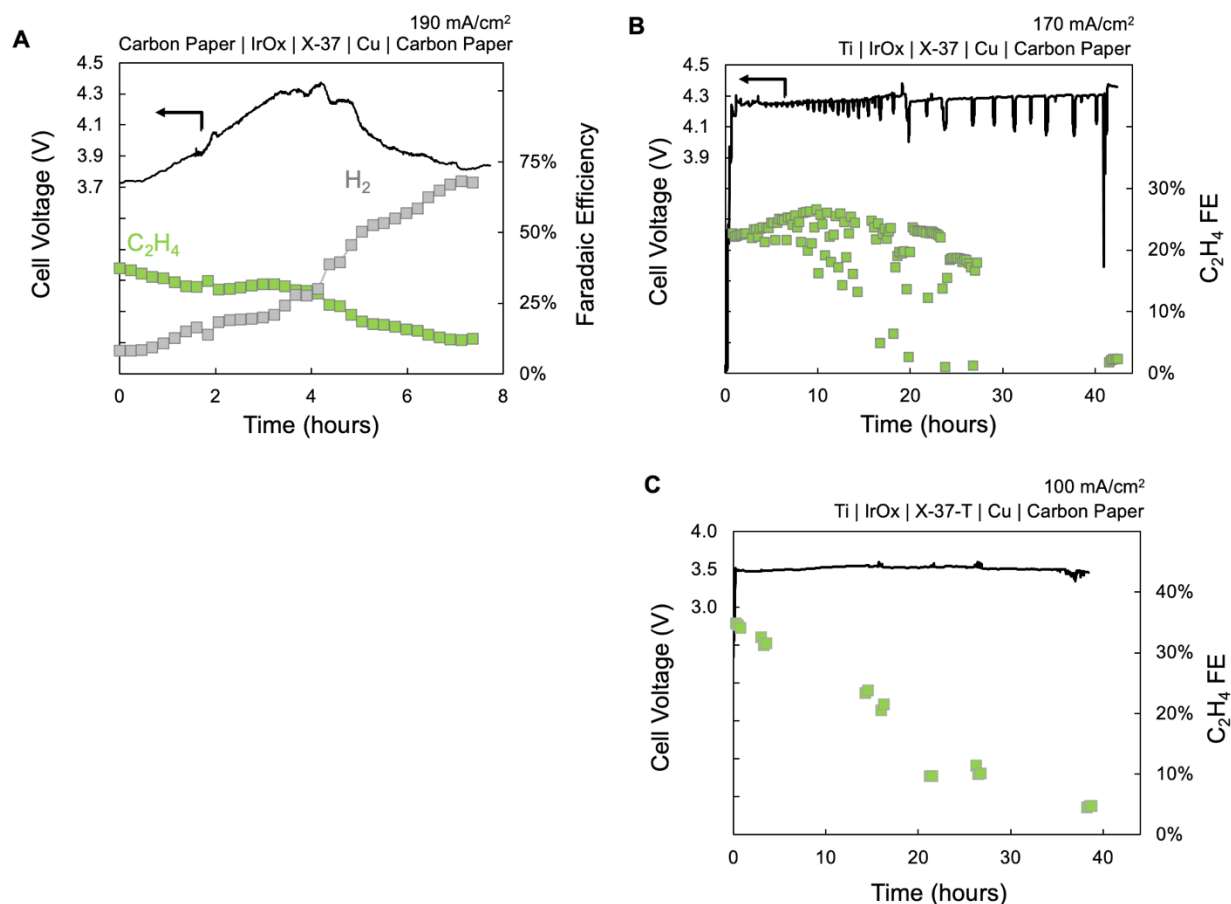


Figure S23: Stability of carbon paper cathodes. A) C₂H₄ FE drops precipitously over the course of a 7 hour stability test with carbon paper cathode and carbon paper anode. A sharp increase in hydrogen generation coincides with decreasing voltage. In order to disambiguate instability modes of the cathode and anode, a titanium-based anode is tested with a carbon paper cathode for 40+ hours with results shown in B). C) Carbon paper stability test under identical conditions as those in Figure 5, with the sole substitution of ePTFE/HCGDE substrate for carbon paper substrate.

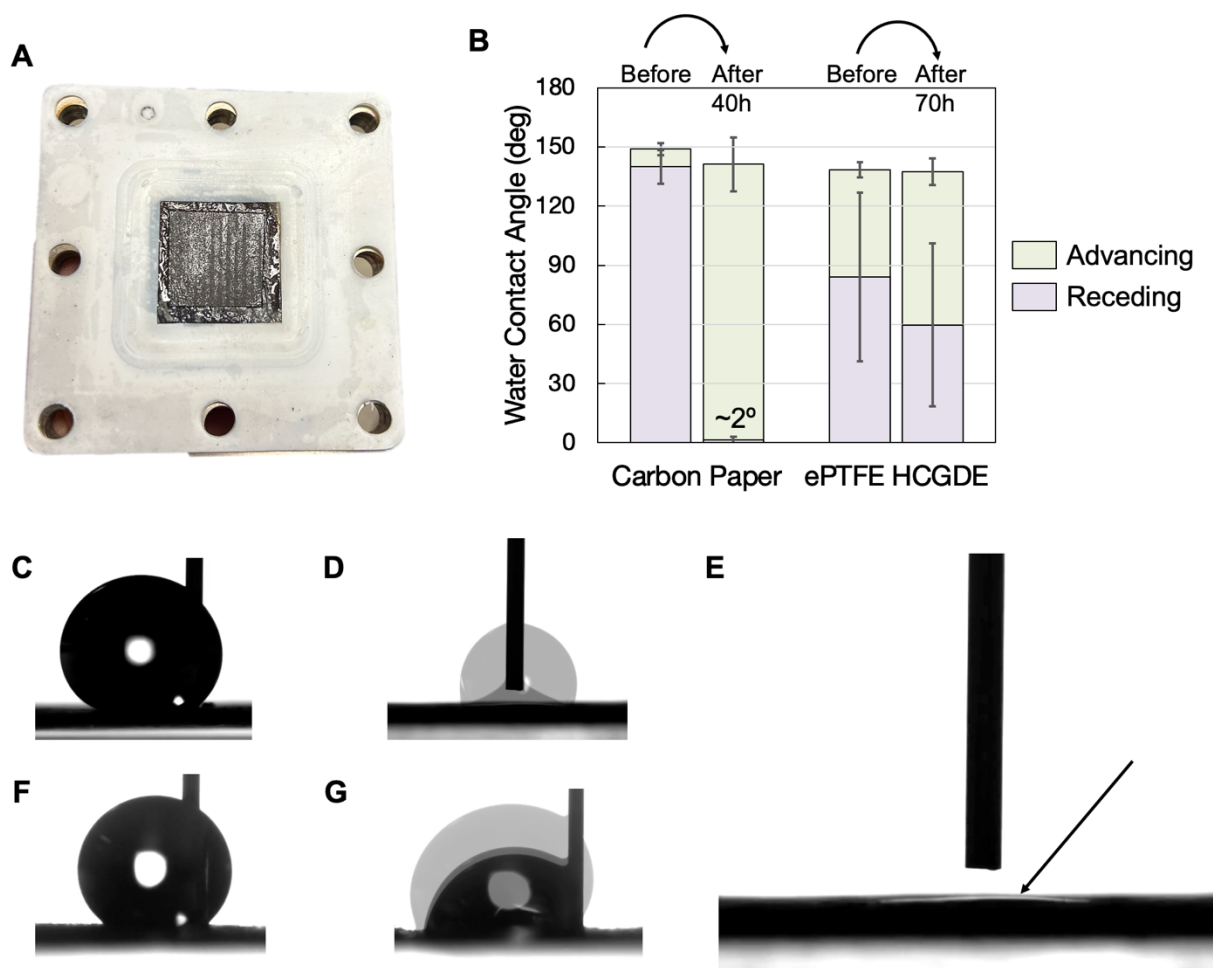


Figure S24: Post-mortem investigation of wetting on GDL substrates after long-term stability tests. A) Image of the back-side of the carbon paper GDL after a 40 hour 100mA/cm² stability test shows visible wetting. B) After the carbon paper and ePTFE HCGDE electrodes were fully dried, contact angle investigation reveals that the hydrophobicity of carbon paper is significantly more affected than that of ePTFE, indicating better flooding resistance and stability of ePTFE-based GDL electrodes. C) Representative droplet advancing on a carbon paper substrate after 40h stability test and drying. D) Overlaid timelapse of a representative droplet receding on a carbon paper substrate after 40h stability test and drying. E) Enlarged image showing wetting of a carbon paper substrate after the droplet has been fully removed, evidenced by the light reflection. This implies a receding contact angle of ~0 deg. F) Representative droplet advancing on ePTFE HCGDE backside after 70h stability trial. G) Overlaid timelapse of a representative receding droplet on the ePTFE HCGDE. The overlay clearly shows the left contact line moving to the right twice with a contact angle of ~90 deg.

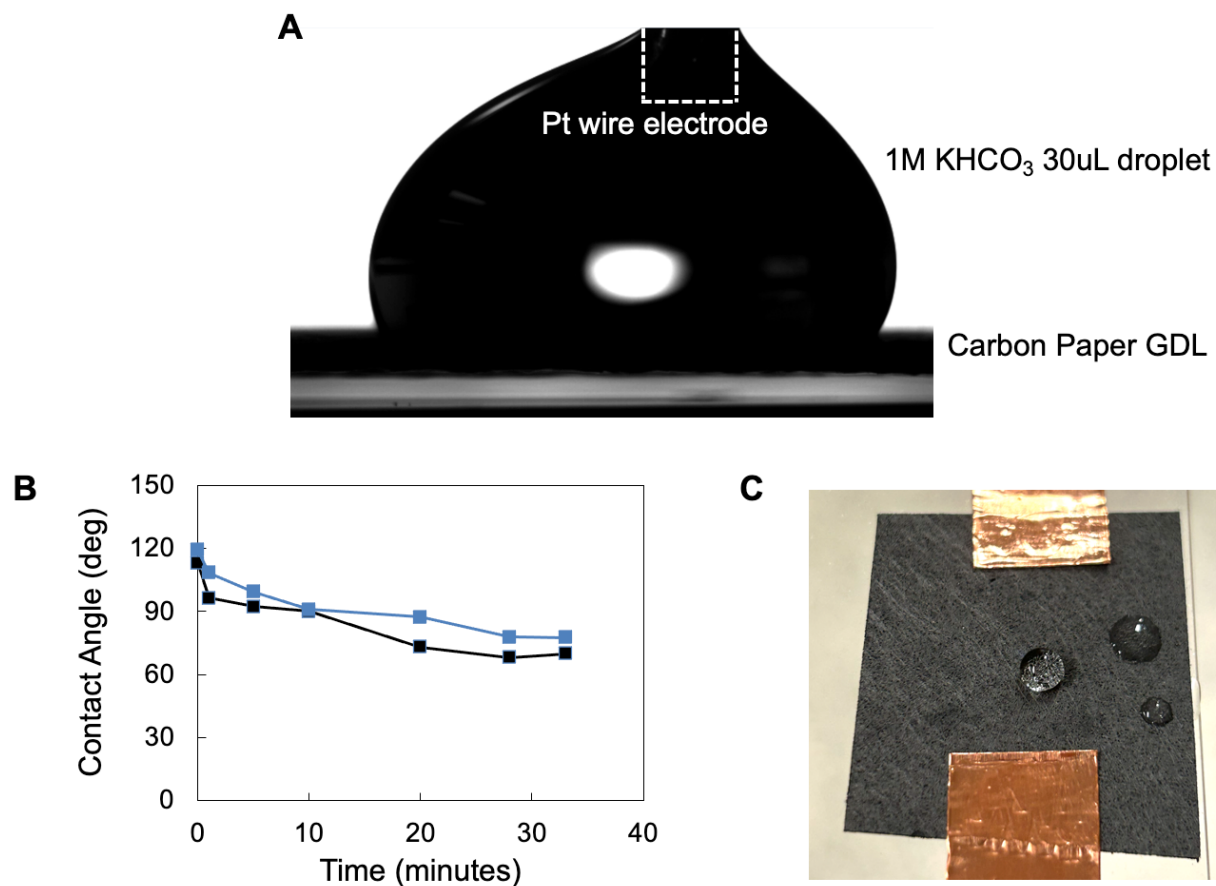


Figure S25: Effect of electrolysis on wettability of carbon paper GDL. A) Experimental setup wherein a droplet is placed atop unused carbon paper GDL, with a Pt wire inserted. The carbon paper is electrically connected as the cathode and the Pt wire as the anode. B) Contact angle degradation as a constant -3.5V is applied to the carbon paper/Pt couple. Note that over 30 minutes only 1% of the droplet volume is electrolyzed at an average current of ~2 mA. C) Air pockets are visible under the left droplet, which was not electrolyzed, while the two right droplets which were electrolyzed do not show visible air pockets. The two right droplets have receding contact angles of ~0 deg, similar to Supplementary Fig S24B, indicating degradation of the PTFE coating hydrophobicity under exposure to electrolysis conditions.

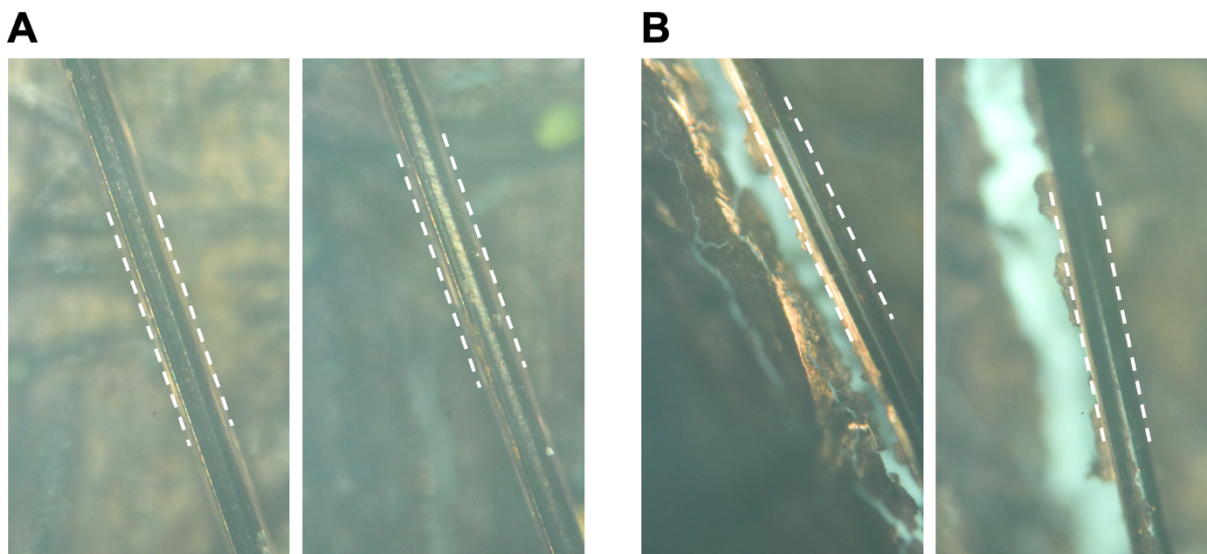


Figure S26: Representative optimal microscope images of the A) virgin wires and B) wires after HCGDE operation and disassembly, showing no noticeable difference or corrosion. The wires are 75 μm in diameter. There is noticeable detachment of sputtered surface copper, exposing the ePTFE substrate. Such irreversible disassembly is common in Membrane Electrode Assemblies.

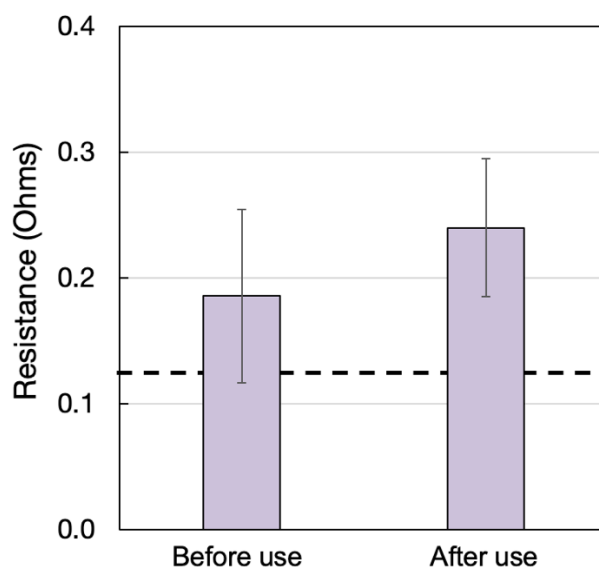


Figure S27: Resistance of 30 mm segments of the 75 μm diameter copper wire before and after 70 h use in the HCGDE assembly measured with a multimeter. The dashed line indicates the theoretically expected resistance given the resistivity of copper of $1.68\text{E-}08 \text{ Ohm}\cdot\text{m}$. The slight increase in resistance seen here would correspond to $\sim 30 \text{ mV}$ of added cell voltage due to the parallelized nature of the wires.

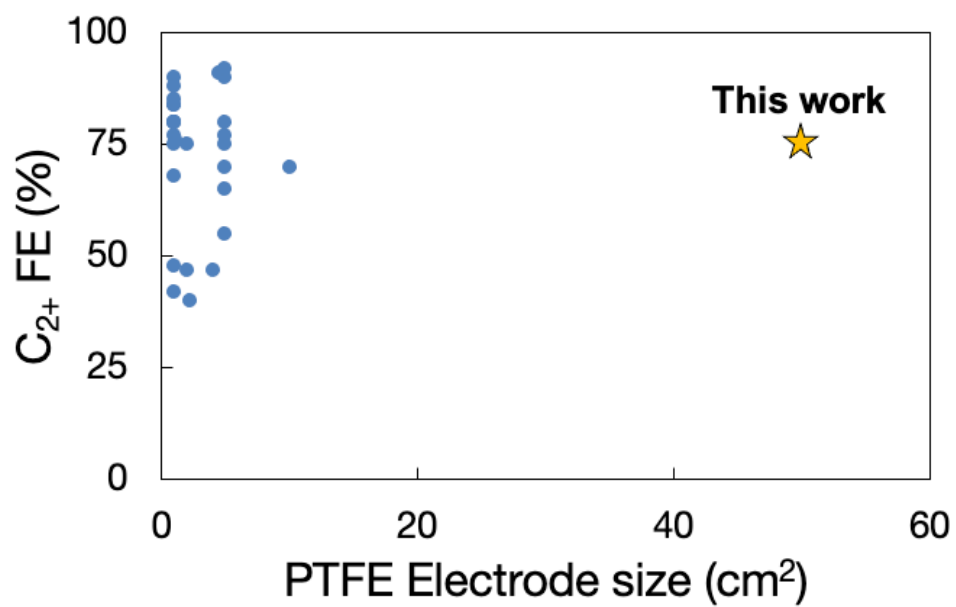


Figure S28: Graphical representation of Table S2.

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