Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

High-throughput parallelized testing of membrane electrode assemblies for CO_2 reduction

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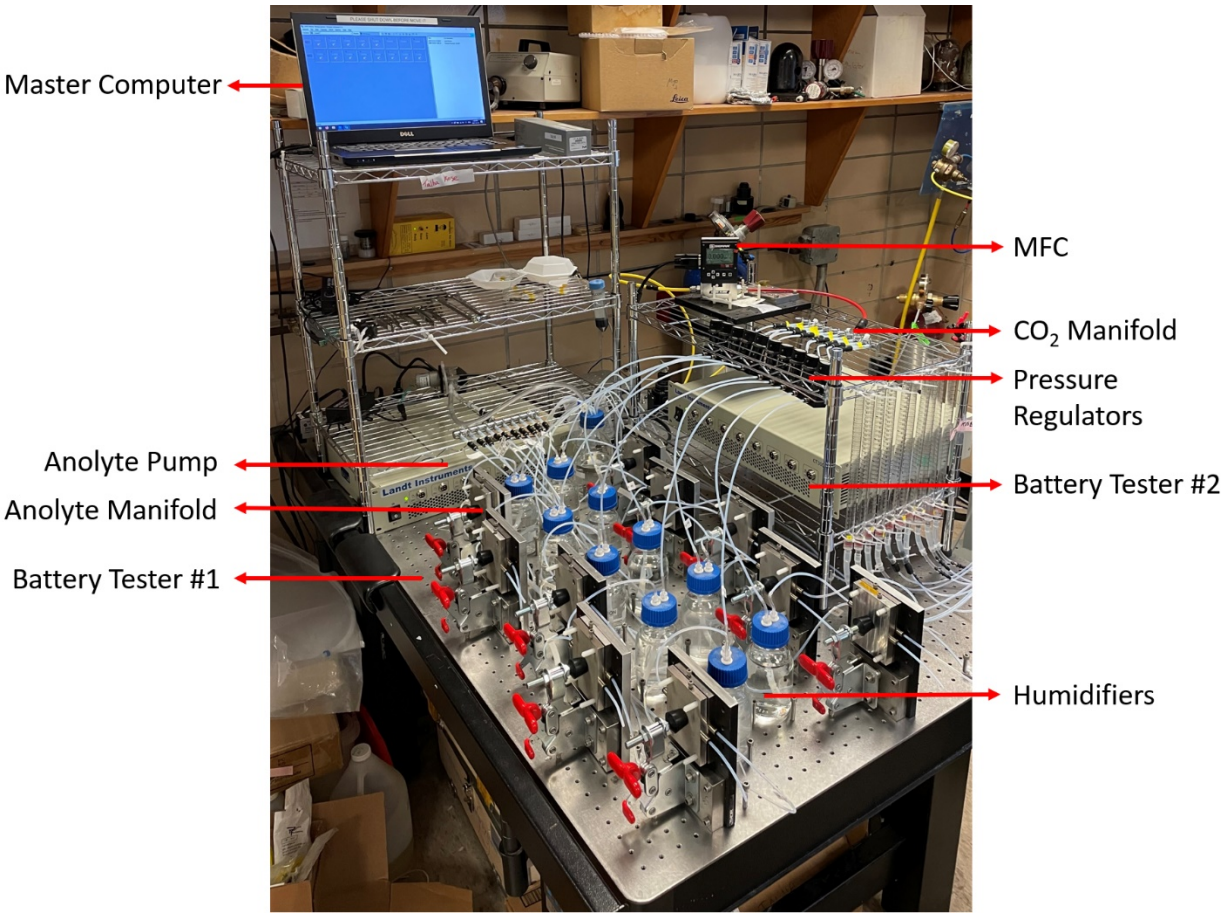

Fig. S1 Overview of the high-throughput experimentation platform.

Table S1 System level comparison of high-throughput experimentation platform presented in this work, a typical single MEA experimental setup, and a scaled up experimental setup for 10 conventional MEAs with respect to space occupied, cost, and features.

	HTE Platform	***Typical Single MEA Testing Setup***	***Conventional Setup for 10 MEAs***
Lab Space Footprint	1.5 m x 0.9 m 1.35 m^2	1.2 m x 0.5 m 0.6 m^2	1.2 m x 0.5 m x 10 ~5-6 m^2
Voltage-Current Source	*Battery Tester* x 2 **Specs**: 1A-9V, 16 Independent Channels **Cost**: 4,000 CAD x 2	*Single Channel Potentiostat/Galvanostat + Booster Module* **Specs**: 10A-10V **Cost:** 12,000 CAD	*Multi-Channel Potentiostat/Galvanostat* **Specs:** 10A-10V, 10 Independent Channels **Cost:** 80,000-90,000 CAD
Anolyte Pump	*Large Flow Peristaltic Pump + Manifold* **Specs:** Flow rate up to 400 sccm **Cost:** Pump – 70 CAD, Voltage Regulator – 20 CAD, Manifold - 30 CAD	*Standard Peristaltic Pump* **Specs:** Flow rate up to 100 sccm **Cost:** Pump – 20 CAD, Voltage Regulator – 20 CAD	*Standard Peristaltic Pump* x 10 **Cost:** Pump – 200 CAD Voltage Regulator – 200 CAD
Mass Flow Controller for CO_2	*SmarTrak 100 + Manifold + 10 Pressure regulators* **Specs:** Flow rate up to 2000 sccm **Cost:** MFC – 3,200 CAD Manifold - 30 CAD, Pressure regulators: 35 CAD each	*SmarTrak 100* **Specs:** Flow rate up to 2000 sccm **Cost:** MFC – 3,200 CAD	*SmarTrak 100* x 10 **Cost:** MFC – 32,000 CAD
Total Cost	~11,700 CAD	~15,300 CAD	~112,400 – 122,400 CAD

MEA Design Details

MEAs presented in this work are comprised of eight main components: Anode electrolyzer plate, cathode electrolyzer plate, shim, O-ring, base board, interconnection part, clamp, and alignment

posts. The interconnection part is used to increase the maximum clearance of the clamps. The clamps have a locking handle which holds the assembly in position and signals the user that clamping is secure. The base is a piece of optical breadboard which has threaded holes 1-inch apart and is made of black anodized aluminium. The material and miscellaneous details are given in Table S2 below. Fig. S2 shows photos of the components of the MEA and the assembled MEA.

Table S2 Materials and other properties used in the MEA design.

Component	**Material**	**Miscellaneous**
Anode Electrolyzer	Titanium Grade II	Thickness: 0.375”
Cathode Electrolyzer	Stainless Steel ST316	Thickness: 0.375”
Shim	Polyether ether ketone (PEEK)	Thickness: 0.0625”
O-ring	Viton Fluoroelastomer	Size: 028, Thickness: 0.0625”
Base	Black Anodized Aluminium	Thickness: 0.5”
Clamp	Steel Arms	McMaster Carr - Compact Hold-Down Toggle Clamp with Locking Handle, 750 lbs. Holding Capacity
Interconnection Part	Stainless Steel ST316	Thickness: 0.75”
Alignment Posts	Nylon Threaded Rods	Length: 2”, Type: 1/4"-20

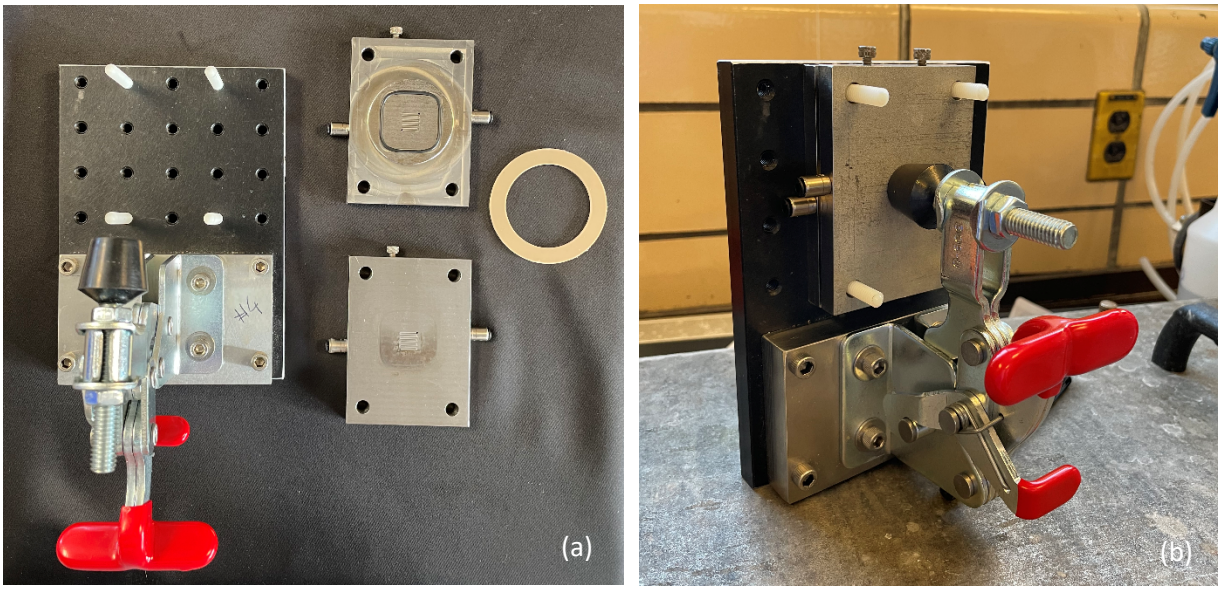

Fig. S2 (a) MEA parts, the base with the clamp, the anode electrolyzer plate, the cathode electrolyzer plate and the shim. (b) Assembled MEA.

Prototype MEA vs Regular MEA

The prototype MEA is the very first design aimed at delivering 1 cm^2 active electrode area with the serpentine flow field. Several tests on the prototype MEA have led to some changes in the design for the rest of the MEAs. The difference between the prototype MEA and the regular MEA designed in the scope of this study is simply based on thickness of the cathode electrolyzer. The thickness of the cathode in the prototype was 1.27 cm (0.5 inches) while it was 0.95 cm (0.375 inches) for the rest. The active area staying inside the O-ring is increased in the final design to ease the assembly of the electrodes. The area was approximately 4 cm^2 in the prototype whereas it is 11 cm^2 in the revised design. The increase in the active area has also increase the inner diameter of the shim from 3.8 cm to 4.8 cm. Fig. S3 illustrates the differences between a regular MEA and the prototype MEA.

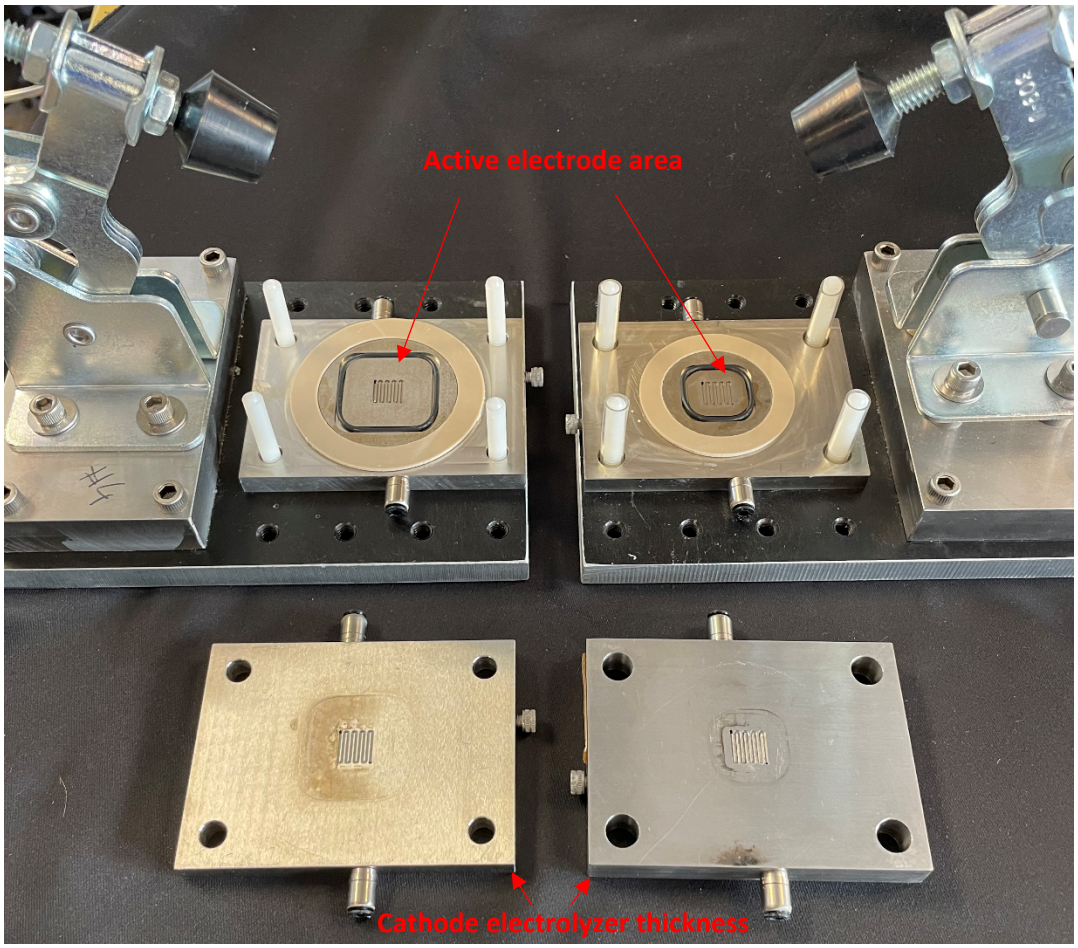

Fig. S3 Differences between the regular MEA and the prototype MEA employed in this work. The major differences are denoted in red on the photo.

Assembly Time Comparison

In order to investigate the acceleration factor of the presented MEA design in the assembly process, we conducted an experiment asking experienced researchers in the field to assemble a conventional MEA and our new MEA and timed their process. Eight willing participants are selected from Sinton Lab members who were not part of the design process. The authors of this paper are excluded from the experiment to avoid any potential biases. Each participant is informed about the MEA presented in this work for 30 seconds and has the opportunity to make themselves familiar with the clamping mechanism before timing tests. Participants repeat both assembly procedure three times. Table S3 presents the data collected from this experiment.

Table S3 Data collected from assembly time comparison experiment.

Participants	Assembly Time (seconds)				Acceleration Factor
	Typical MEA		MEA presented in this work		
	Measurements	Average	Measurements	Average	
#1	84.9	78.4	6.5	6.1	12.8x
	77.7		6.0		
	72.7		5.9		
#2	63.8	57.4	7.5	7.1	8.1x
	51.9		7.5		
	56.4		6.4		
#3	61.9	64.0	6.8	7.5	8.5x
	64.7		7.5		
	65.6		8.3		
#4	107.6	113.4	16.1	16.5	6.9x
	115.5		18.2		
	117.1		15.3		
#5	75.9	76.9	6.5	7.0	11.0x
	80.7		7.5		
	74.1		7.0		
#6	56.2	57.1	8.4	8.4	6.8x
	65.2		8.8		
	49.7		8.1		
#7	58.7	50.7	8.5	7.6	6.6x
	41.4		7.2		
	52.1		6.9		
#8	46.1	43.3	6.6	6.7	6.4x
	41.8		6.9		
	41.9		7.1		

The data presented in Table S3 indicate that the acceleration factor as high as 12.8x can be reached for a researcher experienced in the field. The interpretation of the data should consider the fact that all participants were familiar with the standard MEA at the time of the experiment while it was their first time assembling the MEA presented in this work. Although they had the opportunity to try before the timing experiments, that should affect the final results presented here in favour of further acceleration. Based on the statistical analysis shown in the main text, the MEA presented in this work has accelerated the assembly time by 8.5x.

Overall Acceleration Factor Calculation

Output gas product analysis is a crucial step in the cycle of a CO_2RR experiment. In this work, a gas chromatograph (GC) (PerkinElmer Clarus 590) was utilized to analyse the gas products of the experiments conducted. Analysis of a gas injection completes in 20 minutes per sample. A researcher can inject up to 6 samples in a 20-minute analysis cycle provided that the injections should be 2.5 minutes apart in order to avoid overlapping of the gas peaks which would cause failure to extract the correct data from the analysis. Each injection in a CO_2RR experiment also experiences a CO_2-peak after 10-12 minutes that can cover 3-4 minutes in the analysis span. Hence, to avoid any overlap, the researchers should wait for the CO_2 peak to decay for proper data extraction.

In a CO_2RR experiment with a single MEA, the reaction should arrive a steady state after application of a new current/voltage level. Depending on the experiment, the reaction settling time may vary between 20-30 minutes. In order to compare a traditional single-MEA testing and a multi-MEA testing, we have to make certain assumptions based on the waiting times and time of the injections. Table S4 illustrates a comparison table for the conventional single-MEA testing and the high-throughput MEA testing for CO_2RR experiments.

Table S4 Comparison of experiment time in a typical single-MEA testing versus the High-throughput Experimentation platform employing 10 MEAs.

	Conventional Experiment with a typical MEA	**High-throughput Experiment with 10 MEAs**
MEA assembly	1-2 minutes (x10)	1-2 minutes
Experiment time *	80 minutes (x10)	240 minutes
Total Time Spent	~81 - 82 min (x10) = 13.5 – 13.7 hours	~241 - 242 minutes = 4.0 hours
Overall Acceleration factor	~3.4x	

* Assuming reaction settling time of 20 minutes at each current density level, and one injection per current density level using GC, and total of four different current levels.

In Table S4, the experiment time in HTE platform is calculated based on 5 injections belonging to 5 MEAs running in parallel in a 20-minute window. These 5 injections produce CO_2 peaks beyond 20-minute cycle and hence, the researcher should wait additional 10 minutes before starting a new set of 5 injections for the other MEAs. Therefore, between the injections of the same MEA at different current densities, the reaction runs for 1 hour which is more than enough for settling. It is assumed that the experiment ends after the final injection which happens at 10-minute mark of the last 20-minute window. Considering 20-minute settling time before the first injections, the total experiment time for 10 MEAs running in parallel, it took 240 minutes to complete the experiments. Similarly, for a reaction-settling time of 20 minutes at the beginning and between the injections, and one injection per current density, the experiment time can be estimated as 80 minutes in a typical MEA setting for a CO_2RR experiment. Based on the assumptions and estimations presented in Table S.4, the overall acceleration of 3.4 times can be achieved in CO_2RR experiments using the proposed HTE platform with the given MEA design combined with manual gas injections to the GC. The overall acceleration factor can be enhanced further using an autonomous gas output direction pipeline to a gas product analysis tool such as SIFT-MS which has in-line gas analysis capability.

Preparation of Catalysts

The catalyst gas diffusion electrode (GDE) that was employed in the first experiment was prepared by airbrushing catalyst inks with a nitrogen carrier gas. The catalyst copper ink was prepared with 5 mL methanol (Greenfield Global Inc., >99.8%), 200 mg Nafion (Fuel Cell Store D521 Alcohol based 1100 EW, 5 wt%), and 83 mg copper nanoparticles (Sigma-Aldrich 774081-5G, <25 nm particle size). The catalyst ink mixtures were sonicated for one hour, and then sprayed on a gas diffusion carbon paper (Fuel Cell Store Sigracet 39 BC, with a microporous layer) with a

spray density of 0.2 mL/cm^2. After airbrushing, the GDE was dried for 24 hours at room temperature (~20 ℃). An additional Carbon layer was sprayed on top of the Cu layer. The carbon ink was prepared with 3 mL methanol, 16.25 mg Sustainion ionomer (Sustainion XA-9 Alkaline Ionomer 5% in ethanol), and 3.75 mg of carbon nanoparticles (Alfa Aesar 39724, 75 m2 g-1). Catalyst inks were sonicated for 1 hours and then sprayed on the same carbon layer with cu layer sprayed on. The spray density of carbon layer was 0.12 mL/cm^2. After airbrushing, the GDE was dried for 24 hours at room temperature (~20 ℃). In the second experiment, the Cu ink was modified by increasing the Cu mass to 186 mg, 249 mg, and 332 mg for Cu:Nafion ratio of (4:5), (6:5) and (8:5), respectively, while keeping the Nafion mass the same at 200 mg. Please note that Nafion and Sustainion solutions were added to the ink over their mass instead of their volume.

Calculation of Gas FE

All CO_2RR experiments were performed using an MEA electrolyser with an active area of 1 cm^2. During a CO_2RR experiment, the aqueous 0.1 M $KHCO_3$ anolyte was circulated through the anode flow channel at a flow rate of 25 mL/min using a large peristaltic pump. An anion exchange membrane (Sustainion X37-50, Dioxide Materials) was used as the solid cathode electrolyte. The CO_2 gas flow rate, supplied at a rate of 220 standard cubic centimetres per minute (sccm) from the main line and diverted into 10 lines using the manifold with a flow distribution varying between 10-30 sccm for individual line. Each CO_2 line was bubbled through water for humidification prior to entering each electrolyser. All voltages reported are full cell voltages without *i*R compensation.

The CO_2RR gas products were analysed in 1 mL volumes using a gas chromatograph (PerkinElmer Clarus 590) possessing a thermal conductivity detector (TCD) and a flame ionisation detector (FID). For the screening of samples with different Cu:Nafion ratios, gas samples were

taken after 45 minutes of CO_2RR to ensure that the system was at steady state. Faradaic efficiency (FE) of CO_2RR gas product was calculated by the following equation:

$$FE_{gas} = v_i \times q \times \frac{z_i F P_0}{RT} \times \frac{1}{j_{total}} \times 100\% \quad (1)$$

where v_i is the volume fraction of gas product i, q is the outlet gas flow rate in sccm, z_i is the number of electrons required to have one molecule of product i, F is the Faraday Constant, P_0 is atmosphere pressure, R is the ideal gas constant, T is the temperature, and j_{total} is the total current.

Pressure test results

Compression among the MEAs is measured using commercially available pressure recording films (Mcmaster-Carr, Pressure Recording Film 28-85 psi, 31705K632). The films contain two 0.004”-thick sheets. After placing the cathode and anode electrodes on the electrolyzers, these two films are sandwiched using the clamps of the MEAs. The films are left under pressure at least one minutes which means they are evaluated as extended exposure. Based on the color grade on the film, the pressure of the MEAs can be roughly determined thanks to the reference color chart (Mcmaster-Carr, Color Chart for Pressure Recording Film, 31705K711) and reference graphs provided by the manufacturer. Fig. S4 presents the results of the pressure recording films after assembly, the reference color chart and graph for the extended exposure.

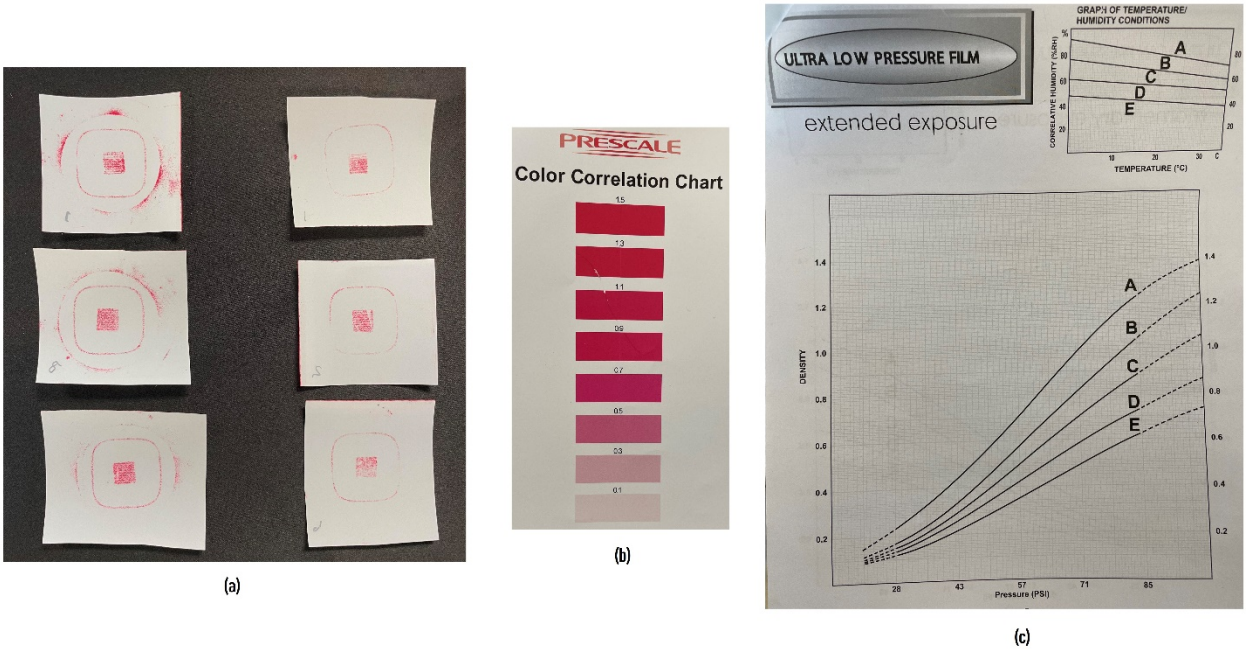

Fig. S4 (a) Pressure film recordings from the over-compressed MEAs and regular MEAs used in the second experiment. (b) Color correlation chart provided by the manufacturer. (c) Color correlation vs pressure graph provided by the manufacturer.

As seen in Fig. S4-a, the circle trails on the films staying on the left column represent the pressure on the shims due to the increased compression for MEA#7, MEA#8, and MEA#9 from top to the bottom, respectively. The films presented on the right column in Fig. S4-a demonstrates the pressure recording film results after assembling three regular MEAs (MEA#1, MEA#2, and MEA#3 from top to bottom.) without over-compression. There are no circle inks on these films which means the shim is in no action for these MEAs. The circular trail on MEA#9 has lower density than the one in MEA#7 and MEA#8 which explains the cell voltage anomaly in the results presented in Fig. 5 in the manuscript. Referring the color chart presented (Fig. S4-b), the pressure on the shim ring of MEA#7, MEA#8 and MEA#9 would correspond to the density of 0.9, 0.5 and 0.3, respectively. Using the graph presented in Fig. S4-c, compression in MEA#7, MEA#8 and

MEA#9 should be, roughly, >85 psi, 75 psi and 50 psi. Please note that these readings highly depend on the person and may not be accurate.

Comparison of Repeatability Experiment Results Using a Conventional MEA

In this section, we presented the results obtained from a conventional MEA (Dioxide Materials, 68732)[1] employing larger electrode size (5 cm^2) than the ones presented in the manuscript. The catalyst used in this experiment is the same with the one utilized in the repeatability experiment whose results are presented in Fig. 4 in the manuscript. The recipe for this catalyst is also presented under *Preparation of Catalysts* section in this document. Fig. S5 presents the data collected from the conventional MEA with 5 cm^2 electrodes.

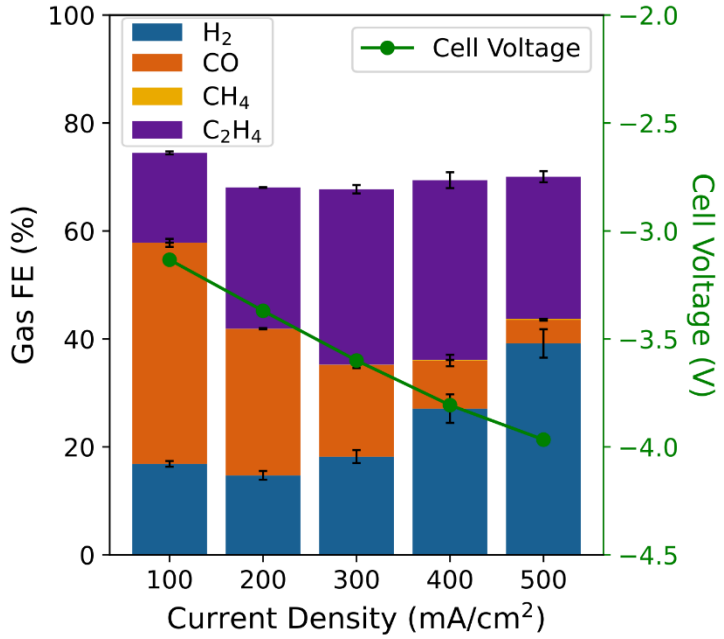

Fig. S5 Faradaic efficiencies of gas products collected from a typical MEA with 5 cm^2 electrodes. The results indicate selectivity of ethylene of 26% at 200 mA/cm^2 and reaches its maximum as 33% at 400 mA/cm^2.

The results shown in Fig. S5 indicate the selectivity towards ethylene of 26% at 200 mA/cm^2 which is in good agreement with the ones presented in Fig.4 in the manuscript (~28% at 200 mA/cm^2).

That supports the expectation of scaling up the MEA systems used in the HTE platform without a major drawback in the performance.

Design and Integration of Automated Gas Sampling

This section presents the design of a fluid handling system in order to interface the HTE with a gas analysis tool such as Gas Chromatography or selected ion flow tube mass spectrometry (SIFT-MS). We assumed the analysis tool is capable of handling one gas product at a time hence, our design focused on the sequential analysis of gas products coming out of each MEA. Our gas sampling system is designed to employ 10 solenoid valves which can be activated by applied voltage between its terminals. Upon activation, these valves can direct the inlet gas to the analysis port while in the idle mode, the inlet passes to the waste port. All valves are designed to be manifold-mounted. The manifold is custom-designed for this specific operation to accommodate the valves and combines all analysis ports of valves together in a channel which is directed to the analysis tool. Fig. S6 presents the schematics of the designed system.

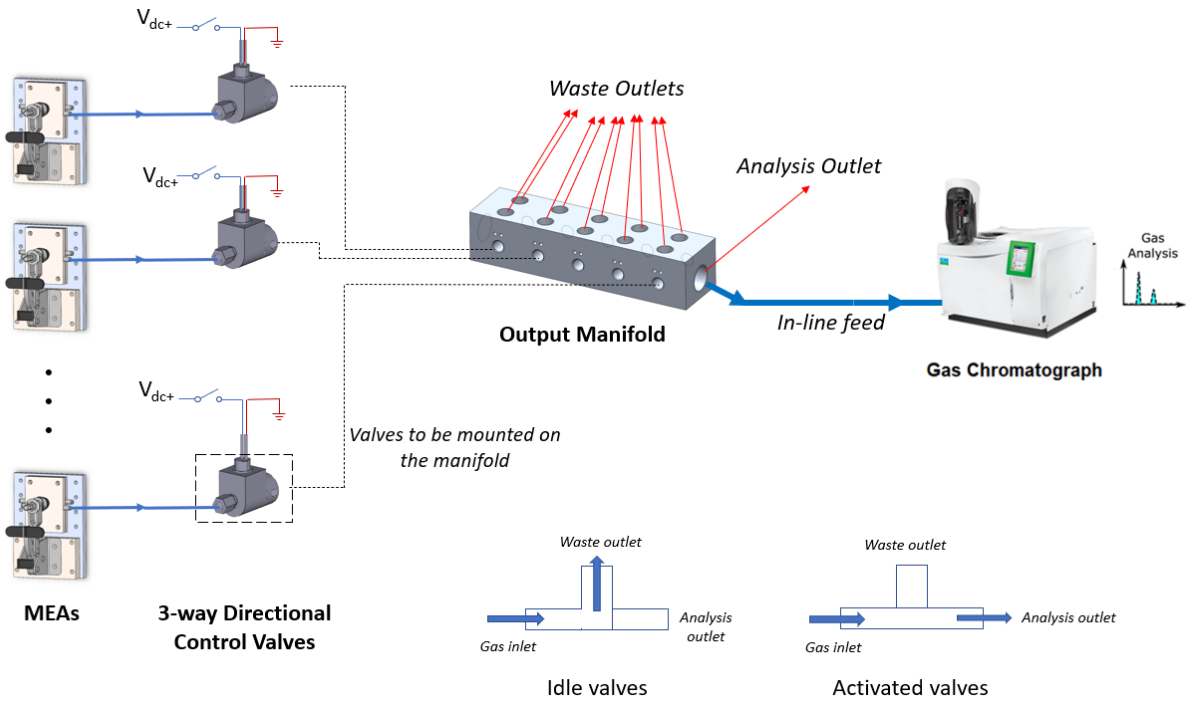

Fig. S6: Schematics of the automated gas sampling system designed to interface the gas outputs with the product analysis tool.

The manifold's analysis channel is designed to be connected to a gas source (Ar) in order to flush the channel after sending a gas to the analysis. Moreover, automated volumetric flow measurement feature can be also added to the system as described in this study[2]. The designed system was not integrated with the GC or SIFT due to logistics problems Covid-19 pandemic caused. Hence, the integration is left as a future work at time of paper submission.

References (SI)

1 D. Materials, Complete 5 cm2 CO2 Electrolyzer, https://dioxidematerials.com/products/carbon-dioxide-electrolyzers-components/.

2 G. O. Larrazábal, P. Strøm-Hansen, J. P. Heli, K. Zeiter, K. T. Therkildsen, I. Chorkendorff and B. Seger, *ACS Applied Materials and Interfaces*, 2019, **11**, 41281–41288.