

Enhancing C_{≥2} product selectivity in electrochemical CO₂ reduction by controlling the microstructure of gas diffusion electrodes

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1. Experimental methods

Methods

Poly-(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP, Merck, Mw ~400k, Mn ~ 130k), tetraethylammonium bromide (TEABr, Merck, 98%), and dimethylformamide (DMF, Merck, 227056, 99.8%), potassium chloride (99-100.5% ACS, Thermoscientific), potassium carbonate (KHCO₃, ACS 99.7% ACS, Merck), CO₂ (Linde, 4000 ppm N₂), CO (Pangas, 4.7N), Nafion 117 (20 mm disk) and Cu sputtering target (AJA International, 99.995%) were employed without purification or cleaning. MilliQ pure water was used for the preparation of electrolytes and for the liquid product analysis.

2. Fabrication of GDEs

GDEs substrates for CO₂RR were prepared by electrospinning PVDF-HFP solutions. Specifically, 15, 30, and 32 wt% PVDF-HFP, 1 wt% solution TEABr in dimethylformamide DMF were prepared by steering at room temperature overnight. These solutions were placed in a 20 mL syringe and injected through a metal needle (21 G) at 10 μl/min by a syringe pump (MTI) mounted on sliding arm (MTI). A potential of 30 kV was applied between the metallic needle and a rotating disk collector (MTI, 10 cm diameter) by two high voltages sources (GenVolt) at a distance of ~ 8 cm. The resulting fibers were collected on the collector rotating at 400 rpm to produce PVDF-HFP fiber mats with similar thicknesses ranging from 100 to 150 μm.

PVDF-HFP fiber mats were used as substrates to prepare GDEs by single-side deposition of a Cu catalyst layer with a nominal thickness of 500 nm employing physical vapor deposition. In a typical deposition, Cu was sputtered at 100 W and direct current mode, and at 3 mtorr Ar (Pangas, 5N) plasma for 20 minutes (AJA International Orion series). Sheet resistance of the obtained GDEs was below 0.5 Ω/cm, which is negligible compared to the final cell resistance.

The presence of Cu on the fiber mat was investigated by X-rays diffraction (XRD) as shown in Fig. S1. The measurements were performed in Bragg-Brentano symmetric geometry by using a PANalytical X'Pert Pro instrument (Cu-K α radiation, 40 kV and 30 mA) equipped with an X'Celerator detector. Each sample was fastened with a Kapton tape on a Si support and was measured in a 2 θ range from 5 to 90° for 3 hours.

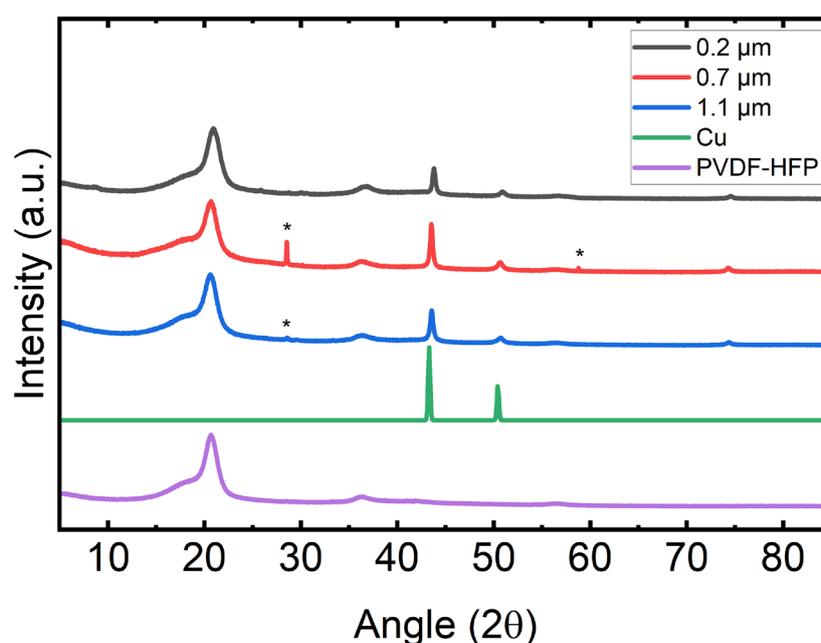


Figure S1. XRD pattern of the three sample (black, red and blue curve) and of a Cu reference (green curve, 10.1016/j.nanoso.2021.100727). Signal coming from Si background are marked with (*).

3. Microstructure imaging of GDEs

Morphology of the GDEs by scanning electron microscopy (SEM, Hitachi TM3000) with 15 kV electron acceleration voltage. Trenches were milled by focused ion beam to image the cross sections of the GDEs. Corresponding top view images SEM are provided in Fig. S2.

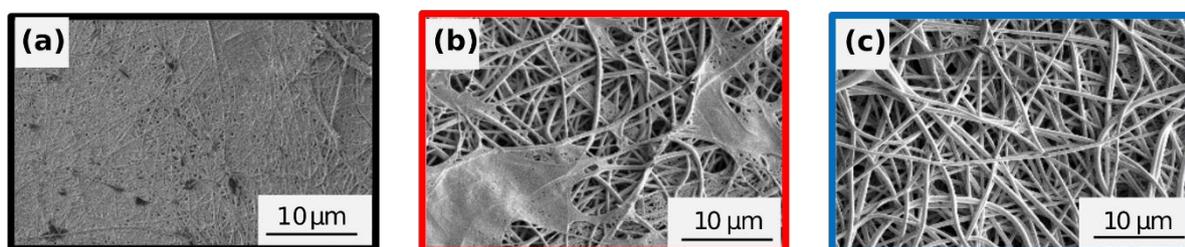


Figure S2. Top view SEM images of (a) 0.2, (b) 0.7, and (c) 1.1 μm Cu GDE. The thin, sheet-like metal layer between the fibers do not appear to modify the pore structure of the substrate nor the catalytic performance of the GDE.

4. Mean pore size and water entry pressure determination

Pore size and water entry pressure (WEP) measurements are carried out using a porometer system (Porolux 1000, Porometer) with liquid permeability capability. For the mean pore size measurement, the substrate under examination (13 mm diameter) is first soaked in a fluorinated hydrocarbon (PoreFill liquid, Porometer, surface tension 16 dyn/cm²) and an increasing pressure of N₂ gas is imposed on top of the substrate, until first displacement of the liquid takes place (bubble point). The pressure is increased until a sudden increase of the flow is observed, this way the 'wet' curve is acquired. Then, the pressure is released and the N₂ gas pressure is imposed again, this time without any wetting liquid, to obtain the 'dry' curve. An example of the 'dry' and 'wet' curves during porometry is given in Fig. S3.

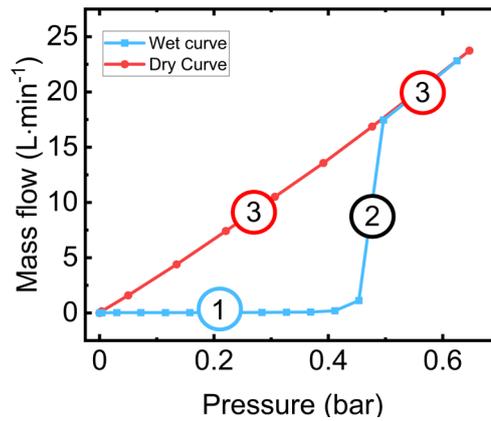


Figure S3. Typical wet and dry porosimetry curves recorded for the determination of the mean pore size of the porous substrate. W is the mass transport of gas.

From the two curves, the mean pore size and pore size distribution can be obtained using the Young-Laplace equation and the following formula:

$$\Delta p = \frac{2\gamma}{R}$$

where Δp is the applied gas pressure, γ is the surface tension of the liquid and R is the pore size. Finally, the first derivative of the difference between the dry and wet curve is taken, the resulting curve is shown in Fig. S4. When the pressure reaches the value at which most pores are permeable, there is an abrupt step-function-like increase in the flow (see Fig. S4). This leads to the typical delta-function-like peak in the plot of the differential flow in Fig. 1d, even when acquiring pressure-flow data with high frequencies. From this differential flow we estimate that the typical uncertainty of the measured pore size for our samples is 0.1 μm . To check for possible variation of the microstructural properties by metal deposition, we performed porometry experiments before and after coating the metal layer onto the hydrophobic substrates and we observed no noticeable difference.

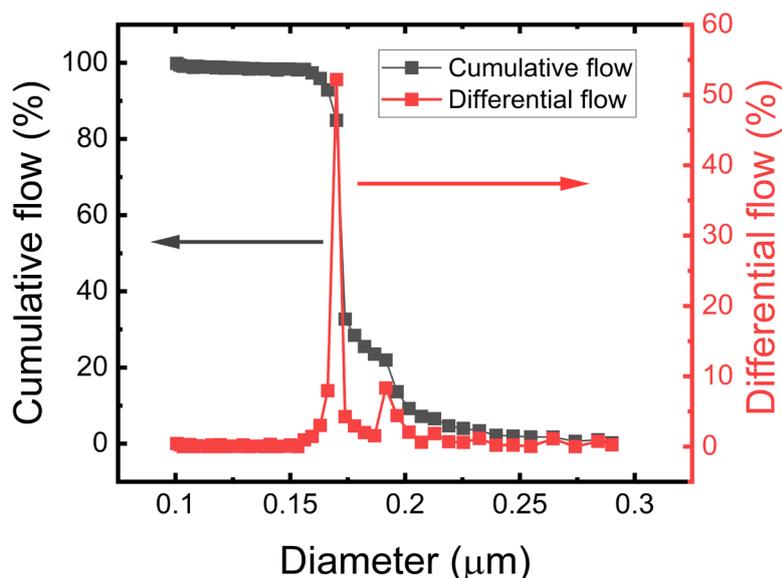


Figure S4. Cumulative flow and derivative flow of a 0.2 μm GDE. The sudden increase of flow around 0.17 μm (black curve) is reflected by an almost direct delta in the derivative plot (red curve).

For the WEP measurement, a dry substrate (13 mm diameter) is used and deionized water is slowly pressurized on top of the substrate until it starts permeating. A laboratory scale is used to record the amount of water that passes through the porous substrate. The first consistent increase in weight, typically in the order of 100 mg, is used to determine the WEP.

5. Electrochemical analysis

To assess the selectivity and activity of the prepared GDE, these were inserted in a modified PEEK electrochemical cell (Redox.me) with a round active area of 1 cm^2 . The electrolyzer, shown in Fig. S4, consists of 3 chambers, one dedicated to the CO_2 gas flow (3 mL), and two for the cathodic and anodic electrolytes (catholyte and anolyte, 15 mL each). The GDEs are used as cathodes, with their hydrophobic polymer side facing the CO_2 gas, and the active side hosting the sputtered metal catalyst facing the catholyte. A Nafion 117 membrane is used in all experiments to separate the two liquid chambers, to avoid product crossover. The catholyte chamber hosts the reference electrode (Ag/AgCl in saturated KCl) and the anolyte chamber the anode (IrO_x electrodeposited on a Ti gauze). The CO_2 gas flow is controlled by Mass Flow Controllers (Bronkhorst) and set in the range of 22.5 mL/min. The gas flow leaving the GDE and containing products is also flushed through the catholyte chamber to collect any products formed on that side, before being injected in a gas chromatography for analysis. Pressure was controlled using a needle valve. Two pressure sensors (Elveflow, MPS-V2-S-2) were placed at the outlet of the gas and of the catholyte chambers to measure the pressure of the gas and of the electrolyte flows.

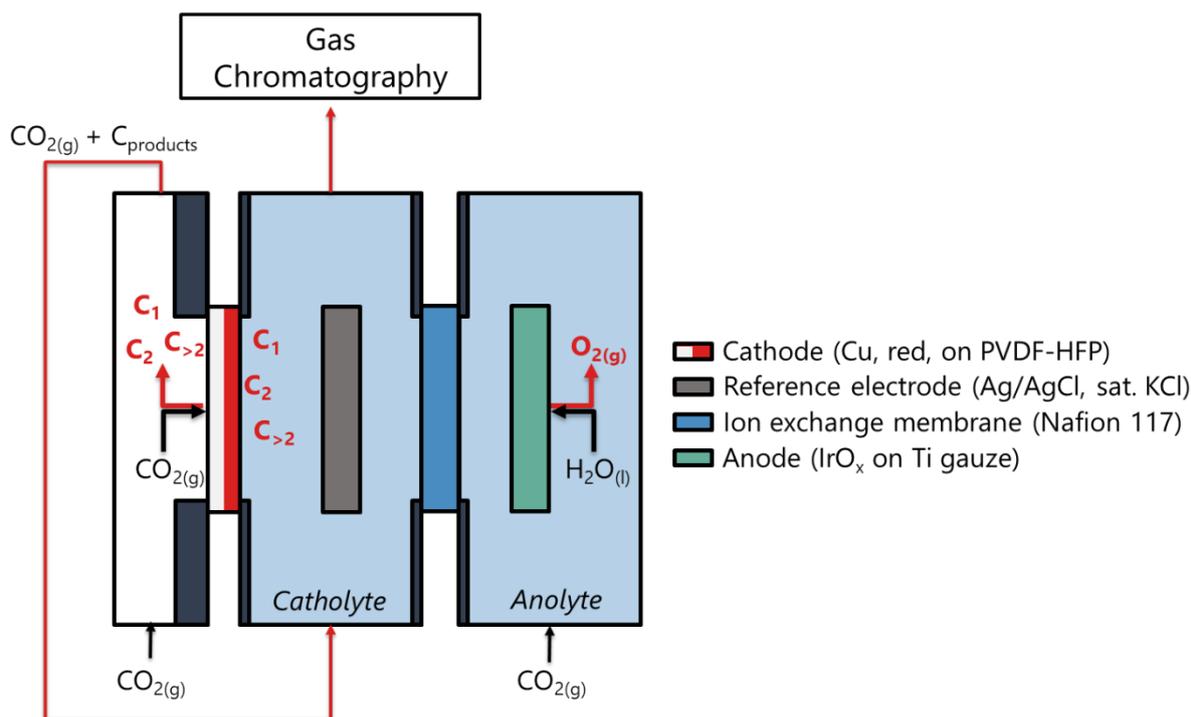


Figure S5. Schematics of the electrolyzer cell used for the electrochemical characterizations.

The electrolyte used in all characterization was 1 M KCl (99-100.5% ACS, Thermoscientific) for the catholyte and 1 M KHCO₃ (ACS 99.7% ACS, Merck) for the anolyte. Conductive Al tape is used as an electrical contact, but no area of the tape is exposed to the liquid electrolyte nor to the CO₂ gas. In a typical experiment, the GDE is loaded and the CO₂ flow is started. The electrolytes are saturated with CO₂ by bubbling the gas in both chambers in two separate streams. The electrolysis is started after saturation, with an initial linear scan voltammetry to -1.2 V vs Ag/AgCl for 1 to 5 minutes to reduce eventual CuO_x species on the surface of catalyst. With a second linear voltammetry the desired conditions are reached, and a subsequent chronoamperometric step is added to apply the desired current for the duration of at least 1 h. Every 10 minutes, an impedance spectroscopy measurement is performed to assess the cell resistance and its variations. The voltage of the working electrode (E_{WE}) is corrected for this resistance, and normally both the E_{WE} starting value and the E_{WE} end value (after 1 h) are corrected for their respective impedance measurements, to verify that there were no significant variations in the electrochemical conditions experienced by the sample. In addition, the E_{WE} value is corrected for the reference electrode shift to be brought back in the RHE scale. The reference electrode shift is measured with respect to a pseudo reversible hydrogen electrode, obtained by trapping a bubble of H₂ in contact with a Pt wire, which is immersed in 1 M H₂SO₄. Typical shift values for our Ag/AgCl reference electrodes (saturated KCl) are within 5 mV of the thermodynamic value (199 mV).

6. Product analysis

During the 1h electrolysis, the gas leaving the electrolyzer is bubbled through the catholyte chamber (to collect the CO₂RR products released in the liquid) and subsequently connected to a gas chromatograph (MicroGC Fusion, Inficon), with a Molecular Sieve (Ar as carrier gas) and a RT-Q (He as carrier gas) columns. The GC samples the gas flow every 5 minutes, to yield a time resolved product analysis. The gas flow is also measured at the entrance of the GC using a Volumetric Mass Flow Meter (Defender, MesaLabs).

The Faradaic Efficiency for the gases is calculated using the following formula:

$$FE_{gas,x} = \frac{W \left(\text{STP}, \frac{\text{L}}{\text{min}} \right) \cdot t \text{ (min)} \cdot [c]_{gas,x} \cdot n_{e,x} \cdot F \left(\frac{\text{C}}{\text{mol}} \right)}{Q \text{ (C)} \cdot 22.414 \left(\frac{\text{L}}{\text{mol}} \right)} \cdot 100$$

where W is the gas flow measured by the flow meter at standard temperature and pressure, t is the electrolysis time, $[c]_{gas,x}$ is the concentration of the gaseous product x (fraction of the gas flow taken up by the product x , dimensionless), $n_{e,x}$ is the electrons required to produce product x , F is the Faraday constant, and Q is the charge passed during the electrolysis time, measured by the potentiostat.

To quantify the liquid products by HPLC we employ an ion-exchange ligand-exchange column. For the HPLC measurement, we use a HiPle-H column (300 mm length, 7.7 mm diameter, Agilent 1260 system,) and a solution of 5 mM H₂SO₄ as eluent, with a flow of 0.6 mL/min and a column pressure (including backpressure) around 30-35 bar. Prior acidification of the solution with 1M H₂SO₄ in a 1:1 quantity minimizes a strong negative peak in the chromatogram attributed to carbonates.

The Faradaic Efficiency for the liquid products is calculated with the following equation:

$$FE_{liquid,y} = \frac{V \text{ (L)} \cdot t \text{ (min)} \cdot [c]_{liquid,y} \left(\frac{\text{mol}}{\text{L}} \right) \cdot n_{e,y} \cdot F \left(\frac{\text{C}}{\text{mol}} \right)}{Q \text{ (C)}} \cdot 100$$

where V is the electrolyte volume, t is the electrolysis time, $[c]_{liquid,y}$ is the molar concentration of the liquid product y , $n_{e,y}$ is the number of electrons required to produce liquid product y , F is the Faraday constant, and Q is the charge passed during the electrolysis time. For accuracy, the electrolyte volume was inserted in the electrolysis cell using a 10 mL adjustable volume pipette (Eppendorf).

The typical uncertainty of the FE values is estimated to be ~10% due to fluctuations in the product analysis and in the gas flow and electrolyte volume measurements. This can also affect the total FE, leading, e.g., to FE > 100% in some situations.

7. Data analysis

Electrochemical and product analysis data are combined in a single file abiding to the FAIR data practices³⁹ and are automatically processed by python-based scripts as reported in a previous work⁴⁰.

2. Product distribution including liquids as a function of pore size and current density

The normalized product distribution of Fig. 3 is found in Fig. S6.

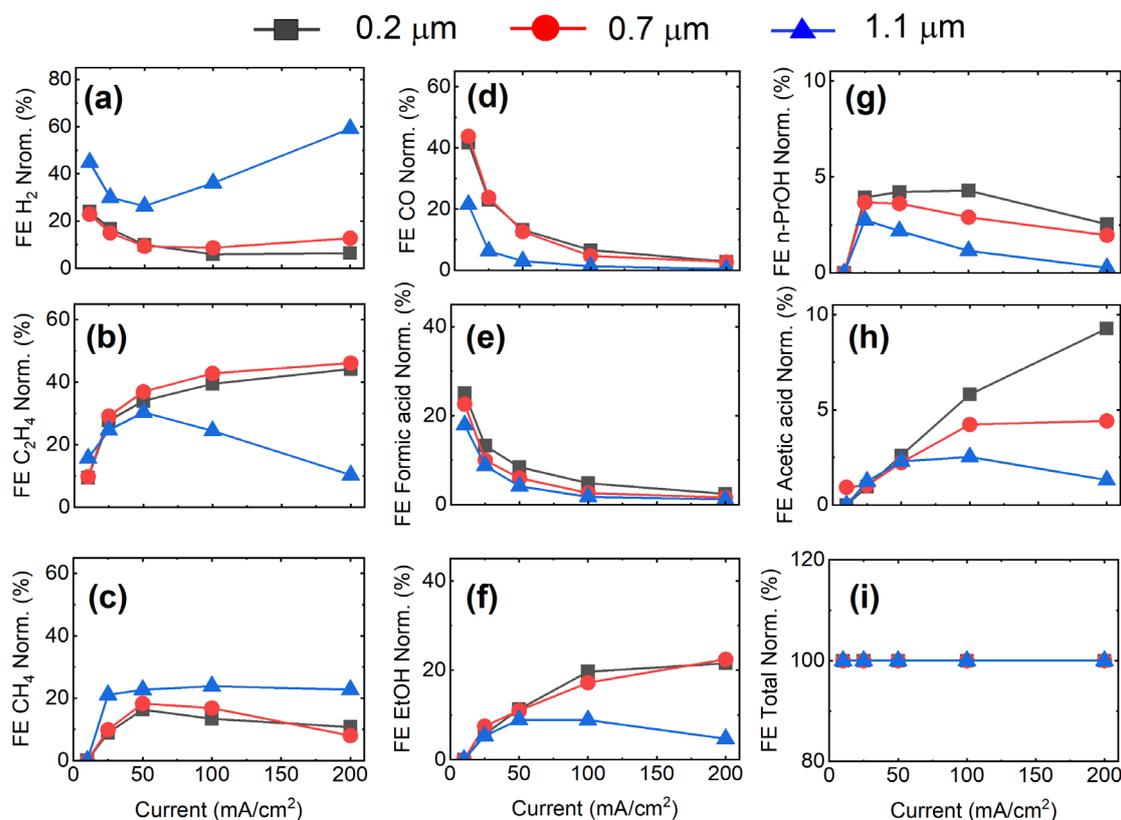


Figure S6. Normalized Faradaic efficiency of Cu-GDEs with different mean pore size as a function of current density towards (a) H₂ (b) C₂H₄, (c) CH₄, (d) CO, (e) formic acid (f) EtOH (g) n-PrOH (h) acetic acid and (i) total FE. Additional trace compounds (FE < 1 %) including allyl alcohol, propane, propene, propionaldehyde, acetaldehyde, and acetone were detected in the gas products and are accounted for in the total FE.

The potential of the reactions reported in Figure 2 is found in Fig. S7

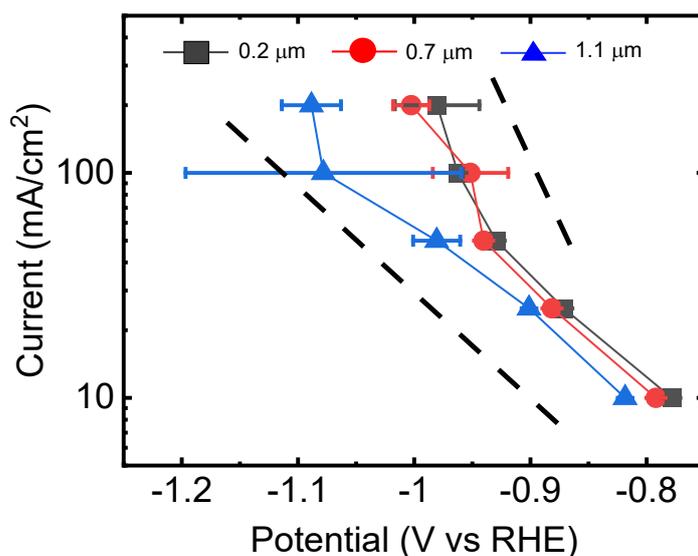


Figure S7. Current density as function of the reverse hydrogen electrode (RHE) potential. Two different Tafel slopes are visible for GDE with lowest and intermediate pore size at 50 mA/cm², which marks a change in selectivity from

products requiring few electrons (H_2 and CO) to those requiring more electrons (C_2H_4 and CH_4). This switch is not observed for the GDE with largest pore as its main selectivity is towards H_2 and CO even above 50 mA/cm^2 . Error bars are obtained as 95% confidence interval assuming Gaussian distribution.

The potential of the reactions reported in Fig. 3 is found in Fig. S8

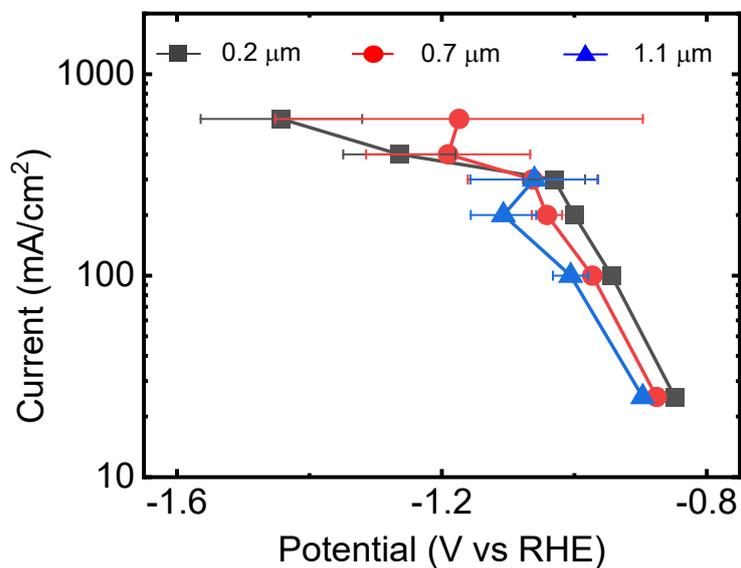


Figure S8. Current density as function of the reverse hydrogen electrode (RHE) potential. The analysis at current densities above 200 mA/cm^2 is complicated by the noise introduced by bubble formation. An increase in potential is observed when the selectivity switches from C_2H_4 and CH_4 to H_2 . Error bars are obtained as 95% confidence interval assuming Gaussian distribution. The errors bars are particularly large because of the impossibility to accurately measure the cell resistance (and therefore to correctly account for the IR drop) when the bubble formation is severe, especially above 200 mA/cm^2 .

3. Product distribution including liquids as a function of pore size and time

The complete product distribution of the GDEs as function of pore size and time are found in Fig. S9

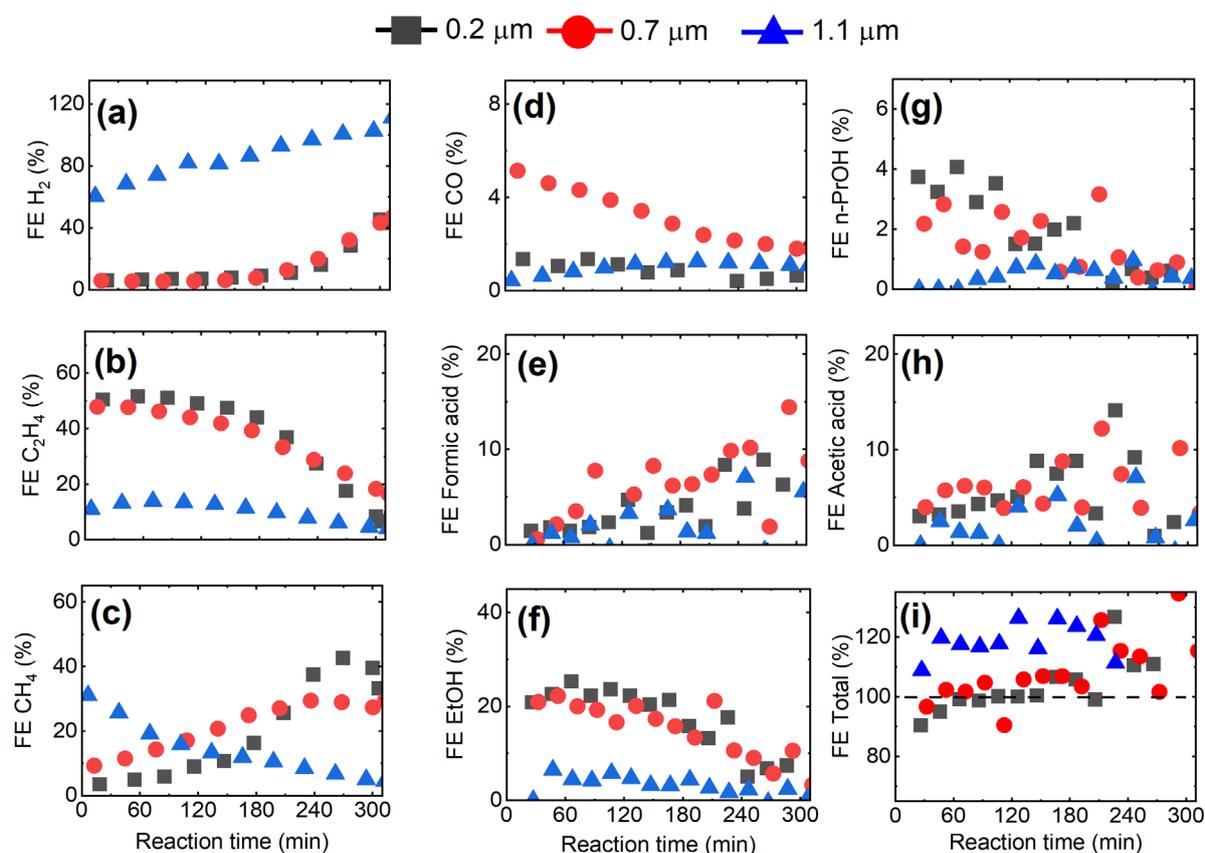


Figure S9. Faradaic efficiency of Cu-GDEs with different mean pore size as a function of reaction time towards (a) H₂ (b) C₂H₄, (c) CH₄, (d) CO, (e) formic acid (f) EtOH (g) n-PrOH (h) acetic acid and (i) total FE. Additional trace compounds (FE < 1 %) including allyl alcohol, propane, propene, propionaldehyde, acetaldehyde, and acetone were detected in the gas products and are accounted for in the total FE.

4. Evaluation of the statistical error on FE

The statistical error was assessed by running three nominally identical GDEs with 0.2 μm pore size for one hour at 200 mA/cm^2 . As shown in Fig. S10, the FE towards the main products of the reaction, i.e. H_2 , C_2H_4 , and CH_4 is comparable across the three samples, but their similarity decreases with time. As such, the statistical error depends on the time window considered, and is expected to become larger with longer reaction times. The relative statistical uncertainty considering a 1 h experiment was estimated to be around 5% of the FE value, yielding e.g. for C_2H_4 a FE of $50 \pm 3\%$.

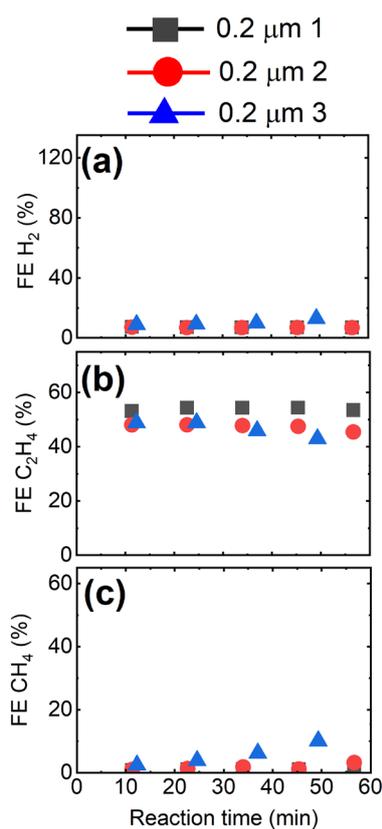


Figure S10: Faradaic efficiency (FE) towards (a) H_2 , (b) C_2H_4 , (c) CH_4 as a function of time for three identical gas diffusion electrodes with 0.2 μm pore size at 200 mA/cm^2 . The statistical error for each FE is estimated to be $\sim 5\%$. The relative statistical error for each FE value is estimated to be $\sim 5\%$.