Supporting Information:

An Introductory Guide to Assembling and Operating Gas Diffusion Electrodes for Electrochemical CO_2 Reduction

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Modelling of the local reaction environment in Fig. 2a

The local reaction environment was modelled similar to previous works and is included in this Viewpoint to highlight operational differences between low and high current density cell operation.[1] For the simulation, a catalyst thickness of 100 nm and porosity of 60% was assumed. The reaction selectivity was assumed to be 90% CO_2 to CO and 10% H_2 evolution, each two-electron processes. A boundary layer thickness to the bulk electrolyte of 200 μm was assumed.

Step-by-step assembly of a gas-diffusion cell for electrochemical CO_2 reduction

The assembly of a standard gas-diffusion cell for rapidly testing catalysts is shown in this section. First, the entire cell assembly is shown in Fig. S1 followed by a step-by-step cell assembly with descriptions in Fig. S2.

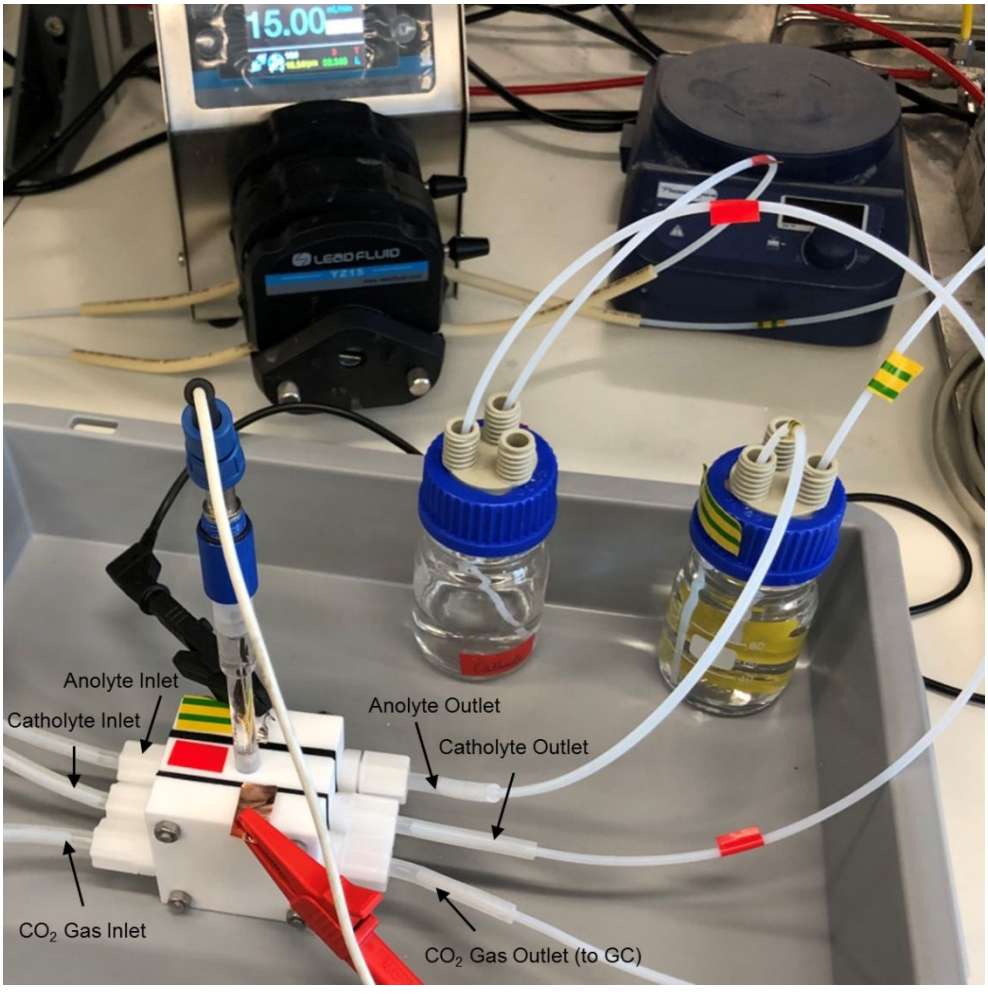
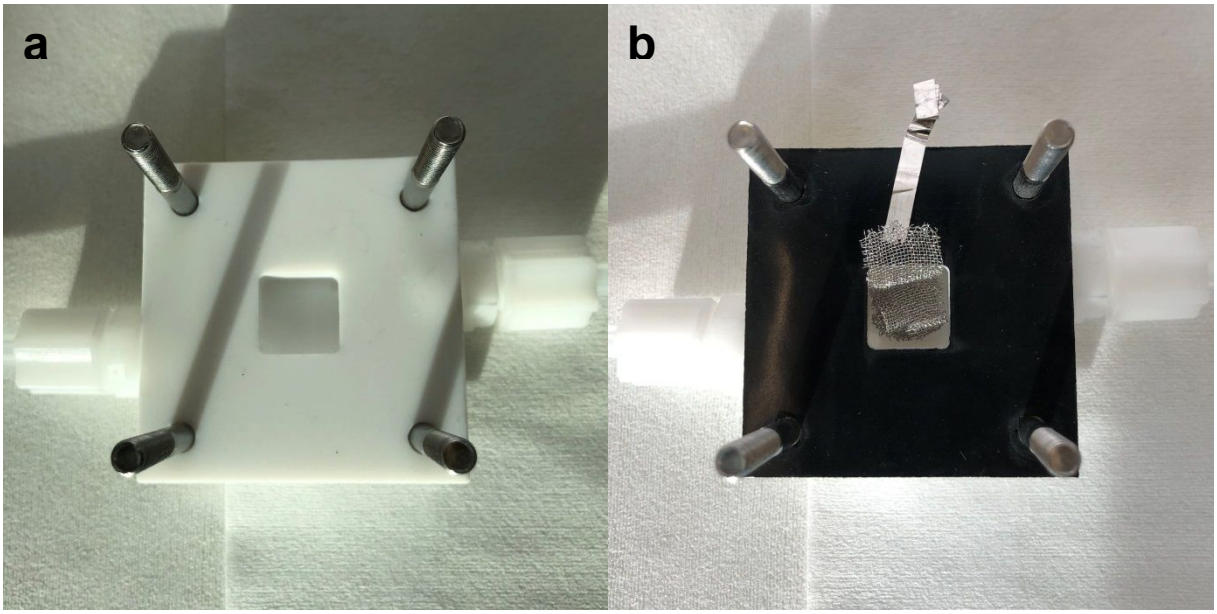
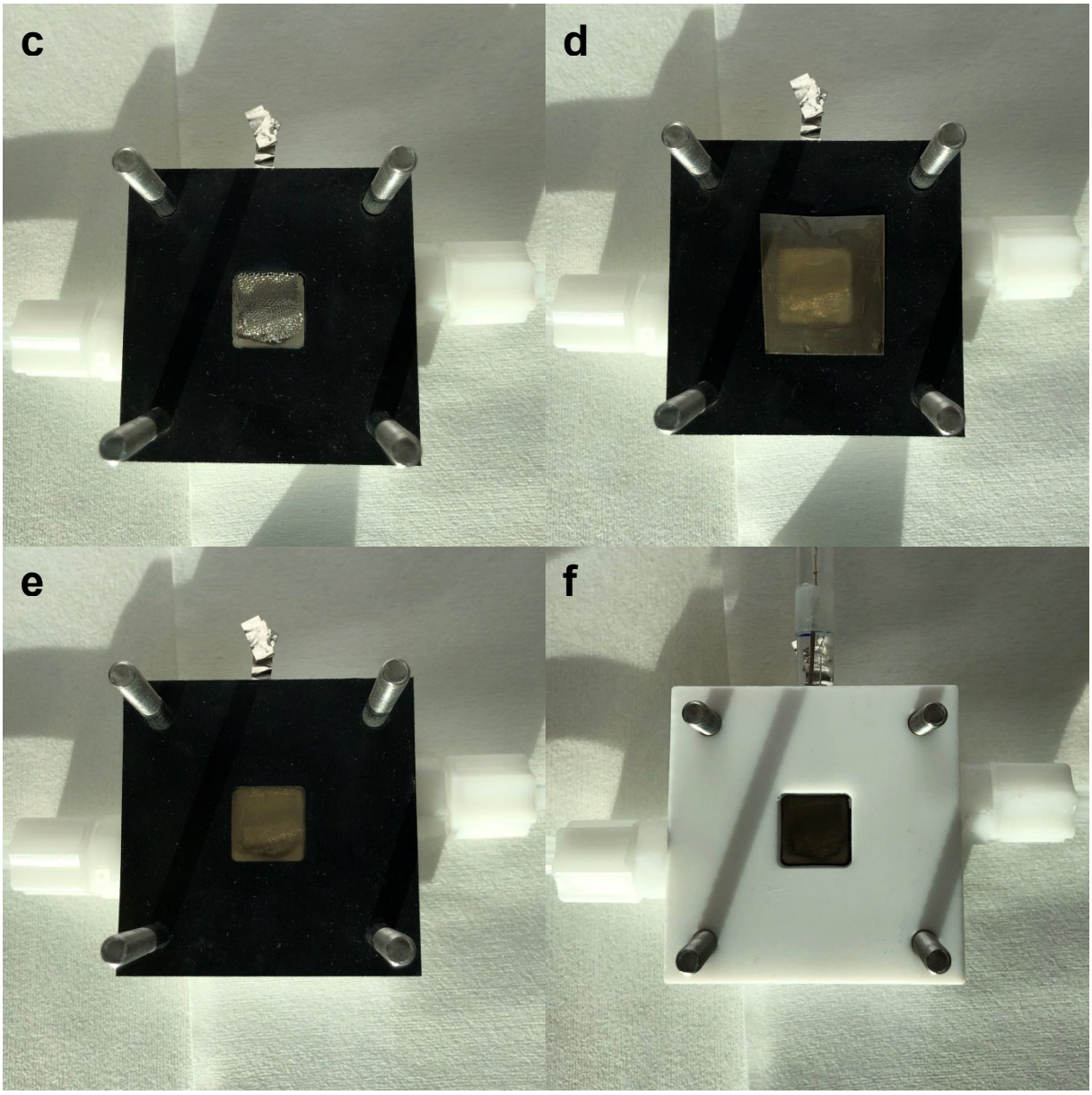


Fig. S1: Assembled cell and labelled inlet and outlets for the electrolyte and CO_2. The catholyte and anolyte are pumped through the cell from separate reservoirs.

Starting with the anode and anolyte chamber flat on the table (a), Fig. S2(a-j) shows assembly of the Polytetrafluoroethylene (PTFE) cell and components used for electrochemical CO_2 reduction. Fig. S2a highlights the anolyte inlet and outlet fittings and the four bolts used to hold all components in place after assembly. Here, the cavity measures 1.5 cm by 1.5 cm with a depth of 0.8 cm. A gasket with the same hole and cavity cut-out is then placed on top of the PTFE anode chamber (Fig. S2b), followed by a nickel or platinum mesh which functions as the anode for the oxygen evolution reaction in alkaline and neutral pH anolyte, respectively. A piece of copper or aluminium tape holds the anode in place while acting as a contact lead for the potentiostat cable external to the cell. A second gasket is then placed over top, sandwiching the anode in place and, once compressed by bolt tightening, prevents electrolyte from leaking outside the cell (Fig. S2c). An ion-exchange membrane, here an anion exchange membrane, is then placed on top (Fig. S2d), followed by another sealing gasket (Fig. S2e). The PTFE catholyte compartment is then placed over top, with a port in the top for the reference electrode, enabling 3-electrode measurements of the cathode (Fig. S2f). The gas-diffusion layer attached to a sealing gasket as described in Supplementary Video 2 is then placed on top of the catholyte chamber with the catalyst side facing down. The exposed carbon fibers from the back of the gas-diffusion layer are now visible, in addition to the copper conducting tape sealing the electrode in place (Fig. S2g). A final gasket then seals the cathode in place (Fig. S2h). An overhead view of the cell up to this point shows the full assembly prior to the addition of the PTFE CO_2 gas chamber (Fig. S2i). Once the third PTFE chamber is placed on top, nuts can be applied and tightened onto the bolts, giving the complete CO_2 reduction cell in (Fig. S2j).

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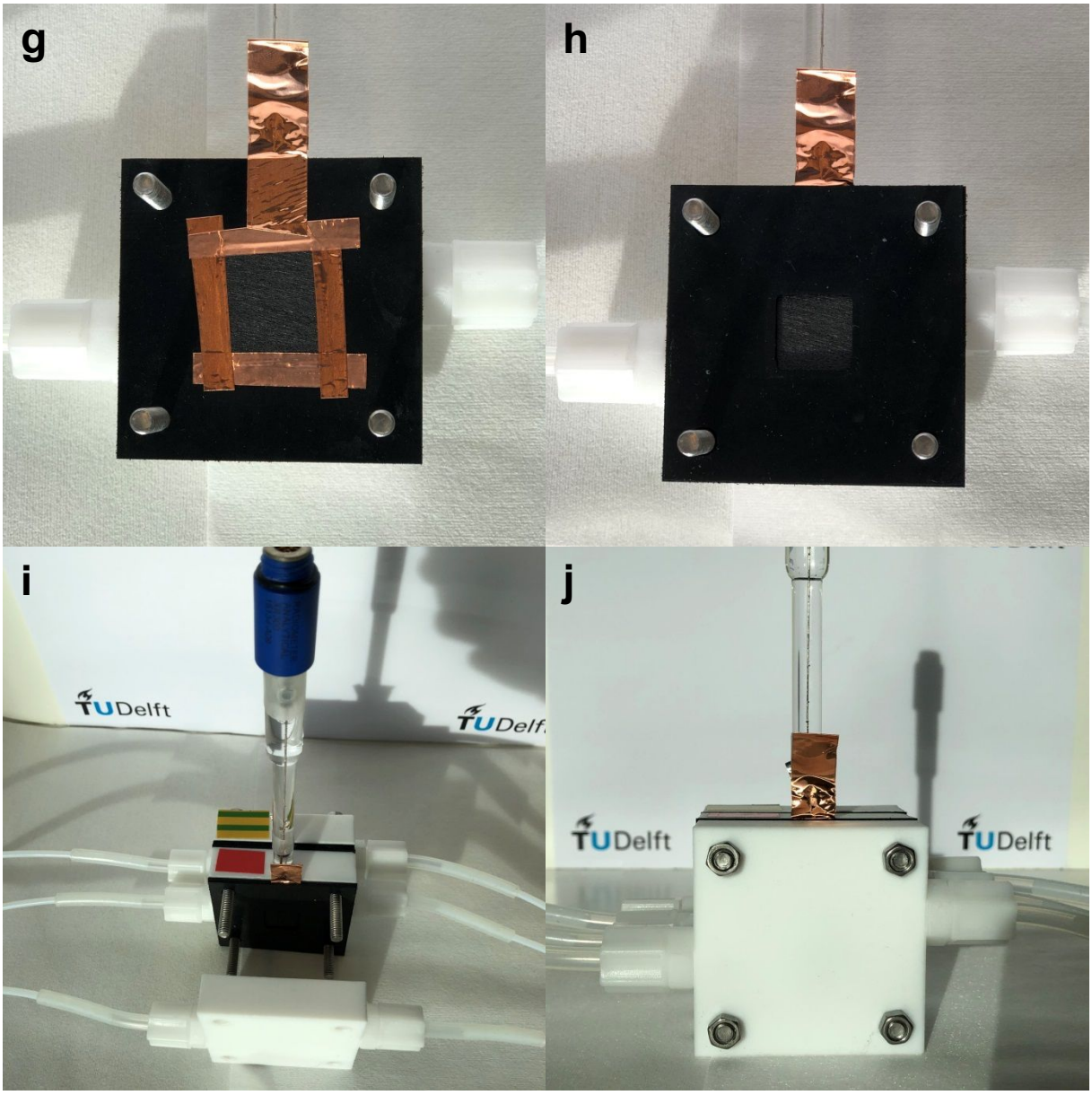

Fig. S2: Step-by-step cell assembly as described within the supporting text.

Securing of the gas-diffusion layer to the sealing gasket

Fig. S3 shows two methods to seal the gas-diffusion layer. On the left, conducting tape is applied around the entire sample, while on the right tape is applied only at the top of the sample. Given the relatively high resistivity of gas-diffusion layers, and the sensitivity of the CO_2 reduction reaction to both current density and potential, applying conducting tape around the entire sample is important for ensuring uniformity of the reaction on the gas-diffusion layer. Further, sample size should either be limited or the current collector should have maximum contact with the gas-diffusion electrode (e.g. copper mesh pressed against the back while still allowing gas flow).

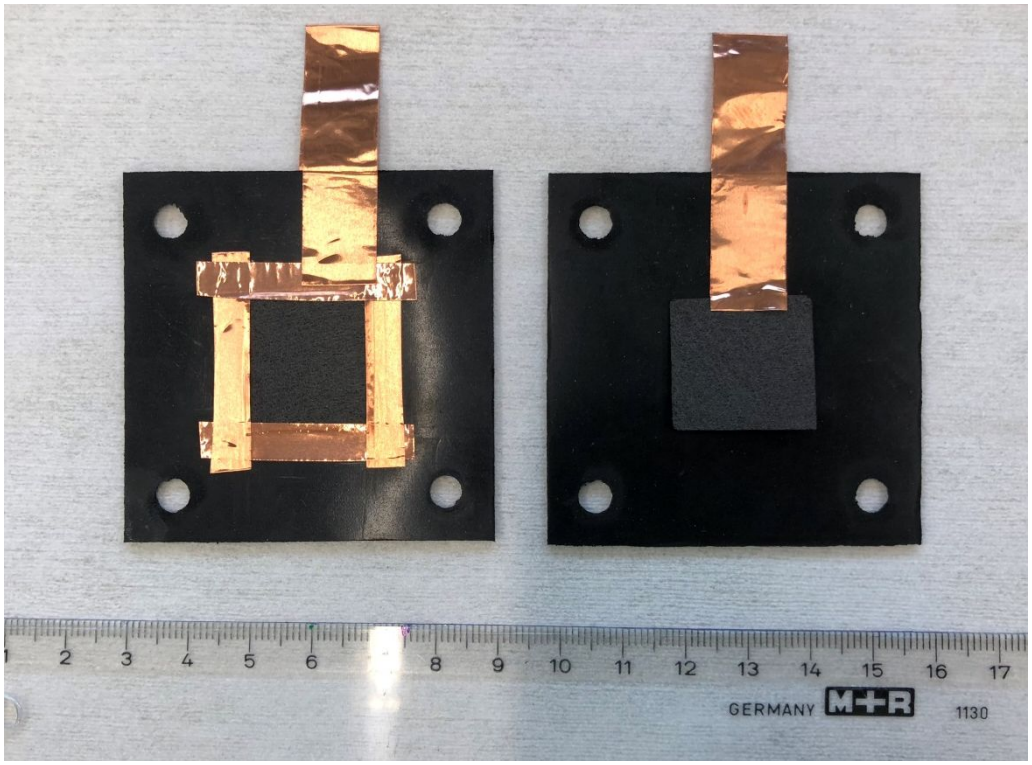

Fig. S3: Sealing of the conducting tape to the gas-diffusion layer.

Determination of solution resistance in Fig. 2c

To determine the solution resistance in Fig. 2c, EIS and CI measurements were conducted in the custom-designed GDE cell in 1M $KHCO_3$ on a potentiostat (Bio-Logic, SP-200) using an electrolyte flow rate of 5 mL/min. The solution resistances under different current densities were recorded by EIS and CI with 3 replicates. Briefly, the GDE was operated at the chosen current density for a fixed period of time, followed by either EIS or CI measurements.

Supplemental References

(1) Burdyny, T.; Smith, W. A. CO2 Reduction on Gas-Diffusion Electrodes and Why Catalytic Performance Must Be Assessed at Commercially-Relevant Conditions. *Energy Environ. Sci.* **2019**. https://doi.org/10.1039/C8EE03134G.