

## **Probing the local activity of CO<sub>2</sub> reduction on gold gas diffusion electrodes: effect of the catalyst loading and CO<sub>2</sub> pressure**

Mariana C. O. Monteiro<sup>a</sup>, Stefan Dieckhöfer<sup>b</sup>, Tim Bobrowski<sup>b</sup>, Thomas Quast<sup>b</sup>, Davide Pavesi<sup>a</sup>, Marc T. M. Koper<sup>\*a</sup>, and Wolfgang Schuhmann<sup>\*b</sup>

a Leiden Institute of Chemistry, Leiden University, Einsteinweg 55, 2333CC Leiden, The Netherlands  
E-mail: m.koper@chem.leidenuniv.nl

b Analytical Chemistry-Center for Electrochemical Sciences (CES), Ruhr-Universität Bochum, Universitätsstr. 150, 44780 Bochum, Germany  
E-mail: wolfgang.schuhmann@rub.de

## **Electronic Supplementary Information**

## Methods

### ***Nanoparticle synthesis***

Gold nanoparticles supported on carbon were synthesized by dissolving 0.034 g of H<sub>2</sub>AuCl<sub>4</sub> trihydrate (>49 % Au, Fisher Scientific) in 95 mL of water and 0.097 g of trisodium citrate dihydrate (≥99 %, Sigma-Aldrich) in 5 mL of water. The Au solution was brought to a boil under vigorous stirring, and the citrate solution was pre-heated. As soon as the gold solution boiled, the pre-heated 5 mL of citrate solution was added. Upon addition, the solution, which was initially yellow, turns transparent, then black and finally, after 15 min dark red. After the solution cooled down, still under vigorous stirring, an amount of VXC72 Vulcan carbon (Cabot) was added to yield a metal loading of 60% Au on the carbon support. The solution was then tip sonicated for 20 min at 31% amplitude with a MS73 ultrasonic probe (Bandelin) and kept stirring overnight. Once all the Au nanoparticles were supported on the carbon, the solution became transparent. The Au/C particles were filtered and rinsed several times with water.

### ***Au-nanoelectrode preparation***

Au-nanoelectrodes suitable for the approach via shear-force based distance feedback were fabricated with a laser puller (Model 2000, Sutter Instruments). The adhesion properties of untreated gold wires to the capillary glass walls are not sufficient for the reliable production of well-sealed Au SECM tips. Therefore, we modified the adhesion characteristics of the gold wire (50 μm diameter, >99.99 %, Goodfellow) by electrochemically coating it with a thin layer of platinum. Platinum deposition was performed in a 3-electrode electrochemical setup with the Au wire as working electrode, a Pt mesh as counter electrode, and a Ag/AgCl/3 M KCl as reference electrode. A commercial Pt plating solution (Met-Pt 209, Metalor) was used as electrolyte. Contact with the electrolyte was made with the gold wire at 0 V, and then three potential pulses of 100 ms to -1 V and 500 ms to 0 V were performed. The coated Au-wire was further immersed into the plating solution for 2 h without any applied bias voltage, and then thoroughly rinsed with water. Once dried at ambient atmosphere, 1 cm long pieces of Pt-plated gold wire were positioned in the centre of soda-lime glass capillaries (Hilgenberg) with an inner diameter of 0.5 mm and an outer diameter of 1 mm.

Next, the filled glass capillaries were fixed in a laser puller. Both capillary inlets were connected to a vacuum pump (Laboport, KNF Neuberger) to avoid the inclusion of air bubbles during the subsequent sealing step. During sealing of the Au wire in 7-9 heating/cooling cycles (20 s and 40 s, laser ON/OFF), the puller bars were fixed with a metal clamp to prevent a continuous pulling force on the capillary. The following laser puller parameters were used during the sealing step: heat: 260; filament: 5; velocity: 90; delay: 140; pull: 0. After confirming a visually complete Au/glass seal with the help of an optical microscope, the capillary was reinserted into the laser puller for the hard pull step. In this step, the Au/glass composite was liquified by laser heating and pulled into two parts using the following parameter set: heat: 300; filament: 5; velocity: 90; delay: 140; pull: 90-110.

The resulting long-tapered glass/Au tips were electrically contacted by conductive 2-component epoxy glue (Polytec EC 151-L, Polytec PT). The glue was filled into the glass capillary using the tip of a Cu-wire (outer diameter of 0.3 mm) up to the non-sealed section of the Au wire. One end of the Cu wire was left inside the filled capillary while curing the glue at 90 °C for 1 h. The tip was polished in a homemade polishing setup which individually rotates the electrode and a hard disc covered with an abrasive film to expose the cross-section of the gold wire. The tip was also subsequently polished on the following abrasive layers: P2000 sandpaper (Starcke), 0.5 μm and 0.1 μm diamond lapping film (661X, 3M Deutschland). Prior to polishing on each lapping film, the Au tip was ultrasonicated in EtOH/water for 10 min.

### ***Focused ion beam (FIB) milling of gas diffusion electrode substrates***

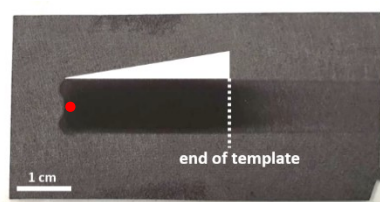
In the first step, the FIB milling process was used to mill a hole into the substrate from the top to create a ramp with a slope of approximately 45° using a FIB current of 65 nA for 2 h. This is a prerequisite for EDX analysis of the cross-sectional view later. In a 90° angle to this cut, another ramp with a 45° slope was milled into the substrate using the same parameters. The sample was then tilted by 2°, and a FIB cross-section polishing procedure was applied for about 10 min to obtain the shown cross-sectional view inside the substrate. EDX of the exposed cross-section after FIB milling was conducted at an acceleration voltage of 30 kV.

### Shear-force based distance control

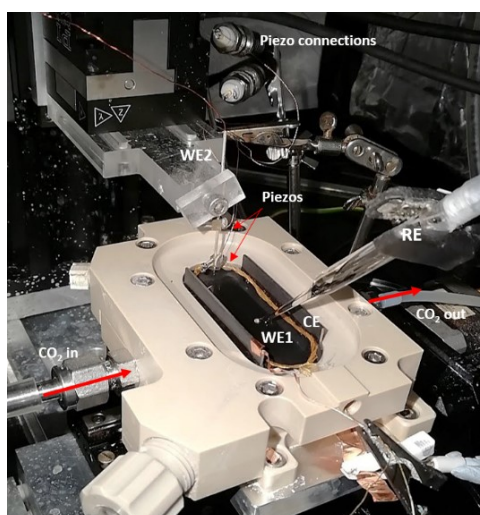
All setup components of the SECM with shear-force-based distance control are located inside of a homemade faraday cage to allow for shielding of electrical noise, with the exception of the lock-in amplifier and the potentiostat. Vacuumed polystyrene panels (Vaku-Isotherm) are used to cover the inner walls of the faraday cage to maintain a constant temperature around the measurement cell. Vibrational noise during SECM measurements was minimized by mounting the faraday cage on an actively damped table (Newport RS 2000). In order to establish a shear-force-based distance control loop two piezo elements were mounted to the Au-tip glass body and connected to a lock-in amplifier (Ametek 7280) via BNC connectors. One of those piezo elements served as the detection element for the magnitude of the oscillation at the tip apex and was mounted as close as possible to the tip's taper. The second piezo unit had the function to generate a tip oscillation at a defined frequency by applying an AC voltage via the lock-in amplifier. This excitation piezo was mounted in a distance of 1-1.5 cm above the detection piezo and was displaced by an angle of around 45°. To establish a reliable distance control, it is crucial to identify a tip resonance frequency with high sensitivity towards the tip-to-surface distance. For that purpose, before every experiment, a frequency spectrum in the range from 200-500 kHz (linear ramp over 300 s, 200 mV magnitude) was recorded while the tip was kept in the pre-approach position above the GDE substrate. Subsequently, electrolyte (1 M  $\text{KHCO}_3$ ) was filled into the electrochemical cell, so that the Au tip got immersed into this different oscillation medium. Another frequency spectrum was then recorded and compared to the one in air (Fig. S6). Resonant frequencies with significantly different oscillation magnitudes in both scans indicate possible tip frequencies for the shear-force based approach, since only resonant frequencies originating from the tip, and not from other system components such as the electrode holder, are altered by a change of the oscillation medium.

### Supporting material

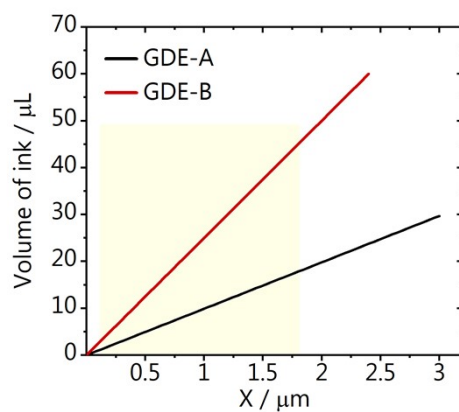
Figure S1 shows a photograph of one of the gas diffusion electrodes after spraying, indicating the Au/C nanoparticle gradient deposited in the exposed area. The red dot marks roughly the starting X-Y position of the array scans, which was established with the help of an optical microscope. Figure S2 shows the setup used for the SECM measurements. The volume of ink dispensed using the spray-coater along the gas diffusion substrate is shown in Figure S3 for GDE-A (shallow catalyst gradient) and GDE-B (steep catalyst gradient). SECM measurements were performed along 1.7 cm of the substrates, corresponding approximately to the area highlighted in yellow in Figure S3.



**Figure S 1.** Photograph of the gas diffusion electrode after spraying showing a 1 x 3 cm<sup>2</sup> catalyst loading gradient.



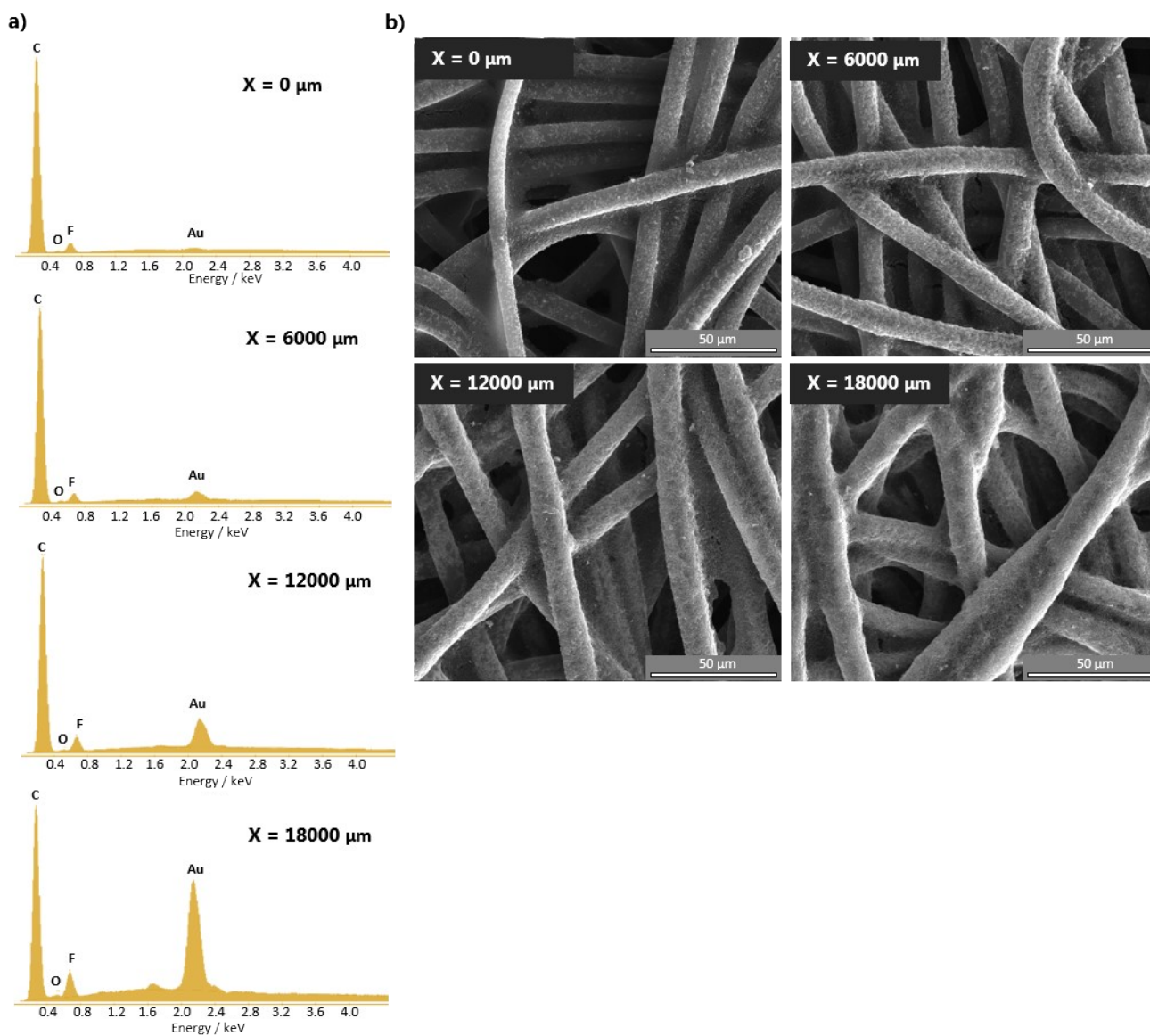
**Figure S 2.** Electrochemical cell mounted in the SECM setup. The GDE substrate and the Au nanoelectrode are indicated as WE1 and WE2, together with the Ag/AgCl reference electrode (RE) and the DSA counter electrode (CE). The piezo elements and connectors are also indicated in the image, as well as the CO<sub>2</sub> gas inlet and outlet.



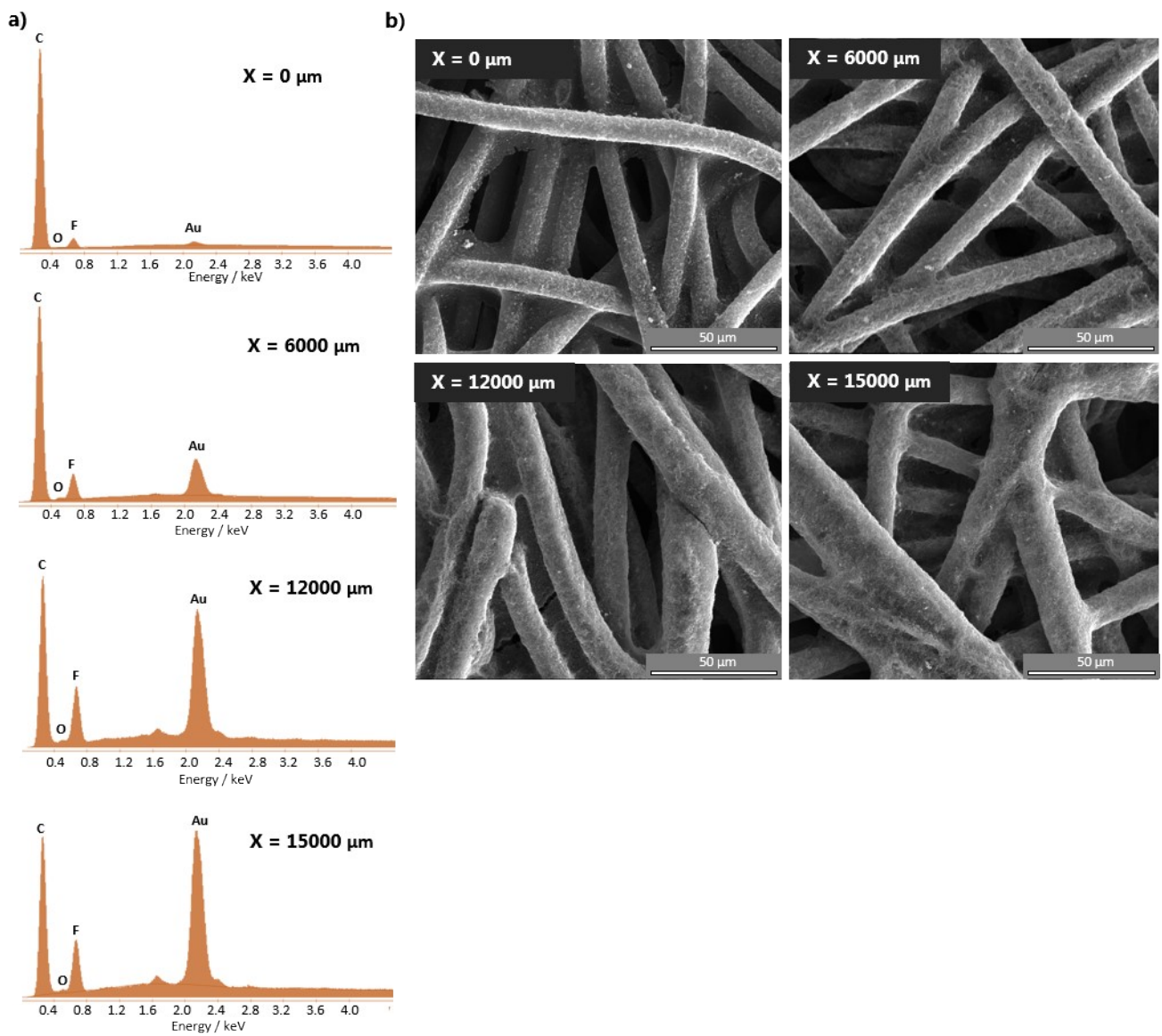
**Figure S3.** Volume of ink dispensed along the gas diffusion layer creating a more (GDE-B) or less (GDE-A) steep catalyst gradient.

### Characterization of the gas diffusion electrodes

The two GDEs were characterized by SEM and EDX at different X-positions along the Au/C catalyst gradient. Results are shown in Figure S4 and Figure S5, for GDE-A and GDE-B, respectively.



**Figure S4.** a) EDX spectra and b) SEM micrographs obtained at different X-positions along the catalyst gradient of GDE-A.

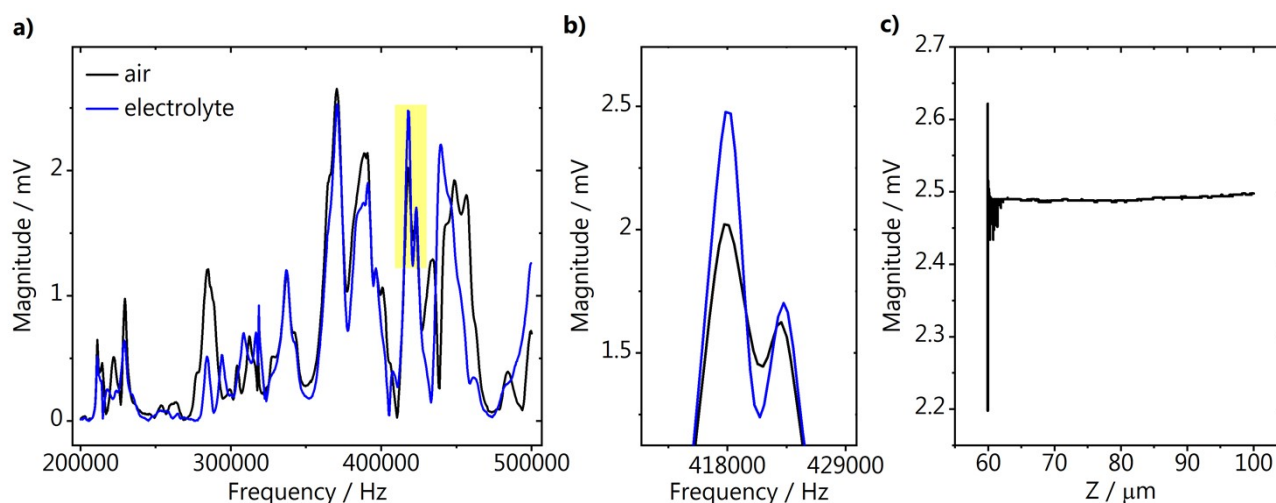


**Figure S 5.** a) EDX spectra and b) SEM micrographs obtained at different X-positions along the catalyst gradient of GDE-B.

## SECM measurements

### Shear-force approach

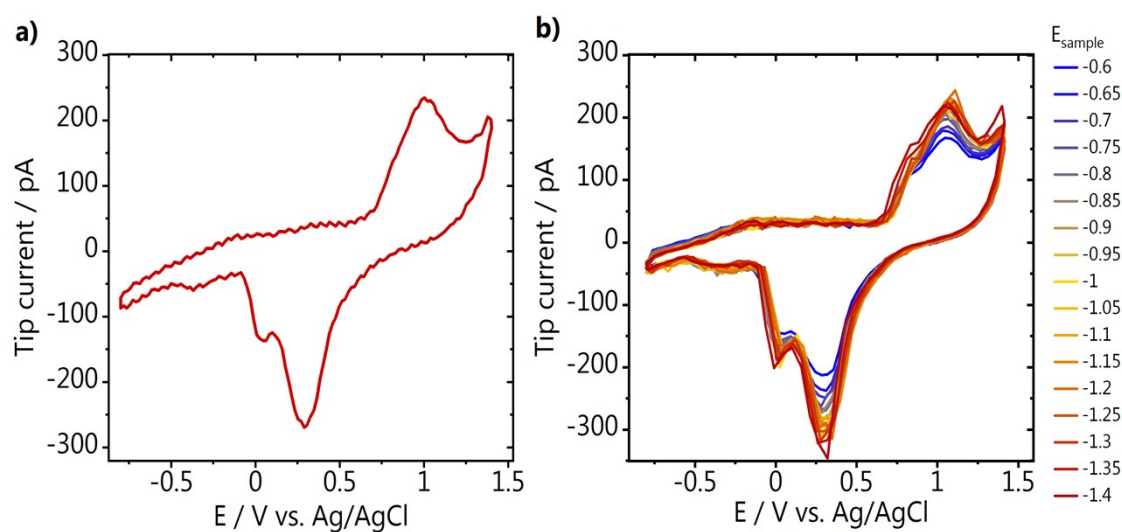
For positioning of the tip above the gas diffusion electrodes, first, a frequency spectrum of the gold nanoelectrode (Figure S 6a) is recorded in air and then in electrolyte in order to determine the resonance frequencies characteristic from the tip. Using one of these frequencies, e.g. shown in Figure S6b (and marked in yellow in Figure S6a), an approach curve (Figure S6c) is performed to place the tip  $\sim 100$  nm from the surface. Approach curves were performed at every XY position of the substrates before the measurements.



**Figure S 6.** a) Frequency spectra recorded in air and electrolyte, b) zoom in of the tip resonance frequency used for the approach curve (yellow area from a)), c) approach curve.

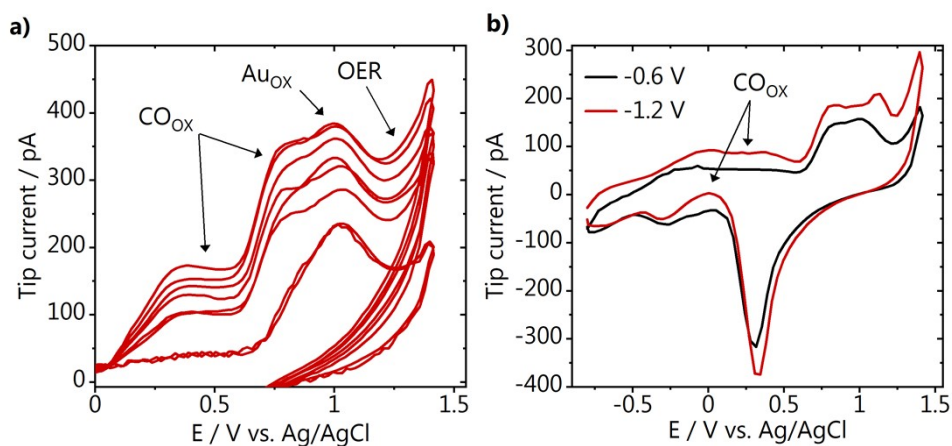
### Gold nanoelectrode response

The blank voltammetry of the gold nanoelectrode was recorded in the shear-force interaction region ( $\sim 100$  nm from the surface) before each measurement to assure a clean and reproducible Au surface. An example of a blank CV is shown in Figure S7a. CVs were also recorded while applying different potentials to the bare gas diffusion layer (without catalyst) in  $\text{CO}_2$  saturated electrolyte (Figure S7b). No CO is produced by the bare substrate, and a reproducible double layer charging current is observed between 0 and 0.55 V vs Ag/AgCl/3 M KCl.



**Figure S7.** a) Blank CV of the gold nanoelectrode and b) voltammetry recorded in the shear-force interaction region while stepping the GDE potential. The sample potentials reported ( $E_{\text{sample}}$ ) are versus Ag/AgCl/3 M KCl, and the CVs were recorded in 1 M  $\text{KHCO}_3$ ,  $\text{CO}_2$  saturated, at  $200 \text{ mV s}^{-1}$ .

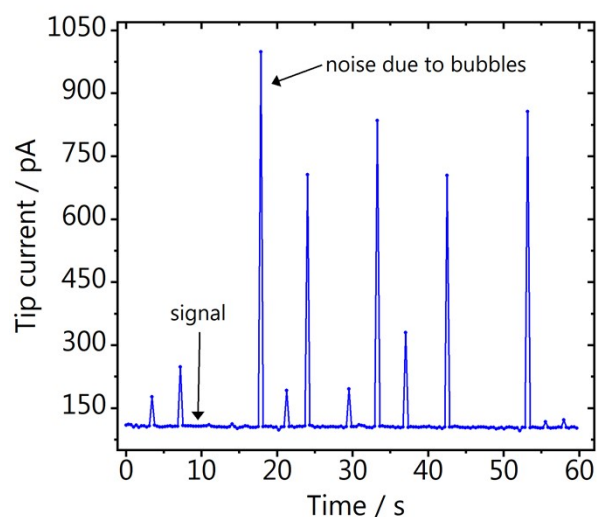
The gold nanoelectrode CVs were also recorded after flowing a calibration gas containing 1% CO for 10 s through the cell (Figure S8a). Two characteristic plateaus show the diffusion-limited oxidation of CO.<sup>1</sup> Additionally, voltammetric features of the gold oxidation and the overpotential of the oxygen evolution reaction (OER) can be observed. In Figure S8b, the voltammetric response of the Au nanoelectrode is shown while different potentials were applied to the gas diffusion electrode. The sample potentials reported are versus Ag/AgCl/3 M KCl, and the CVs were recorded in 1 M KHCO<sub>3</sub>, CO<sub>2</sub> saturated, at 200 mV s<sup>-1</sup>.



**Figure S8.** CVs of the gold nanoelectrode a) after feeding a calibration gas containing 1 % CO through the substrate for 10 s and b) upon applying different potentials to the GDE. The sample potentials reported are versus Ag/AgCl/3 M KCl, and the CVs were recorded in 1 M KHCO<sub>3</sub>, CO<sub>2</sub> saturated, at 200 mV s<sup>-1</sup>.

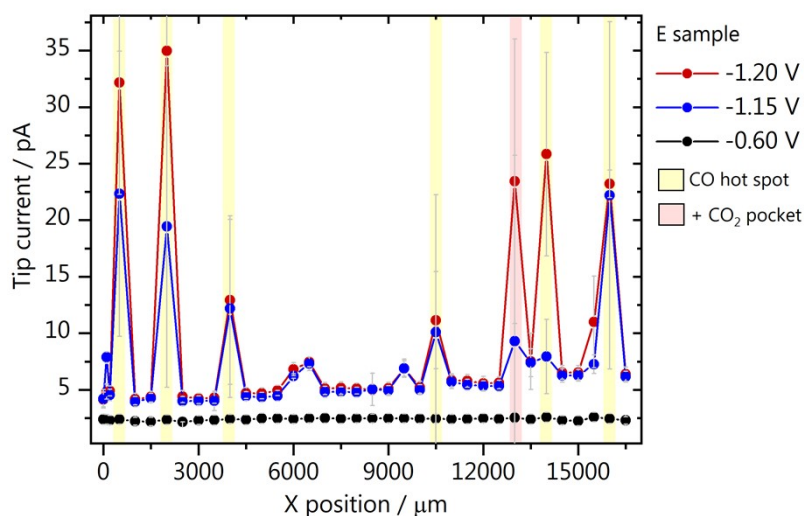
### SECM array scans

An example of how bubbles affect the current measured at the gold nanoelectrode is shown in Figure S9, where the sample (GDE-A) was held at -1.15 V vs. Ag/AgCl/3 M KCl.



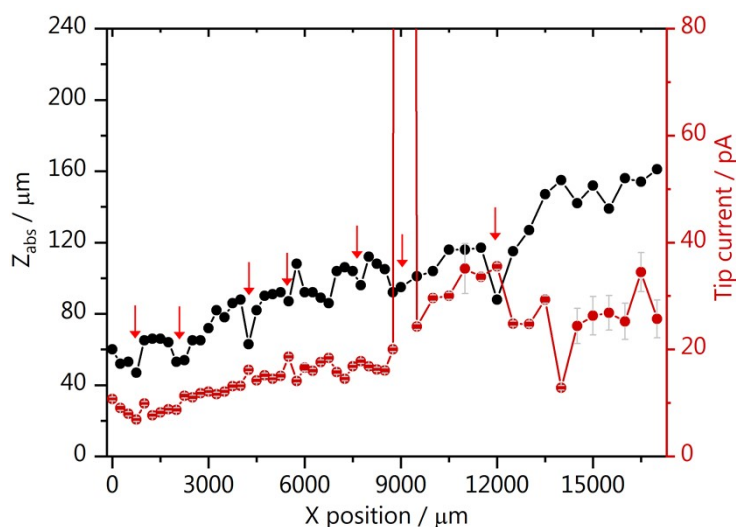
**Figure S9.** Raw tip current data recorded during a measurement where GDE-A was held at -1.15 V vs. Ag/AgCl/3 M KCl.

The activity of GDE-A along the catalyst gradient is shown in Figure S10. The experiment was performed in 1 M  $\text{KHCO}_3$  with a  $\text{CO}_2$  pressure of 2 mbar.



**Figure S10.** SECM array scan of GDE-A in 1 M  $\text{KHCO}_3$  at a  $\text{CO}_2$  pressure of 2 mbar. Potentials are reported versus Ag/AgCl/3 M KCl.

Figure S11 shows the correlation between the sample height profile and the amount of CO detected along the gradient of GDE-B, at a  $\text{CO}_2$  pressure of 0.7 mbar.

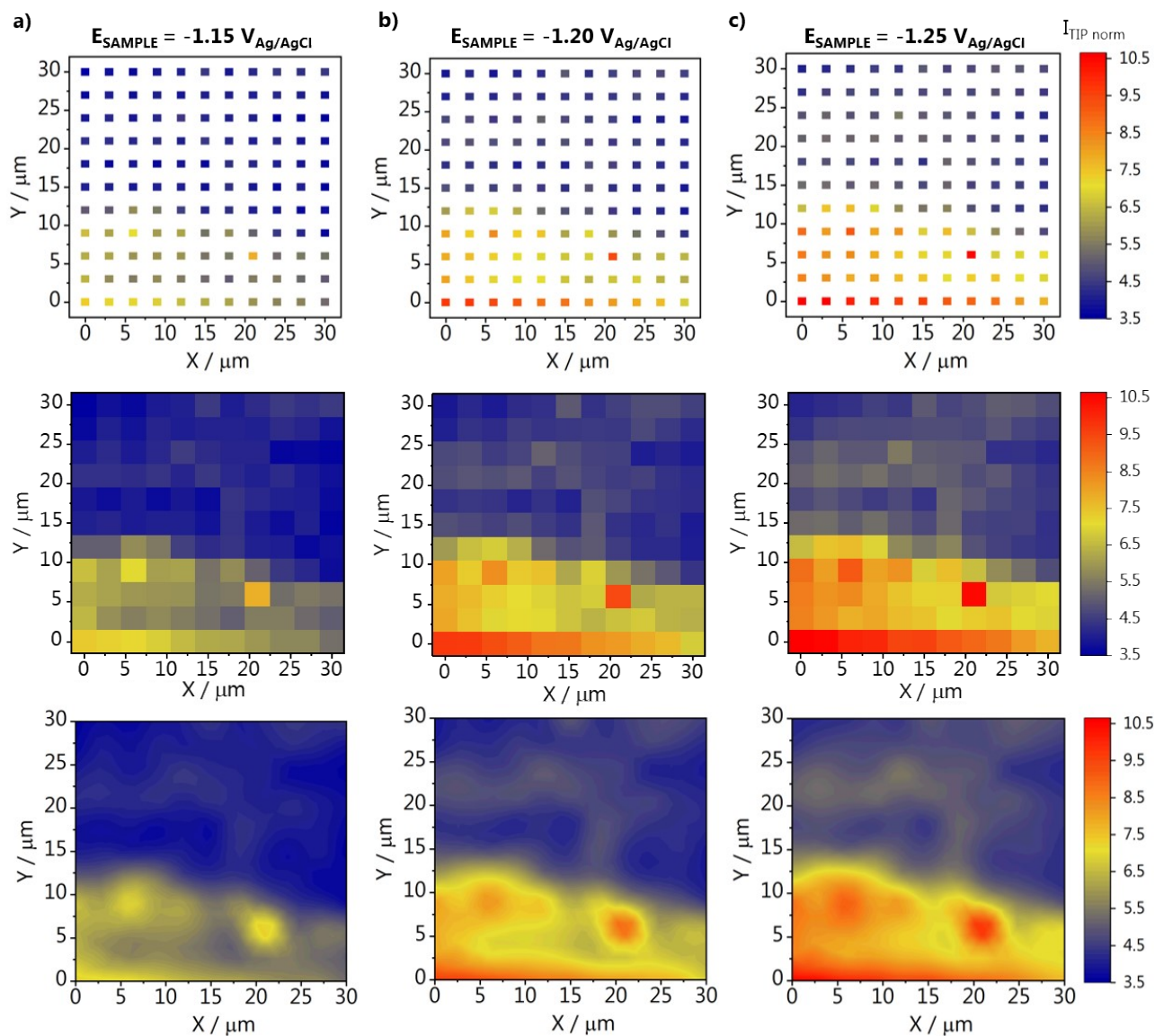


**Figure S 11.** Absolute position of the shear force interaction region along the catalyst gradient of GDE-B, together with the CO activity.



### Activity map data processing

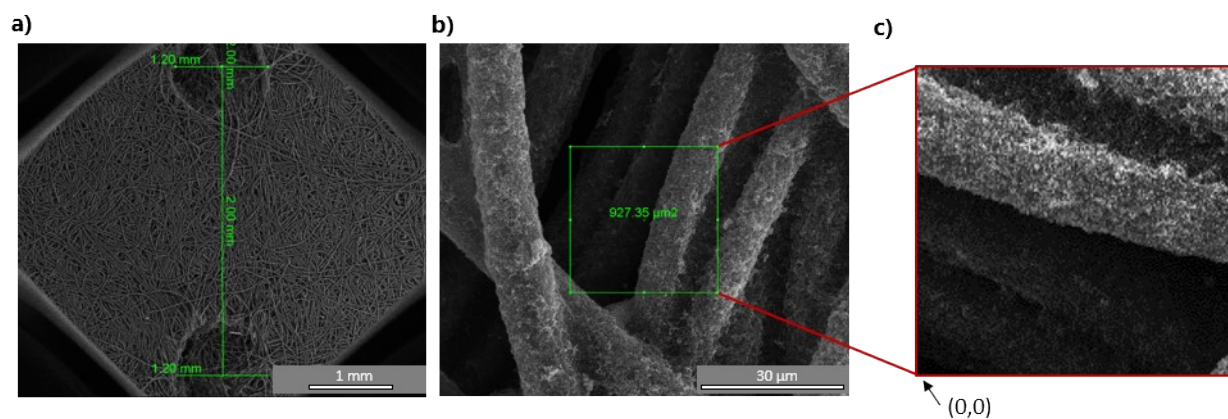
Figure S12 presents the activity maps recorded in a 30 x 30  $\mu\text{m}$  area of GDE-B ( $\text{CO}_2$  pressure 0.7 mbar). Here, three different ways of visualizing the same data are presented for the three different substrate potentials applied. The top panel shows a realistic representation of the data measured, considering the diameter of the Au nanoelectrode, and the middle panel the same data but with the space filled. The interpolated data (using nearest neighbours) are shown in the lowest



**Figure S12.** Activity map of GDE-B recorded at sample potential a) -1.15 V, b) -1.2 V and c) -1.25 V. Three different ways of visualizing the data are presented, namely by plotting the individual data points with and without space filling, and the interpolated data shown in the main text. Potentials are reported versus Ag/AgCl (3 M KCl).

panel and allows for easier visualization and interpretation of the activity trends and is therefore shown in the main text.

After recording the activity maps, we have marked the substrate using a 1.2 mm probe at a distance of 1 mm of the scanned area, as shown in the SEM micrograph in Figure S13a. Although there is an uncertainty in the exact location of the map, Figure S13b shows that the mapped region likely has large variations in topography, i.e. deep pores and fibres at different levels. Taking this into consideration together with the results shown in Figure S11, we are confident that the mapped area is likely the region shown in Figure S13c.



**Figure S 13.** SEM micrographs of a) the marks made in GDE-B after the activity maps were recorded, b) the mapped region, within a confidence interval and c) a suggested topography of the mapped area.

## References

- 1 M. C. O. Monteiro, L. Jacobse and M. T. M. Koper, *J. Phys. Chem. Lett.*, 2020, **11**, 9708–9713.