Probing the Local Reaction Environment During High Turnover Carbon Dioxide Reduction with Ag-Based Gas Diffusion Electrodes

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Experimental section

Chemicals and materials

Potassium hydroxide for the SECM experiments and for the Pt-tip potential calibration was purchased from Fisher Chemicals (85.3 %, analytical reagent grade) and Sigma Aldrich (99.9 % trace metal basis, semiconductor grade), respectively. For the exact determination of KOH concentration by acid-base titration, oxalic acid dihydrate (p.a., Merck) was used as received. All KOH solutions were purified from metal cation impurities utilizing a Chelex®100 column (Sigma Aldrich) as reported elsewhere. Water (MilliQ) was purified by a water purification system (SG Water) and had a conductivity of 0.055 µS cm⁻¹.

Ag-based GDEs were fabricated by a wet preparation process which has been described in detail elsewhere. A suspension consisting of the Ag catalyst, PTFE as binder and a methylcellulose solution as a pore building agent was spray-coated on a conductive supporting material (Ni-mesh) using an airbrush procedure. The preparation of the 1 wt% methyl cellulose solution involved mixing of hydroxyethylmethyl cellulose (WALOCEL MKX 70000 PP 01) with demineralized water and subsequent stirring of the solution for several hours with an Ultra Turrax at 1650 rpm. The catalytic silver particles (SF9ED, Ferro) were dispersed in that solution under addition of water. A homogeneous distribution of the particles in the suspension was achieved by stirring with three repetitions of 5 mins with an Ultra Turrax at 17,500 rpm. In between the mixing intervals a 5 min long resting time step was maintained. An aqueous PTFE suspension with 59 wt% PTFE (PTFE Dispersion TF 5060GZ, 3M Dynene) was added while stirring at lower rotation speed. From that point on the solution was stirred permanently in order to avoid particle agglomeration. The suspension was hand sprayed on the conductive supporting material, a Ni-mesh (106 µm x 118 µm mesh size, 63 µm thickness; Haver & Boecker) using a spray piston with a 0.6 mm pinhole. The Ni mesh was fixed on a heating plate to allow for fast solvent evaporation while spraying. Multiple layers were applied, each new layer after sufficient drying of the previous ones. After every tenth layer the electrode was rotated to ensure surface homogeneity of the sprayed layer. This procedure is repeated until a silver loading of 150 mg cm⁻² is reached. The electrode was hot-pressed with a pressing load of 15 MPa at 130 °C for 5 min. After pressing, the electrode is subjected to heat treatment at 330 °C for 15 min to burn out the methyl cellulose and improve the mechanical stability through PTFE sintering.

Pt-tip preparation

Pt-tip electrodes for the shear-force based distance control were fabricated with a laser puller (Sutter Instruments) following a previously published procedure. First, a 1 cm long piece of Pt-wire (Ø: 25 mm; Goodfellow) was positioned in the center within a quartz glass capillary (outer diameter (D_out): 0.9 mm; inner diameter (D_in): 0.3 mm, L: 90 mm; QSIL). The capillary was fixed in the laser puller unit and its both inlets were connected to a vacuum pump (Laboport, KNF Neuberger). In a first step, the wire was sealed into the capillary during 7 – 12 heating/cooling cycles (20 s and 40 s, laser ON/OFF) using the following laser pull parameters: heat: 780; filament: 5; velocity: 150; delay: 128; pull: 0. After confirming a complete Pt/glass seal in a light microscope, the capillary was reinserted into the instrument and the hard pull step was conducted, meaning that the wire/glass assembly was pulled into 2 parts. That was done using the following parameter set: heat: 775; filament: 5; velocity: 150; delay: 128; pull: 170. The resulting long-tapered Pt-tips were electrically contacted by soldering a Cu wire (Ø 22 mm; BLOCK) to the non-sealed section of the Pt-wire through short heating with a heat gun. The still glass-sealed Pt-tips were transferred into a dual-beam FIB/SEM instrument (Quanta 3D ESEM; FEI) in order to expose a disc-shaped Pt-surface at the tip by focused ion beam (FIB) milling (Fig. S3). For that purpose, a Ga ion beam (1 nA current and 30 kV acceleration voltage) was focused on the desired section of the glass mantle close to the tip. The as-obtained Pt-tips were used without further modification. In between different measurements the Pt-tips were stored in 2 M HNO₃ to avoid contaminations from ambient air.

SECM setup for the shear-force based approach of Pt-tips to operating GDEs

The SECM cell for the local investigation of Ag-GDEs during CO₂RR is depicted in Fig. S1. The precise approach of the probe to the GDE surface is facilitated by a combination of a stepper motor and piezo positioning unit. While the former allows a course pre-alignment close to the GDE surface and at the desired x-y coordinate, the latter enables a more precise approach in nm increments while recording the oscillation magnitude as the distance feedback signal. An integrated CO₂ gas channel in the cell base block provides gaseous reactant to the GDE backside. The setup is located inside a home-made Faraday cage in order to shield it from electrical noise. The walls inside the Faraday cage were covered with isolating vacuumed polystyrene panels (Vaku-Isotherm) maintaining a constant temperature around the measurement cell (panels visible in right photograph of Fig. S1). The Faraday cage was further mounted on an actively damped table (Newport RS 2000) in order to reduce overall vibrational noise. All electronical components were connected to the same ground connection in order to avoid ground loops. While handling of Pt-tips, an electrostatic discharge foot connector was worn at all times to prevent damage to the electrode tip apex.
Shear-force feedback-based approach of Pt-tips towards Ag-GDE surfaces

A close positioning of the Pt-tip to the GDE surface was facilitated by shear force distance-controlled SECM. The approach feedback-mechanism is based on hydrodynamic forces occurring in close proximity to solid surfaces. Such forces exert a measurable influence on the oscillation characteristics of oscillating Pt-tips which renders the methodology independent of electrochemical feedback mechanisms. A shear-force based distance control loop was established by mounting two piezo elements (Piezomechanik Pickelmann, Fig. S1) to the electrode body of the Pt-tip. Both piezo elements were connected to a lock-in amplifier (Ametek 7280). One piezo element was positioned close to the tip’s taper and served as the detection element for the oscillation movements of the tip apex. The second piezo element was fixed 1 – 1.5 cm from the detection piezo away at an angle of around 45°. The latter was used to oscillate the tip at a defined frequency by applying different AC voltages to it. Simultaneously, the detection piezo measured magnitude and phase of the tip oscillation making the use of those as distance feedback parameters feasible.

Prior to each approach, the GDE was mounted in a PEEK cell body that was specifically designed for SECM experiments over GDE substrates (Fig. S1). In that cell the GDE was sandwiched between two gaskets (Ø: 28 mm, Viton®) with an inner hole of 5 mm diameter in order to seal the system from the ambient gas phase. One additional O-Ring (5 mm Øin) was implemented at the GDE surface facing towards the electrolyte to confine the latter to a geometric surface area of 0.2 cm². The gas channel at the GDE backside was purged for over 30 min with CO₂ before starting the Pt-tip approach. Then a coarse alignment of the Pt-tip close to the GDE surface was performed with x-, y-, z stepper motors (OWIS,) using optical control with a video microscope (monochrome USB camera; The ImagingSource).

The shear-force assisted approach necessitated the identification of a tip frequency with sufficient sensitivity to the sample distance. In order to differentiate resonant frequencies of the tip from resonant frequencies of other components in the setup (e.g. the electrode holder) a frequency spectrum (frequency range: 200 – 500 kHz, amplitude: 200 mV) of the Pt-tip was recorded in air and compared to a frequency spectrum in bulk liquid after filling the 1 M KOH electrolyte. Resonance frequencies with significantly different magnitudes in air and liquid marked possible tip frequencies for the approach towards the sample since only resonant frequencies originating from the Pt-tip are altered by a change of the oscillation medium. Fig. S1a illustrates the selection of an exemplary tip frequency (red dashed box) for the Pt-tip approach in a SECM experiment. Due to the significantly higher oscillation magnitude in the electrolyte compared to air, the frequency at 358 kHz could be safely assigned to originate from a tip oscillation mode. While oscillating the Pt-tip at the chosen resonant frequency, the tip was incrementally approached towards the GDE using a piezo-based positioning system (PI, Germany). During the approach the oscillation magnitude was constantly monitored and the approach terminated once a magnitude change of 2 % of the lock-in value was detected (Fig. S2b). This rapid change in magnitude is characteristic for the tip entering the shear-force interaction region in close proximity (around 100 nm) to the substrate surface. In case of a non-sufficient sensitivity of the particular tip resonant frequency, a further frequency scan can be recorded while being in close proximity to the GDE surface (Fig. S1a, dark yellow curve). A comparison of the frequency spectra in surface proximity and bulk liquid can serve as a tool for identifying more sensitive tip resonant frequencies, in case the initially chosen frequency does not show significant magnitude changes upon reaching the shear-force interaction region.

Figure S1. Photographs of the SECM setup for performing shear-force based approaches of Pt-probes to GDE surfaces including assignment of individual system components: 1) x, y, z stepper motor axes, 2) Piezo-based positioning unit, 3) PEEK base block with integrated gas channel for CO₂, 4) Piezo elements mounted to the Pt-tip, 5) Electrolyte exposed side of the GDE and approached Pt-tip.
Figure S2. a) Frequency scans of the Pt-tip oscillation magnitude in different media for identification of tip resonant frequencies. b) Shear-force approach curve of the Pt-tip oscillating at 358 kHz during its incremental approach towards the GDE surface by means of a piezo-based positioning system.

It should be pointed out that positioning of nanosensors that close to a converting substrate electrode can lead to a gap between both electrodes in which hydroxide ions could accumulate due to hindered diffusion imposed by the approached tip. In our particular case we measure the flux of solution species in and out of a porous electrode, so that we do not expect a major contribution to diffusional properties by the sensor itself. That would be only a major concern if a flat substrate would have been used.

Local measurement of ion activities during CO$_2$RR at the Ag-GDE substrate

Electrochemical measurements were recorded using a bi-potentiostat (IPS PG 100, IPS Peter Schrems) controlled by an in-house programmed software. Prior to the actual SECM experiment, all cell cables were connected to a digital potentiostat (Gamry Reference 600, Gamry) in order to determine the uncompensated cell resistance $R_u$ by potentiostatic impedance measurements at three representative DC potentials (Table S1). After preconditioning the electrode for 30 s at one of those potentials, impedance spectra were recorded from 100 kHz to 1 Hz with 10 frequencies per decade and an amplitude of 10 mVpp.

The Pt-mesh counter electrode was located in a glass compartment filled with 1 M KOH which was separated from the analyte solution using a Zirfon Perl UTP 500® membrane. The reference electrode was a Ag/AgCl/3 M KCl/1 M KOH double junction electrode. The Ag-GDE and the Pt-tip were connected as working electrode 1 and 2, respectively. Prior to filling the 1 M KOH electrolyte into the SECM cell, dissolved oxygen was removed by purging the electrolyte more than 20 min with Ar outside the cell. Afterwards, a constant Ar flow was maintained above the electrolyte level to minimize re-dissolution of oxygen from the atmosphere. Directly after filling the electrolyte, i.e. after closing the electric circuit of the electrochemical cell, a resting potential of -0.1 V vs. reference was applied to the GDE resulting in a reductive current of a few µA. Once the approach of the Pt-tip to the GDE was completed, a CO$_2$ flow of around 16 ml min$^{-1}$ was maintained through the gas channel behind the GDE using a mass flow controller (Model: GFC17, Aalborg). The CO$_2$ gas outlet tube was immersed into a water-filled gas column until an overpressure of 5 mbar was reached within the CO$_2$ gas channel at the GDE backside.

Cyclic voltammograms (200 mV s$^{-1}$, start and stop potential: 0 V) were continuously recorded at the Pt-tip. Depending on the local pH value in the tip sensing region, the upper and lower vertex potentials were adjusted to avoid excessive OER and HER. In parallel, the GDE-potential was incrementally stepped from the initial resting potential towards more negative potentials, thus increasing stepwise the overpotential for CO$_2$RR / water reduction. The investigated potential window spans -0.8 V down to -1.9 V vs. reference. For each increment multiple CVs were recorded at the Pt-tip electrode until a stabilization of the PtO-reduction peak potential was observed. After probing the highest overpotential at -1.9 V, the GDE potential was stepped back to the initial resting potential with negligible CO$_2$ conversion. This allowed to follow the time-resolved equilibration of local ion fluxes with the conditions in the bulk electrolyte (Fig. 3c).

Calibration of the PtO-reduction peak potential

Immediately after the SECM experiments, a calibration of the PtO-reduction peak potential was performed by recording CVs of the Pt-tip in differently concentrated KOH solutions. Within this measurement series the Pt-tip working electrode as well as the counter and reference electrode from the SECM experiment were immersed into different calibration solutions (1 M, 2 M, 4 M, 8 M, 12 M and 16 M).
and multiple CVs were recorded. All calibration solutions were prepared as a dilution series from a 16 M KOH stock solution. The accuracy of the concentration in the stock solution was confirmed by its titration with oxalic acid dihydrate (p.a., Merck) with phenolphthalein as indicator. An average titer factor of 0.991 was determined in three independent titrations. The averaged PtO-reduction peak potentials depicted in the calibration curve (main paper, Fig. 2) are a result from three independent calibration experiments with different Pt-tips.

**Product analysis by means of gas chromatography**

Potentiostatic CO₂ conversion experiments were coupled to GC chromatographic product analysis using the same electrochemical cell configuration as in the SECM experiment. For that purpose, the CO₂ gas outlet from the GDE backside was directly connected to a 1 ml sample loop inside a gas chromatograph (GC multiple gas analyzer#1, SRI Instruments). Hydrogen in the product stream was quantified by a thermal conductivity detector (TCD), while CO and possible carbonaceous trace products were analyzed using a flame ionization detector (FID) with methanizer. The system was operated with N₂ as the carrier gas (21 psi) and a constant column oven temperature of 90 °C. During each analysis run, the products were separated over a 3-meter HayeSep D column. During the measurement a CO₂ flow of 16.243 ml min⁻¹ (average from 10 flow measurements done with DryCal Mesalabs, Defender Series) was maintained. The electrolyte was purged with Ar for about 30 min and a constant Ar flow was kept above the electrolyte throughout the analysis. Electrochemical conversion of CO₂ was conducted at similar increments of uncompensated potential compared to the SECM experiment, namely from -1 V towards -1.9 V vs. Ag/AgCl/3M KCl. Each potential was applied for a total of 15 min, while in the last 38 s a potentiostatic impedance spectrum (10 mV amplitude, 10 kHz-2 Hz, 3 frequencies per decade) was recorded for determination of $R_u$. In parallel to the potentiostatic conversion at each potential increment, the GC product stream was separated for 6 min. After each analysis run the sample loop was replenished for 1.5 min with new products preparing the next injection onto the separation column. Altogether every sample was injected each 7.5 min allowing 2 individual injections per investigated GDE potential.

**Scanning electron microscopy (SEM) and focused ion beam (FIB) milling of Pt-tip electrodes**

After the Pt-wire was sealed into the center of a quartz glass capillary, the Pt/glass composite is hard-pulled forming long-tapered tips as depicted in Fig. S3a. Due to the nature of the hard-pull process, the resulting electrode consists of a tapered Pt-wire which is still covered by glass at the very apex. Exposing a well-defined Pt-disc requires an opening of the tip. This can be either achieved by in the mechanical way by cutting the glass tip and polishing it on abrasive polishing surfaces such as Al₂O₃ or diamond-based lapping films. The disadvantage of that methodology lies in the unavoidable contamination of the Pt with constituents from the polishing media, as well as inhomogeneity in the Pt-surface due to the comparably large dimension of polishing particles relative to the small Pt-discs. In the presented work, we utilized an alternative strategy of tip opening, which involves FIB milling with Ga ions. As depicted in Fig. S3b and S3c this method produces very smooth Pt/glass surfaces without any detectable contaminations.

**Figure S3.** a) Photograph from an optical microscope (Olympus BX41, MPlan N 10x/0.25 Microscope Objective Lens) showing the laser-pulled Pt/glass composite at the tip region. Due to the coverage of the tip with glass after the laser pulling, the Pt-disc (dark area) inside the quartz glass (bright areas) was exposed by FIB milling. b) SEM micrograph (5000x magnification) showing the total glass/Pt-disc surface at the Pt-tip. c) SEM micrograph using higher magnification (100000x) from the Pt-disc.
Determination of the uncompensated resistance of the electrochemical cell in the SECM experiment

Once the electrochemical cell was assembled in the final cell geometry for the SECM experiment, potentiostatic impedance spectra were recorded at three DC potentials vs. Ag/AgCl/3 M KCl/1 M KOH representative for low (-0.6 V), intermediate (-1.2 V) and high (-1.6 V) electrochemical conversions. The recorded Nyquist plots were analyzed for the real part of the high-frequency (100 kHz) data point of the plot. The uncompensated resistance was used for the post-correction of the IR drop during all investigated GDE potentials.

Table S1. Real and imaginary parts of the high frequency part in Nyquist Plots obtained from potentiostatic impedance measurements on Ag-GDE at different DC potentials (10 mV AC amplitude). Nyquist plots were measured in a frequency range of 100 kHz – 1 Hz recording 10 frequencies per decade.

| DC potential vs. Ag/AgCl/3 M KCl / 1 M KOH [V] | Z’ - high frequency [Ω] | Z” - high frequency [Ω] |
|-----------------------------------------------|--------------------------|--------------------------|
| -0.6                                          | 18.50                    | 2.05                     |
| -1.2                                          | 18.46                    | 1.46                     |
| -1.6                                          | 18.35                    | 0.46                     |

Determination of the uncompensated resistance of the electrochemical cell in the GC coupled experiment with the SECM cell

Similar to the SECM experiments, potentiostatic impedance spectra were recorded for determination of the uncompensated cell resistance. At each investigated potential, impedance data was recorded after measuring 862 s of chronoamperometry at each potential increment. The uncompensated resistance obtained from the high-frequency part of the Nyquist plot was used for post-correction of the IR-drop.

Table S2. Real and imaginary parts of the high frequency part in Nyquist Plots obtained from potentiostatic impedance measurements on Ag-GDE at different DC potentials (10 mV AC amplitude). Nyquist plots were measured in a frequency range of 10 kHz – 2 Hz recording 3 frequencies per decade.

| DC potential vs. Ag/AgCl/3 M KCl/1 M KOH [V] | Z’ - high frequency [Ω] | Z” - high frequency [Ω] |
|-----------------------------------------------|--------------------------|--------------------------|
| -0.6                                          | 12.69                    | 0.66                     |
| -0.8                                          | 12.85                    | 0.65                     |
| -1.0                                          | 14.62                    | 0.65                     |
| -1.2                                          | 14.56                    | 0.61                     |
| -1.3                                          | 14.55                    | 0.52                     |
| -1.35                                         | 14.39                    | 0.53                     |
| -1.4                                          | 14.29                    | 0.54                     |
| -1.45                                         | 14.79                    | 0.56                     |
| -1.50                                         | 14.60                    | 0.54                     |
| -1.55                                         | 13.25                    | 0.48                     |
| -1.60                                         | 12.53                    | 0.47                     |
| -1.65                                         | 13.18                    | 0.48                     |
| -1.70                                         | 11.96                    | 0.43                     |
| -1.75                                         | 11.58                    | 0.43                     |
| -1.80                                         | 11.09                    | 0.42                     |
| -1.85                                         | 10.50                    | 0.44                     |
| -1.90                                         | 10.84                    | 0.46                     |

Headspace and CO₂ gas phase product analysis during CO₂RR over Ag-GDEs

The GC-coupled product analysis of the CO₂ product stream originating from the GDE backside demonstrated total faradaic efficiencies of CO/H₂ far lower than 100 % for the highest investigated overpotentials (Fig. 4 in main paper). Due to the non-confined headspace in the SECM cell, one possible explanation for this observed product loss before detection is the dissolution of products in the electrolyte and their subsequent release into the headspace. We assume that products escaping through the electrolyte mostly consist of H₂ and therefore that FEs observed beyond -1.7 V vs. Ag/AgCl/3M KCl can be extrapolated to 100% with H₂. We confirmed this hypothesis in a control experiment, where the same type of Ag-GDE was mounted into a closeable glass cell which was connected to a 6-way valve in front of the sample loop inlet (Fig S4). N₂ was purged at 16 ml min⁻¹ into the headspace to continuously flush out products towards the 6-way valve. Depending on the handling position of the valve, either the headspace or the CO₂ atmosphere at the GDE backside was flushed into the sample loop of the GC. In this way, contributions from the headspace and the GDE backside were independently sampled for each potential in a separate GC analysis run (6 min duration, 1.5 min sample loop loading). Figure 4a shows the added FEs of top (electrolyte) and bottom (gaseous) compartments. The measurement first of all confirms the trend as displayed in Fig. 4 in
the main manuscript: the H\textsubscript{2} product dominance grows after reaching a potential beyond \textasciitilde -1.5 V vs. Ag/AgCl/3 M KCl, whereas a different cell geometry was used here with an electrode size of over 2 cm\textsuperscript{2}. More importantly, the individual determination of CO/H\textsubscript{2} faradaic efficiencies in the headspace compartment (Fig. S4ba) shows a significant transition of gas products at high CO\textsubscript{2}RR overpotentials into the headspace. This crossover is far more significant for H\textsubscript{2} as compared to CO, which implies that the main missing part of products in the SECM-cell / GC experiment relates to H\textsubscript{2} (Fig. 4, main manuscript). Hence, we assume that a decreased overall efficiency as observed in the open cell measurement is linked to an increase in H\textsubscript{2} production with a subsequent escape of the product. Also, as apparent in Fig. S4c the increased detected product quantity in the headspace is accompanied by an accumulation of large gas bubbles on the GDE surface, which further underlines the observed H\textsubscript{2} dominance in the headspace, but is also explains the lower overall FE at higher overpotentials, since some product quantity is located on the surface and not within the GC gas stream.

![Graphs](image.png)

**Figure S4.** a) Faradaic efficiencies for CO and H\textsubscript{2} detected for the CO\textsubscript{2}RR in a closed glass cell (top and bottom injection). b) FE\textsubscript{s} determined in headspace the head space glass cell. c) Photograph of glass cell while the Ag-GDE was biased at -1.73 V (iR-corrected) vs. Ag/AgCl/3 M KCl. The red circle depicts the GDE/electrolyte interface region where product gases accumulate in form of visible gas bubbles on top of the GDE surface.

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