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The electrode-electrolyte interface in CO₂ reduction and H₂ evolution: a multiscale approach

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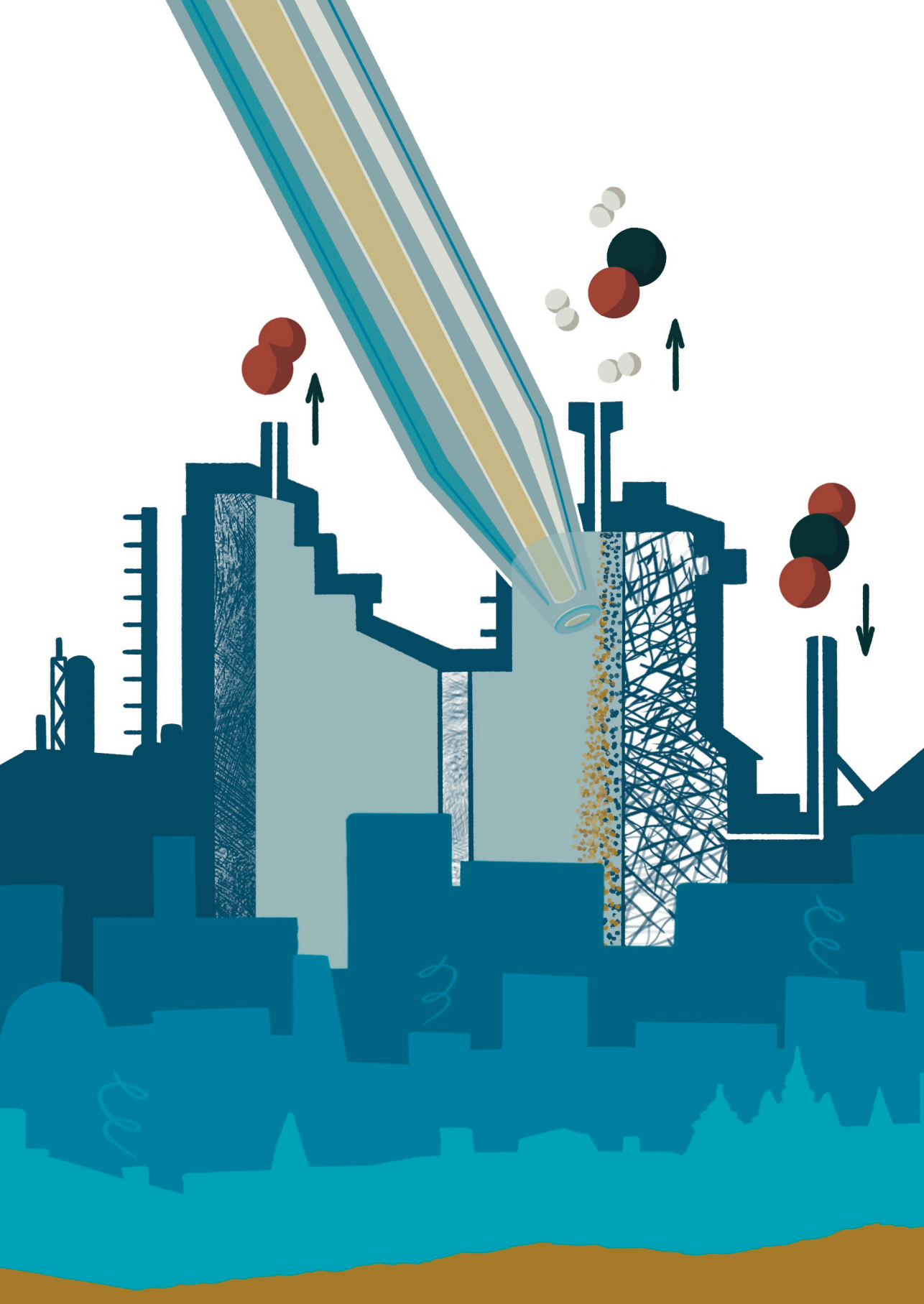
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Probing the local activity of CO_2 reduction on gold gas diffusion electrodes: effect of the catalyst loading and CO_2 pressure

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Abstract

Large scale CO₂ electrolysis can be achieved using gas diffusion electrodes (GDEs), and is an essential step towards broader implementation of carbon capture and utilization strategies. Different variables are known to affect the performance of GDEs. Especially regarding the catalyst loading, there are diverging trends reported in terms of activity and selectivity, e.g. for CO₂ reduction to CO. We have used shear-force based Au nanoelectrode positioning and scanning electrochemical microscopy (SECM) in the surface-generation tip collection mode to evaluate the activity of Au GDEs for CO₂ reduction as a function of catalyst loading and CO₂ back-pressure. Using a Au nanoelectrode, we have locally measured the amount of CO produced along a catalyst loading gradient under operando conditions. We observed that an optimum local loading of catalyst is necessary to achieve high activities. However, this optimum is directly dependent on the CO₂ back-pressure. Our work does not only present a tool to evaluate the activity of GDEs locally, it also allows drawing a more precise picture regarding the effect of catalyst loading and CO₂ back-pressure on their performance.

12.1 Introduction

The electrochemical reduction of CO₂ (CO₂RR) has the potential to replace processes involving fossil fuels for the production of fuels and chemicals. Several studies have been performed to determine how to tune the activity and selectivity towards the various gaseous and liquid products (e.g. CO, HCOO⁻, C₂H₄, CH₄, CH₃CH₂OH) on different catalyst surfaces.^{1,2} However, these studies are often performed at a small scale, using idealized systems. Due to the poor solubility of CO₂ in water, achieving high current densities at conventional electrodes is, among other factors, hindered by CO₂ mass transport.^{3,4} To realize CO₂ electrolysis at more industrially relevant currents, gas diffusion electrodes (GDEs) have been used. GDEs are hence promising, considering potential industrial applications of the CO₂RR.⁵⁻⁹ However, due to the complexity of the reaction itself,¹⁰ the substrate,¹¹ and the electrolyser stack,¹² there is still a lack of understanding on how the GDE performance is affected by different system parameters. Gas diffusion electrodes consist of a porous conducting material with the electrocatalyst being deposited on the surface, which is immersed into the catholyte, while the reactant (CO₂) is fed from the backside, either in a flow-through or flow-by configuration. The reaction happens at 3-phase boundaries formed by the catalyst, the electrolyte, and the gaseous CO₂. This configuration minimizes the depletion of CO₂ at the reaction interface, allowing to operate at higher current densities. Additionally, the porous structure of the GDE needs to be of hydrophobic nature to allow gas transport while preventing electrolyte flooding. Various parameters have been shown to influence the activity of GDEs, such as the catalyst loading, pressure, electrolyte flow rate, reactor geometry, electric resistance, conductivity, wettability of the substrate, among others, and deconvolution of their interrelated effects can be challenging.¹³

For a conventional system in which CO₂ is bubbled into the electrolyte phase, an increased electrochemically active surface area in contact with the electrolyte, would in principle, lead to higher activity assuming sufficient CO₂ mass transport. However, in the case of GDEs, this does not necessarily apply, as not only the catalyst has to be present, but it also has to be simultaneously reached by the CO₂ feed and wetted by the electrolyte. Previous studies on CO₂RR to CO on GDEs have been performed to assess the effect of the catalyst loading on the activity and faradaic efficiency (FE) for CO. Duarte et al. investigated the reaction on 10 cm² Ag-GDEs with catalyst loadings between 0.5 and 2 mg cm⁻².⁶ Their results show little effect of the loading on the reaction selectivity, but an increase in activity was

observed with higher loading. On the other hand, Bhargava et al.⁷ conducted CO₂ electrolysis on 1 cm² Ag-GDEs with catalyst loadings ranging from 0.3 to 3 mg cm⁻². They observed an increase in the CO partial current density with increasing loading up to 1 mg cm⁻², with the highest mass activity as a function of potential being obtained with a loading of 0.3 mg cm⁻². Along the same line, we recently reported on the selectivity and efficiency of CO₂ reduction to CO in acidic media on 10 cm² Au-GDEs with different loadings (Chapter 11).¹⁴ In galvanostatic measurements, we observed slightly improved selectivity for CO with the GDE having lower catalyst loading (1 mg cm⁻²) than the one with higher loading (2 mg cm⁻²). Through scanning electron microscopy (SEM) analysis of the two GDEs, we attributed those differences to agglomerates within the catalyst layer at a loading of 2 mg cm⁻², which prevents access of the reactants to the catalyst nanoparticle surface. These contradicting results show that in-depth knowledge concerning the parameters determining an optimal catalyst loading is not available. Additionally, a systematic comparison becomes difficult as the experimental conditions and fabrication procedures vary from one work to another.

Another approach to improve the activity of GDEs, is to increase the CO₂ pressure at the back of the GDE or the CO₂ flow rate in a flow-through electrolyzer.^{15–17} However, operating at too high CO₂ pressures, with the aim to supply sufficient CO₂ to the whole catalyst surface, can be detrimental to the GDE stability and may lead to flooding.¹⁸ It is important to point out that even though activity and selectivity values are reported as a function of the CO₂ flow rate or pressure and catalyst loading, a comparison between different studies is nearly impossible due to differences of at least some of the experimental conditions. Electrolyzers and GDEs have different sizes, the substrates have different compositions, and there is always limited information about the actual flux of CO₂ reaching the electrocatalyst surface/electrolyte interface. The ability to probe the activity of GDEs *in situ* may contribute to the understanding of the interplay between these parameters as well as the impact of the surface topography, the formation of the 3-phase boundary, and ultimately provide the basis for the optimization of the performance of CO₂RR electrolyzers. Such information cannot be obtained using conventional product detection techniques such as gas/liquid chromatography, mass spectrometry, rotating-ring-disc electrodes (RRDE), due to their lack of spatial resolution and sensitivity. In contrast, scanning probe techniques are powerful tools for investigating activity locally with high resolution.^{19–26} Mayer et al.²² used a Pt ultramicroelectrode (Pt-UME) to detect formate, CO and H₂ during CO₂RR on

Sn/SnO_x arrays. However, here, the tip-to-surface distance was determined using O₂ reduction diffusion limitation, which may mainly practical for probing flat electrodes. Similarly, in Chapter 5 of this thesis, we have used a Pt-UME in the surface-generation tip-collection (SG-TC) mode to detect CO produced during CO₂RR on Au, Cu and Ag electrodes.^{25,26} Although these previous measurements were performed on non-permeable substrates, it has also been demonstrated that probing the local pH during the oxygen reduction reaction (ORR) and CO₂RR on GDEs can be achieved with SECM by shear-force positioning of Pt nanoelectrodes at ~100 nm above the GDE surface.^[23,24] This experimental approach allows for simultaneously deriving modulations of the local pH value in correlation with the current density, and the topography *in situ* and with high resolution.

In this Chapter, we have developed a method using SECM and shear-force positioning to probe the local activity of gas diffusion electrodes under *operando* conditions. We investigate how the catalyst loading and CO₂ back-pressure affect the local activity of Au-GDEs under different applied potentials. For that, we prepared 3 cm² Au-nanoparticles modified GDEs containing different catalyst gradients ranging from low to high loading regions, and we used SECM in the SG-TC mode to probe the activity during CO₂RR to CO. By approaching the surface using shear-force positioning, we are able to map the local CO product fluxes along these Au-catalyst loading gradients at a very short distance of about 100 nm above the GDE surface. The diffusion-limited CO oxidation current is constantly recorded at the positioned Au nanoelectrode while the SECM tip is scanned across the loading gradient. Simultaneously, the applied sample potential and the CO₂ back-pressure are varied, and the interplay between catalyst loading and CO₂ back-pressure is evaluated for optimum operation of GDEs. These measurements and the obtained information opens up pathways towards investigating these systems on a deeper level. This should eventually help to better design and optimize GDEs for CO₂ electrolysis.

12.2 Characterization of the gas diffusion electrodes

To investigate the effect of the catalyst loading on the CO₂RR activity of gas diffusion electrodes (GDEs), we prepared two different GDEs containing loading gradients of 60% Au/C nanoparticles. The Au nanoparticles, with an average diameter of 20 nm (inset Fig. 12.1a), were sprayed on a porous gas diffusion layer using an automated air-brush type spray-coater.^{27,28} Different volumes of the catalyst ink were sprayed along 2 cm of carbon/PTFE GDE surfaces (Fig. 12.2a),

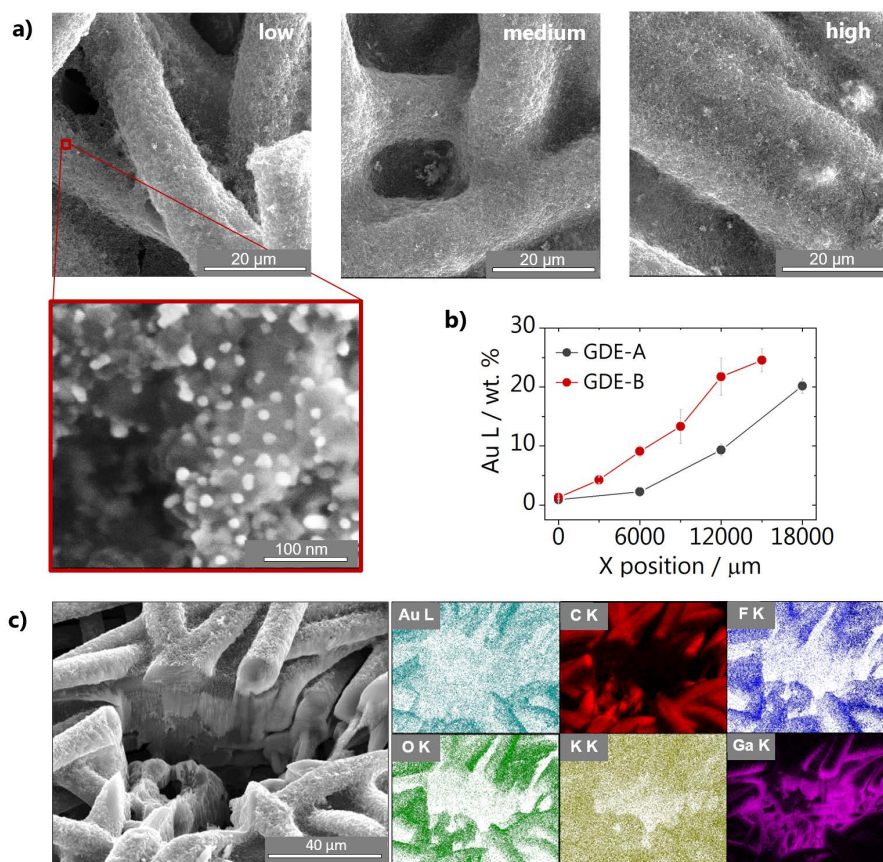


Fig. 12.1. Characterization of the gas diffusion electrodes. **a)** SEM micrographs taken in the low, medium and high loading regions of a Au/C catalyst gradient sprayed on the gas diffusion layer. The zoomed-in image (red box) shows the shape and distribution of the 20 nm particles on the GDE. **b)** Gold weight percentage measured with EDX along the loading gradient showing a shallow (GDE-A) and steep (GDE-B) gradient. Each data point is an average of three measurements around the same X-position, and error bars are the respective standard deviation. **c)** SEM micrograph of the cross-section of GDE-B exposed after milling with a focused ion beam, together with the EDX elemental maps recorded in the same area.

leading to GDE-A, exhibiting a shallow Au/C gradient, and GDE-B, having a steep increase in the amount of Au nanoparticles along the length of the sample. It is important to point out that the substrate used for this work does not contain a microporous layer, so the catalyst ink was applied directly onto the gas diffusion layer. Fig. 12.1a shows SEM images, representative of the different loading regions of the resulting GDEs. At the low loading area, the carbon fibers are not entirely covered by the Au/C nanoparticles. As moving to regions of higher loading, the coverage increases as the shape of the fibers becomes less evident and the gaps between the fibers are filled with the catalyst ink. The volume of catalyst ink dispensed at each spray increment along the length of GDEs A and B indicates the steepness of the two different catalyst gradients (see Fig. I.3; Appendix I). In addition, we characterized the different loading regions using energy dispersive X-rays (EDX) mapping for comparing the amount of Au along the length of the GDEs. The percentage of Au found along GDE-A and GDE-B is displayed in Fig. 12.1b, showing that, as expected, for GDE-B, a higher loading and a faster increase along the gradient is achieved compared with GDE-A. The values are an average of three measurements around a given position. The EDX results are exemplarily shown in Fig. I.4 and Fig. I.5 in Appendix I, together with SEM micrographs of GDE-A and GDE-B at the corresponding positions. Due to the complex morphology of the GDEs, we used focused ion beam (FIB) milling in combination with EDX to evaluate the composition of the GDEs through a cross-sectional cut perpendicular to the surface. Results for GDE-B are shown in Fig. 12.1c, and the SEM image suggests that the GDE exhibits dense areas together with a few long pore-type channels connected throughout the fibers. EDX elemental analysis shows the presence of Au, C, F, O, K, and Ga (which originates from the ion source of the FIB). The majority of the Au/C nanoparticles are located on top of the fibers. As EDX characterization was performed after CO₂ electrolysis in KHCO₃, K is found throughout the whole imaged area. As recently shown by Cofell et al.²⁹, this is due to KHCO₃ deposition due to concentration gradients and increased local alkalinity developed during electrolysis.

12.3 SECM and shear-force positioning

The activity of the GDEs was evaluated in the SG-TC mode of SECM, as schematically shown in Fig. 12.2a. The GDEs were mounted on a specifically designed cell (see experimental details in Appendix I) so that the whole catalyst gradient was in contact with the electrolyte, while CO₂ was constantly fed through the gas channel at the backside of the GDE. A Au nanoelectrode was used to detect

the local amount of CO produced while CO₂RR occurred at the GDE. The Au wire was platinized before it was inserted into the laser puller to improve the adhesion between the Au wire and the insulating quartz capillary to fabricate a well-sealed Au nanoelectrode. SEM micrographs of a Au nanoelectrode with a tip radius of $1.0 \pm 0.02 \mu\text{m}$ are shown in Fig. 12.2b. During the SECM measurements, the tip was brought as close as about 100 nm to the GDE surface at every XY position by performing a shear-force based approach.³⁰ A frequency spectrum and an example of an approach curve, can be seen in Fig. I.6 (Appendix I). A blank voltammogram of the Au nanoelectrode was recorded in the shear-force interaction region before each experiment (Fig. I.7a, Appendix I), showing that at the chosen experimental conditions in CO₂ saturated 1 M KHCO₃ only voltammetric features characteristic of the Au oxide formation, reduction and double layer charging are present.³¹ To assure that applying different potentials to the GDE does not affect the nanoelectrode current and that the catalyst-free GDE is inert, we have also consecutively recorded voltammograms of the Au nanoelectrode in the shear-force interaction distance while stepping the potential at the catalyst-free GDE from -0.6 to -1.4 V vs. Ag/AgCl (Fig. I.7b, Appendix I). We did not observe any CO formation at the catalyst-free GDE, evidenced by the stable double layer charging current in the potential range between -0.25 and 0.6 V vs. Ag/AgCl. To demonstrate that the Au nanoelectrode responds to CO, a calibration gas containing 1 vol. % CO was fed through the back of the GDE for 10 s while a potential of -0.6 V vs. Ag/AgCl was applied to the GDE (Fig. I.6a, Appendix I). Two characteristic anodic current plateaus become visible due to diffusion-limited CO oxidation to CO₂. These two plateaus appear only in a specific alkaline pH range, as shown previously, confirming that they are due to CO oxidation limited by the diffusion of two different species.^{26,32} At more positive potentials, more specifically at 1.2 V vs. Ag/AgCl, the anodic current is due to oxygen evolution. The two voltammetric cycles recorded before the gas mixture was introduced show the difference in magnitude between the double-layer charging and the faradaic current due to CO oxidation. In the next step, we evaluated the voltammetric response of the Au nanoelectrode, which was positioned in the shear-force interaction distance above the GDE, at potentials of -0.6 and -1.2 V vs. Ag/AgCl applied to GDE-A (shallow catalyst gradient) in 1 M KHCO₃ under a CO₂ back pressure of 2 mbar. The voltammograms for the two GDE potentials are shown in Fig. I.8b in Appendix I. At -0.6 V vs. Ag/AgCl applied at the GDE only current

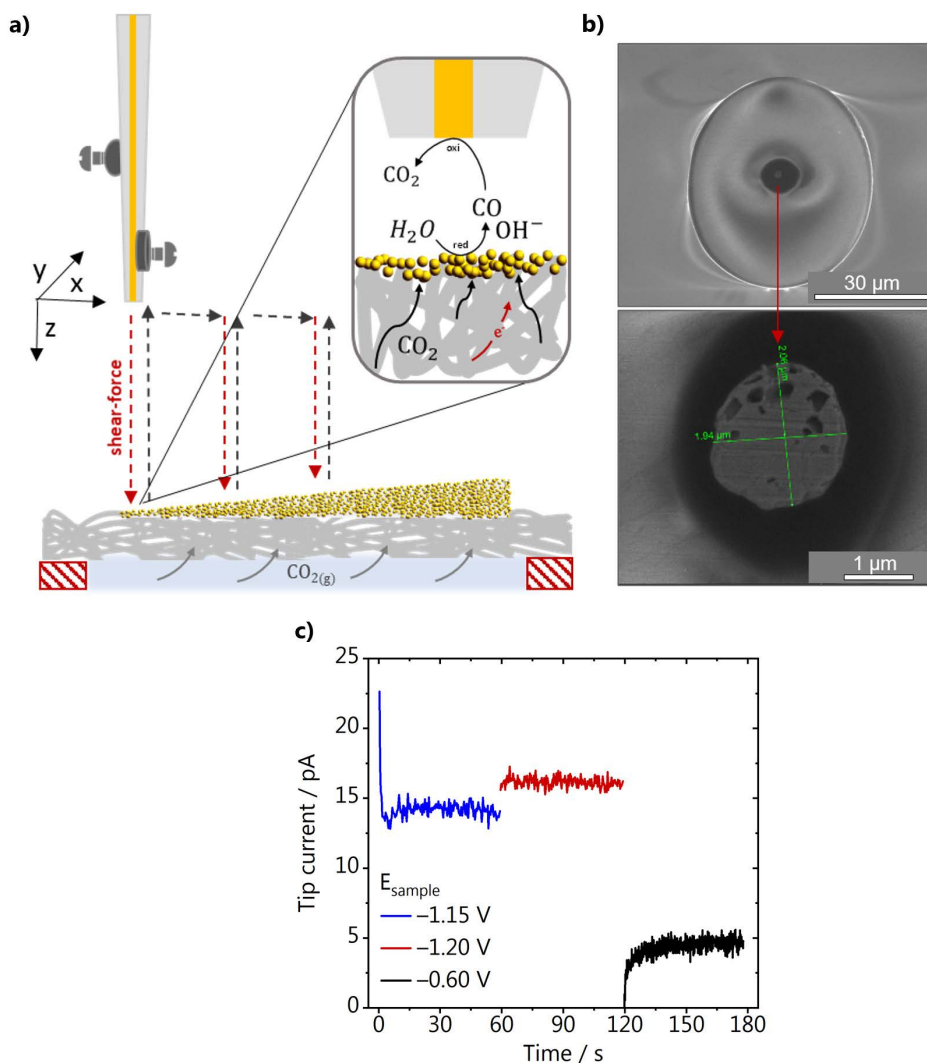


Fig. 12.2. **a)** Schematic representation of the SECM experimental setup, with piezo elements mounted at the Au nanoelectrode tip, approaching a catalyst loading gradient in hopping mode. The SECM is operated in SG-TC mode, as shown in the inset; **b)** SEM micrographs of the gold nanoelectrode; **c)** tip current recorded at a constant potential of 0.19 V vs. Ag/AgCl, upon applying different potentials to the GDE in 1 M CO_2 saturated KHCO_3 .

due to double layer charging is observed at the Au nanoelectrode, whereas at -1.2 V vs. Ag/AgCl a diffusion limited plateau arises. Although the voltammetric features are very similar to the ones observed when using the calibration gas (Fig. I.8a), a distinct shift of the CO oxidation current plateau to more negative potentials is observed due to the concurrent formation of OH^- and an increase in the local alkalinity. The Au nanoelectrode current was recorded at a fixed potential of 0.190 V vs Ag/AgCl during the SECM scans to account for these possible shifts, a potential which is located in the middle of the diffusion-limited CO oxidation plateau. An example of the current that is recorded at the Au nanoelectrode in the shear-force interaction distance during a SECM scan is shown in Fig. 12.2c. Stable diffusion-limited currents increasing from GDE potentials of -1.15 to -1.2 V vs. Ag/AgCl due to the concomitantly increasing amount of CO produced at the GDE are observed. In contrast, when the GDE potential is -0.6 V, the current drops and is only due to the charging of the Au nanoelectrode double layer.

12.4 Effect of the catalyst loading

We have evaluated the amount of CO produced along the catalyst gradients of GDE-A and GDE-B using the diffusion-limited CO oxidation current recorded at the Au nanoelectrode. All SECM experiments were performed in the hopping mode, where at each XY-position, a shear-force approach curve was performed. The Au nanoelectrode current at different GDE potentials was recorded in the shear-force interaction distance (~ 100 nm above the GDE surface), and then the Au nanoelectrode was retracted and moved to a new XY-coordinate (Fig. 12.2a). The average diffusion-limited CO oxidation current recorded at the Au nanoelectrode during 60 s at every X-position and constant Y-position along the GDE is shown for different GDE potentials. Results for GDE-A, at a CO_2 back pressure of 2 mbar, are shown in Fig. 12.3a. We observe that the increase in catalyst loading along the X-direction leads to a nearly linear increase in the amount of CO produced, as the tip current rises from 4 pA (at $X = 0 \mu\text{m}$) to almost 6 pA (at $X = 17000 \mu\text{m}$). However, surprisingly, most of the activity comes from localized hot spots, which are present both in the low and high loading regions of GDE-A. CO hotspots and CO_2 pockets (marked with a yellow and red shade in the SECM array scan, respectively; Fig. 12.3) were detected at certain X-positions where not only relatively higher CO oxidation currents were measured at the Au nanoelectrode, but also constant bubble formation was disturbing the Au nanoelectrode signal. Bubbles were identified due to the signature of the noise they

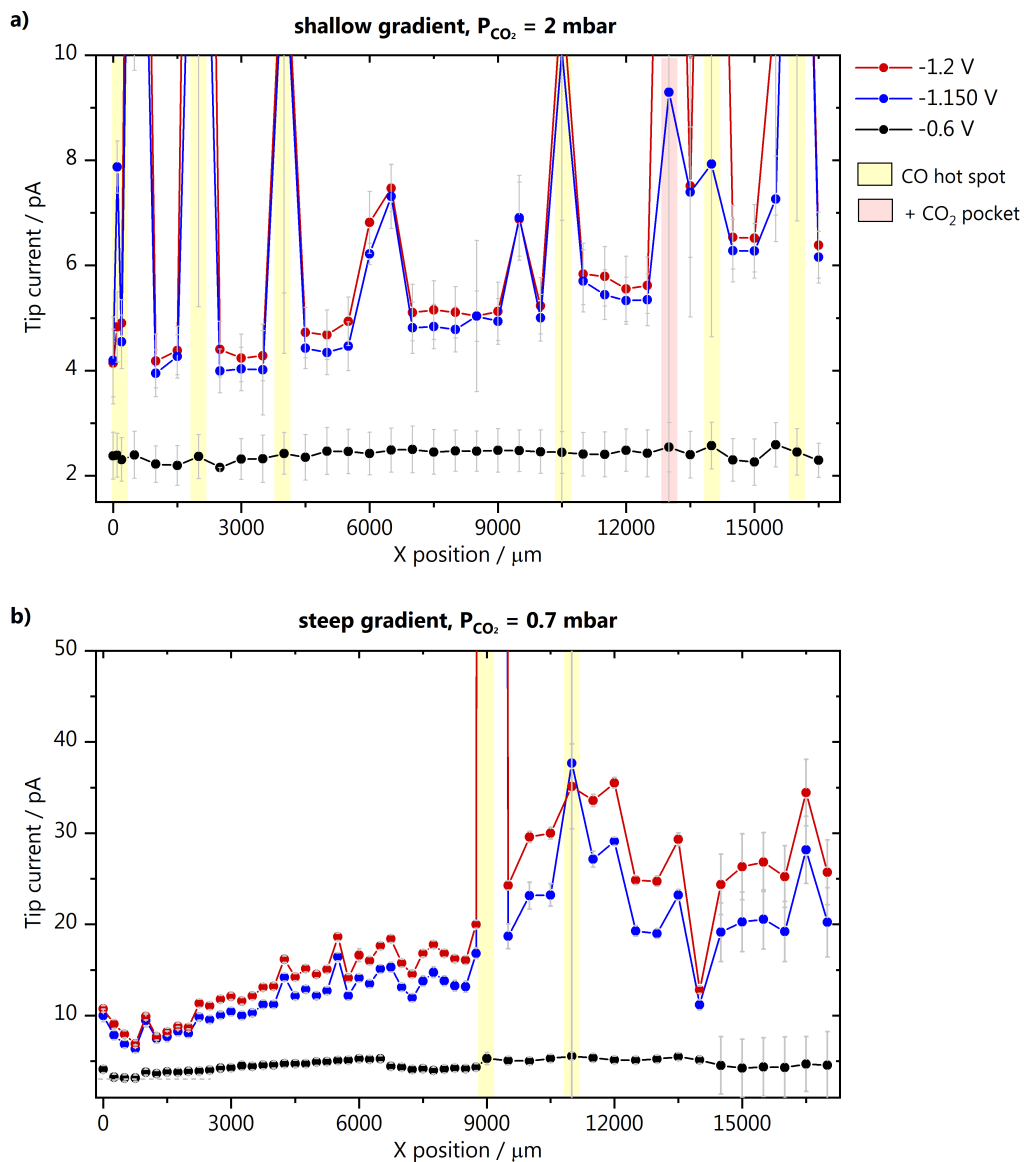


Fig. 12.3. SECM array scans along **a)** the catalyst gradient of GDE-A at a CO₂ back-pressure of 2 mbar, and **b)** the steep gradient of GDE-B at a CO₂ pressure of 0.7 mbar. The potentials applied to the GDEs were -1.2 V (red), -1.15 V (blue) and -0.6 V (black) vs. Ag/AgCl in 1 M KHCO₃ as electrolyte. CO hot spots and CO₂ pockets are marked with a yellow and red shade, respectively.

cause in the Au nanoelectrode current response (see Fig. I.9 in Appendix I). CO hot spots (marked with a yellow shade in the SECM array scan; Fig. 12.3) were identified at positions where the noise in the Au nanoelectrode current was detected upon applying potentials of -1.20 or -1.15 V vs. Ag/AgCl to the GDE. CO₂ pockets are found at positions where even at a potential of -0.6 V vs Ag/AgCl (no CO produced at the GDE), the Au nanoelectrode current was showing the characteristic noise due to bubbles. We observed that every CO₂ pocket was also a CO hot spot, but not every CO hot spot was a CO₂ pocket. The bubble-associated noise was not considered for calculating the average diffusion-limited currents as it is not representative of the CO concentration. Fig. 12.3a zooms in the low current range, and a plot displaying the complete current range is shown in Fig. I.10 in Appendix I. The current at the hotspot locations is up to 5-6 times higher than the maximum current obtained at the other measurement areas of the catalyst gradient. This suggests that at the relatively low catalyst loading along the gradient, the formation of the three-phase boundary within the GDE is more critical to assure high activity than the amount of catalyst on the GDE surface. Additionally, it is important to point out that the pore network and transport properties of the gas diffusion layer may play an important role on the formation of these hot spots. For example, CO can accumulate in the pores near highly active areas of the GDE. These gas-filled pores find the optimal pore system for breaking through and therefore the surface of the GDE where the gas-filled pore network opens to the bulk electrolyte is detected as a hot spot. An example of such a pore system can actually be seen in the FIB cross section depicted in Fig. 12.1c. Despite the complexity of these processes, our measurements show how inhomogeneous the activity is along the gradient and that a higher catalyst loading alone, does not assure high activity.

The activity along GDE-B with a steeper catalyst gradient was also evaluated, however, at a lower CO₂ back pressure of 0.7 mbar (Fig. 12.3b). In general, higher activity is observed in comparison to GDE-A, despite the lower CO₂ pressure. Up to $X = 11000$ μm , a steeper increase in the amount of formed CO is seen, which is in good agreement with the EDX characterization (Fig. 12.1b). In contrast to the results obtained from GDE-A, the activity starts to decrease for GDE-B at $X > 11000$ μm . Due to the lower CO₂ availability and the higher density and thickness of the catalyst layer, it seems that at higher loading, a part of the Au/C nanoparticles is less accessible to the CO₂. At lower backpressure, no CO₂ pockets and nearly no CO hot spots along GDE-B are detected. We have also investigated the relationship between activity and GDE topography to better understand the effect of the CO₂

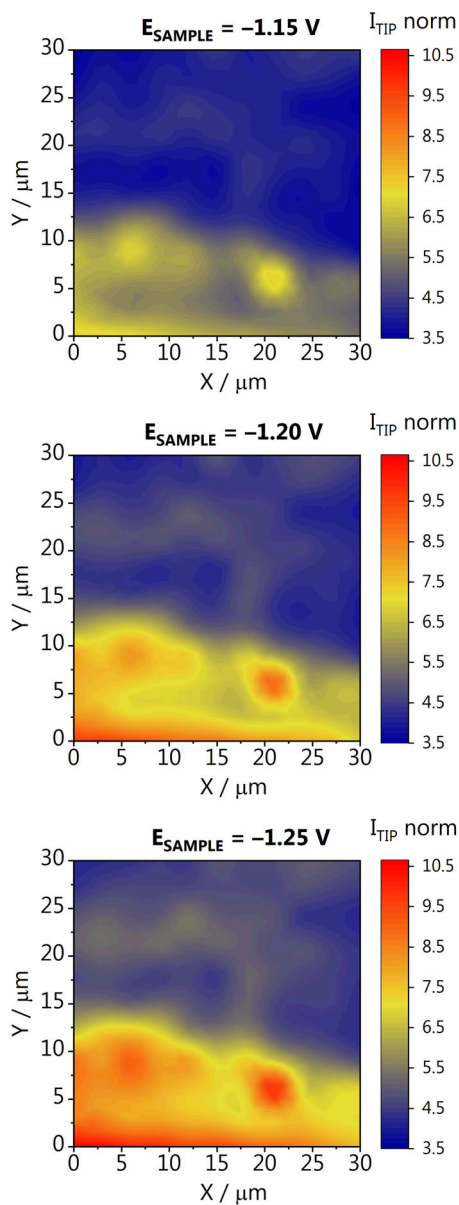


Fig. 12.4. Activity map recorded for GDE-B at a CO_2 back-pressure of 0.7 mbar. The different GDE potentials are reported versus Ag/AgCl in 1 M KHCO_3 . The tip current ($I_{\text{TIP}} \text{ norm}$) is normalized to the double-layer charging current recorded at -0.6 V .

gradient through the gas diffusion layer. A height profile was derived from the absolute Z-position of the shear-force interaction distance of the closest approach of the Au nanoelectrode above the GDE surface. This topography profile is plotted together with the Au nanoelectrode current from Fig. 12.3b at -1.2 V vs. Ag/AgCl (Fig. I.11 in Appendix I). Interestingly, locations where more CO is detected (indicated by red arrows) coincide with lower absolute Z-positions of the Au nanoelectrode. This suggests a CO₂ concentration gradient from the back towards the surface of the GDE, and hence at these lower Z-positions, e.g. above a pore, the local concentration of CO₂ is likely higher, yielding more CO. The same analysis cannot be done for the measurement from Fig. 12.3a (GDE-A), as the large amount of bubbles leads to an uncertainty in the positioning of the Au nanoelectrode over CO₂ pockets and CO hotspots.

12.5 High-resolution activity map

To better understand how localized the hot spots are, and how much the activity can vary within a small area of the GDE, we have recorded activity maps on a $30 \times 30 \mu\text{m}$ area of GDE-B. The origin of the map ($X,Y = 0,0$) corresponds to position $X = 10000 \mu\text{m}$ in Fig. 12.3b within the high activity region along the catalyst concentration gradient. For constructing the activity maps, at each XY position a Z-approach was carried out and the CO oxidation current was recorded at the tip while four different potentials were applied to the GDE (-1.15 , -1.20 , -1.25 and -0.60 V vs. Ag/AgCl). The current determined at each position was normalized to the double-layer charging current recorded at -0.6 V, to account for slight changes of the tip response, which can occur during these long-term measurements (~ 14 h). The activity maps at different GDE potentials are shown in Fig. 12.4, and the data processing in Fig. I.12 in Appendix I. We observe a similar activity trend as for the array scans in Fig. 12.3a and Fig. 12.3b, where more CO is formed at more negative potentials. Interestingly, large differences in activity are observed, demonstrating the inhomogeneity of the lateral response over the GDEs. For example, at position ($X,Y = 0,0$), the activity is seven times higher than at the center of the mapped area ($X,Y = 15,15$). As the catalyst gradient was formed over a much wider length of the GDE (1.7 cm) than the one visualized in the array scan in Fig. 12.4 ($30 \mu\text{m}$), we hypothesize that the detected differences are not due to a difference in the catalyst loading. These differences highlight that apart from a high catalyst loading, it is imperative to supply enough CO₂ and to provide a homogeneous distribution of pores of the GDE accessible for CO₂, in order to form

a three-phase reaction boundary. The used experimental SECM-based strategy allows to spatially resolve inhomogeneous CO₂RR activity, which is a direct result of inhomogeneous three-phase boundary properties within the GDE pore system. Thus, different CO fluxes detected at the Au nanoelectrode are not only a function of catalyst quantity at a given location, but are additionally related to the gas transport of CO₂ through channels below the actual accessible GDE surface as well as the local reaction rate and the concomitant local change in the pH value.

We have marked the region where the activity maps were measured to analyze the morphology-activity relationship of the GDE. After the experiments, GDE-B was marked with a 1.2 mm tip, at two known and safe distances from the area that was mapped (Fig. I.13 in Appendix I). SEM images of the marked GDE area were obtained, and although we cannot assure the location of the specific area of the SECM activity map with a sufficiently small confidence interval, a quite high number of larger pores can be seen in this region. From Fig. I.11 in Appendix I we are confident that the area is very similar to the area selected as shown in Fig. I.13b (Fig. I.13c). Above and in the pores, the concentration of CO₂, and consequently the formed CO, is significantly higher than above the topmost fibers of the GDE. These deeper pores and differences in the pore network are most likely responsible for the significant activity differences shown in Fig. 12.4.

12.6 Effect of the CO₂ pressure

As most results so far point out the importance of CO₂ reaching the wetted catalyst layer, we have also performed an array scan along GDE-B, but now at a CO₂ back-pressure of 4.2 mbar (Fig. 12.3b). This is the highest possible CO₂ pressure at which we could perform SECM measurements without gas bubbles disturbing the electrolyte. Surprisingly, compared to Fig. 12.3b, we see that upon increasing the CO₂ pressure, the activity in the low loading region ($0 < X < 7000$) increases by an order of magnitude (Fig. 12.5). However, here the effect of the catalyst gradient is much less pronounced. Due to the higher back-pressure, more hot spots and CO₂ pockets are formed along the catalyst loading gradient. In contrast to the low loading region, above $X = 7500 \mu\text{m}$ (compare Fig. 12.3b), a large increase in the Au nanoelectrode current is seen reaching a maximum at a higher catalyst loading than at a CO₂ back-pressure of 0.7 mbar. This suggests that a large portion of the catalyst layer is not utilized at lower back-pressure because it is not reached by the reactant. Once the CO₂ pressure is increased, the maximum activity is shifted to a higher

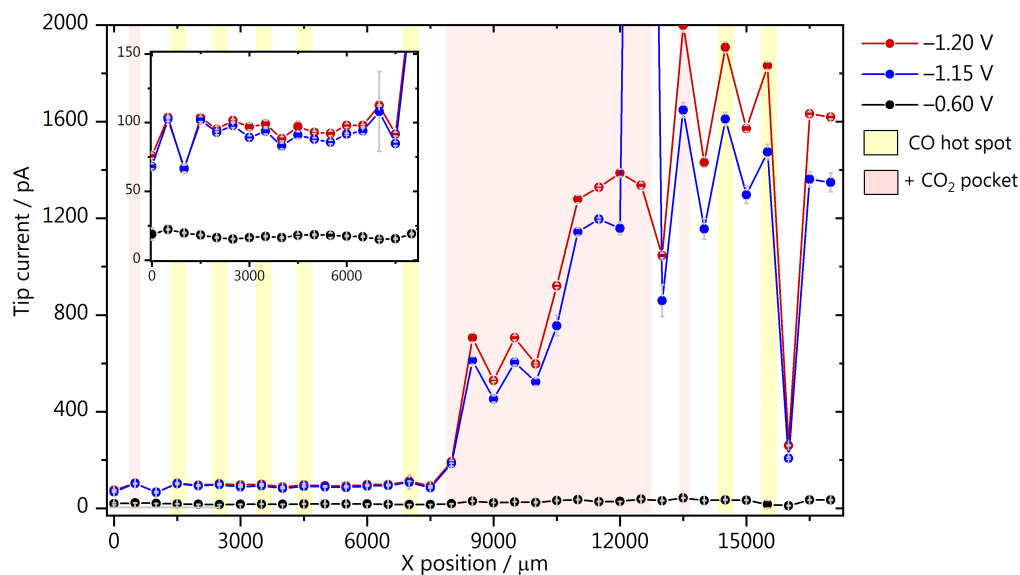


Fig. 12.5. SECM array scans through the catalyst gradient of GDE-B at a CO_2 back-pressure of 4.2 mbar. The applied GDE potentials were -1.2 V (red), -1.15 V (blue) and -0.60 V (black), reported versus Ag/AgCl and measurements were performed in 1 M KHCO_3 . CO hot spots and CO_2 pockets are marked with a yellow and red shade, respectively.

catalyst loading area. If the loading is too high, the surface will be blocked and it will be more difficult for CO_2 to reach the active sites at the catalyst surface.

12.7 Discussion

These results have implications for the design and optimization of GDE-based CO_2 electrolysis systems. We see that overall, higher catalyst loadings lead to higher activity for CO, provided enough CO_2 is supplied. However, we can now also better understand why results in literature show opposing dependencies regarding the relation between local CO_2 R activity and catalyst loading in GDEs. The optimal loading to achieve the highest activity is strongly dependent on the CO_2 back-pressure and the permeability of the gas diffusion substrate (Fig. 12.3b and Fig. 12.5). For example, we previously performed experiments with a large excess of CO_2 , and the GDE with lower catalyst loading exhibited a higher faradaic efficiency for CO.¹⁴ On the other hand, Duarte et al.⁶ observed an increase in CO partial current density with increasing loading but with no effect on the faradaic efficiency. This also points out to the fact that different gas diffusion layers highly differ in terms of how the pore channels are distributed and how permeable and hydrophobic the layer is. All these parameters will play a role and should be tested for and taken into

account when establishing optimum operation conditions for GDEs. Despite the complexity of GDE-based CO₂ electrolyser systems, we have now a tool at hand to go one step further in finding the optimal operation parameters based on the local information which can be attained using the experiments we show here. Even though we could already obtain valuable insights into the effect of catalyst loading on the activity of GDEs, a more systematic study would allow to establish more quantitative system design rules. Additionally, we propose that spray-coating, the currently most used production process for GDEs, may not be ideal in the sense that most of the catalyst particles are located only at the topmost layer of the GDE, where the CO₂ concentration is lowest in a flow-through or flow-by configuration. This suggests that the catalyst particles should be dispersed within the GDE matrix and homogeneously distributed along the electrode cross-section, while still, of course, allowing for electrolyte to percolate. In that way, most of the catalyst will be utilized, and the CO₂ back-pressure can be moderate.

12.8 Conclusions

We have assessed the effect of catalyst loading and CO₂ pressure on the activity of Au GDEs. We used shear-force based Au nanoelectrode positioning, and the SG-TC SECM mode in combination with catalyst loading gradients on the GDE. CO₂ reduction to CO was carried out and the formed CO was detected using the Au nanoelectrode. Our results show that higher catalyst loadings lead to higher activity for CO, provided that enough CO₂ is supplied. We confirm experimentally, that an optimum balance between the available amount of catalyst and the supplied CO₂ is necessary to achieve high activity for CO₂ reduction. Evidently, employing a large amount of catalyst without providing enough CO₂ does not sufficiently utilize the catalyst. The proposed methodology opens up opportunities for probing the activity of GDEs locally in a more controlled manner than using conventional product detection techniques. On top of that, the shear-force positioning used here, allows to directly correlate the activity data with the electrode topography. With that, the influence of other variables on the activity of GDEs can be investigated, such as gas diffusion layer composition and GDE porosity.

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