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

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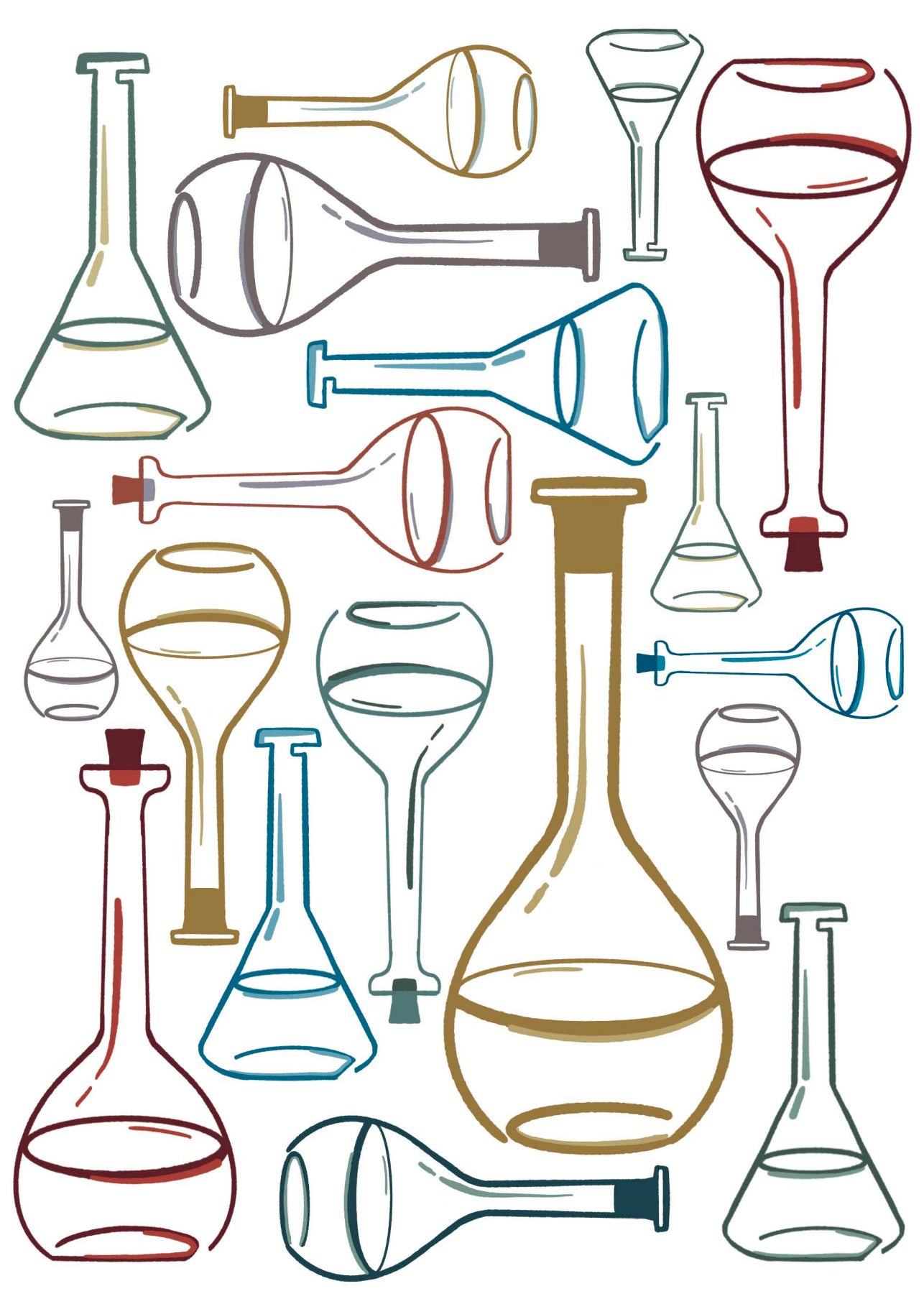
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Summary and Outlook



Summary

Electrocatalysis allows for storing electricity or converting it into chemical bonds, producing chemical building blocks and fuels using renewable resources. Therefore, it plays an important role in the transition towards a more sustainable future for our society through electrification. Still, to bring electrochemical technologies to industrial scale and make them competitive, optimization of various aspects of electrocatalytic reactions are needed. To improve a system, one must first (at least roughly) understand it. Many fundamental studies focus on understanding the catalyst surface, however, different components of the electrolyte, as pH and cations, have also shown to significantly affect the reaction activity and selectivity. In view of that, in this thesis, various aspects of the electrode-electrolyte interface are studied at different scales, using Scanning Electrochemical Microscopy (SECM), stationary and rotating-disc electrode voltammetry techniques, and bulk electrolysis.

During electrocatalytic reactions that consume or produce protons or OH^- , the pH at the electrode surface may differ drastically from the pH in the bulk of the electrolyte. These pH gradients may affect the reaction taking place at the surface and homogeneous reactions taking place in the electrolyte, therefore quantifying them is desired. **Chapter 2** presents a review on different methods to probe pH locally in electrochemistry and highlights SECM as a powerful and versatile technique. In **Chapter 3**, we describe the development of a voltammetric pH sensor based on the 4-hydroxiaminothiophenol/4-nitrosothiophenol (4-HATP/4-NSTP) voltammetry. We apply this sensor to study the local pH developed during hydrogen evolution on gold at different potentials, using SECM. These proof-of-concept experiments show that the 4-HATP/4-NSTP pH sensor is highly selective and sensitive, allowing to measure differences as small as 0.1 pH unit with high time resolution. Thereby, in **Chapter 4** we employed the same pH sensor to also perform SECM local pH measurements during CO_2 reduction. Here, we investigate the diffusion layer dynamics and how the different homogeneous reactions involving CO_2 modulate the local pH. Beyond that, we show through Finite Element Method (FEM) simulations how the SECM tip affects the diffusion of species leading to an additional alkalization of the local reaction environment and discuss ways to avoid that.

In **Chapter 5**, we use SECM to understand the voltammetric features of CO electrooxidation on gold as a function of pH. We probe CO oxidation using a

platinum ultramicroelectrode positioned above an electrode that is reducing CO_2 (therefore locally producing CO). We also perform local pH measurements at the same tip-to-surface position, and the correlation of these two experiments allow to draw a better understanding on the nature of the distinct CO oxidation voltammetric features. Different peaks in the voltammetry appear as a function of the local pH, and are related to CO being oxidized by H_2O or OH^- and the reaction being limited by the diffusion of different species, namely CO or OH^- .

Among the techniques reviewed in Chapter 2, rotating ring-disc electrode (RRDE) is the only one that currently enables local pH measurements to be performed under well-defined mass transport control conditions. However, pH sensors used in combination with RRDE, so far, lacked in temporal resolution, sensitivity, and selectivity. Considering the potential of the 4-HATP/4-NSTP voltammetric pH sensor, in **Chapter 6** we assessed the feasibility of its application to a RRDE system. We show that the 4-HATP/4-NSTP redox couple can be successfully incorporated to a gold ring electrode and we use it to measure the local pH at a gold disc evolving hydrogen. This is successfully done during cyclic voltammetry, chronopotentiometry and chronoamperometry under different rotation rates and potentials, in buffered and unbuffered electrolytes.

In Chapter 7 we investigate a different aspect of the electrochemical interface, namely how surface contamination can affect electrocatalysis. Electrodes must be prepared before they are used for an experiment, and the simplest and most used surface preparation method is polishing. In **Chapter 7**, we show how polishing gold electrodes with alumina paste leads to an enhancement in the hydrogen evolution reaction in acidic media. This is due to the release of Al^{3+} ions in the electrolyte, which promote the water reduction reaction. This should in many cases be avoided, as water reduction competes with various reactions taking place in aqueous media at cathodic potentials, as CO_2 and nitrate reduction.

Apart from the local pH and contamination, ions dissolved in the supporting electrolyte can also strongly affect electrocatalytic reactions. However, the mechanism describing this phenomenon is in many cases still under debate. In **Chapter 8**, we elucidate how metal cations in the electrolyte affect the CO_2 reduction reaction. Through cyclic voltammetry and SECM experiments, we make the remarkable observation that CO_2 reduction to CO happens on gold, copper, and silver electrodes only if a metal cation is added to the electrolyte. By combining the experimental results with density functional theory (DFT) and *ab initio* molecular dynamics simulations, we suggest a new mechanism for the reaction, in which metal cations favor CO_2 adsorption,

and explicitly interact with the CO_2^- reaction intermediate. Furthermore, we see that differences in activity for CO formation among alkali cation species come from the different driving force cations with different hydration energies have to accumulate near the surface. Owing to the complexity of the cation-electrode-reactants interactions, in **Chapter 9** we have extended the study from Chapter 8 to multivalent cationic species. Here, we define which cation properties dictate the activity for CO_2 reduction and for the competing hydrogen evolution reaction at different potentials. We see that electrolytes containing acidic and weakly hydrated cations favor the water reduction reaction, and are therefore detrimental to the activity of CO_2 reduction at high overpotentials. Again, in combination with *ab initio* molecular dynamics, we see that this happens because these species lower the barrier for water dissociation and accumulate more near the surface. Simulations and experiments show that cation acidity is an appropriate activity descriptor and dictates the competition between CO_2 reduction and water reduction. In **Chapter 10**, we look further into the effect alkali cations have on water reduction, as opposite trends as a function of alkali cation identity have been reported for platinum and gold electrodes. We find that weakly hydrated cations (K^+) favor water reduction on gold at low overpotentials (lower alkalinity) while at high overpotentials (more alkaline pH) these are detrimental to the reaction, and higher activity is found using electrolytes containing strongly hydrated cations (Li^+). A similar trend is found for platinum, however this inhibition effect on platinum is already pronounced at lower alkalinity and lower cation concentrations, suggesting that platinum interacts stronger with metal cations in the electrolyte than gold.

The knowledge obtained in the fundamental studies from Chapters 8-10 and in the work of Bondue et al.¹, is transferred to a larger scale device in **Chapter 11**. Normally, CO_2 reduction is performed in neutral to alkaline media, as it is believed CO_2 cannot outcompete proton reduction in acidic media. Nevertheless, in Chapter 11, we show that CO_2 electrolysis can be carried out in acidic media using 10 cm^2 gold gas diffusion electrodes (GDEs). Up to 90% selectivity for CO is obtained at industrially relevant current densities ($50\text{-}200\text{ mA cm}^{-2}$) using a Cs_2SO_4 electrolyte, at pH 2-4. We show that this is comparable to results obtained in similar systems operating in neutral to alkaline conditions, with the advantage that in acidic media we can improve the process energy efficiency by 30%. Additionally, we observe that weakly hydrated cations like Cs^+ or K^+ are essential to run the reaction in acidic

media, as in Li_2SO_4 electrolytes at pH 2-4 nearly no CO is produced, in agreement with the findings from Chapters 8 and 9.

In Chapter 11, we also study the effect of the amount of catalyst applied to the GDE on the activity for CO, by running the reaction in gold GDEs with 1 and 2 mg cm^{-2} catalyst loading. The GDE with 1 mg cm^{-2} shows slightly better performance, but no clear trends can be observed, also not when comparing with similar work in the literature. To address that, in **Chapter 12** we used a system to locally probe the activity of GDEs using SECM with a shear-force based positioning, which also allows to a certain extent, to obtain information about the surface topography. We prepared GDEs having a gradient of gold nanoparticles going from a low to a high loading region. A gold nanoelectrode is used to detect the amount of CO produced along the GDE catalyst gradient. We see that more CO is produced as the loading increases. However, hot spots are found throughout the whole gradient, showing that more important than the amount of catalyst, is how accessible the catalyst particles are to the reactants. We confirm that by measurements at different CO_2 pressures which show that at the highest pressures there is an optimum loading necessary to achieve high activity. Finally, this system opens up a new path for locally probing the activity and topography of GDEs under *operando* conditions and with high spatial resolution.

Outlook

The work presented in this thesis addresses a number of research questions, especially concerning CO_2 reduction and hydrogen evolution, using a multiscale approach. With that, we believe the tools developed to probe local pH and local activity, and the findings on how cations interact at the reaction interface, contribute not only to the existing research in these fields, but to the field of electrocatalysis in general. The following sections present ongoing and future directions for the different topics discussed in this thesis.

Local pH measurements

The pH sensor developed in Chapter 3 and used in Chapters 4-6 showed to be robust enough and its applications can be numerous. Both in the SECM and RRDE configurations, the 4-HATP/4-NSTP functionalized gold electrode can be used to probe local pH during other electrocatalytic reactions as nitrate reduction, oxygen reduction, CO oxidation. It can also be applied, for instance, to monitor the

pH during electrodeposition or corrosion processes. In fact, testing its functionality in these various systems would be beneficial for finding out its limitations. The main advantage of this sensor is the fact that it is just formed by a monolayer of molecules on the gold surface, therefore the response time upon changes in proton concentration is fast. On the other hand, currently, the main drawback of using the 4-HATP/4-NSTP sensor is the instability of the redox couple under current or potential overloads, caused e.g. by bubble formation. This is especially relevant in the RRDE system, and overcoming it should still be addressed, i.e. by applying a hydrophobic coating to the ring-disc spacer.²

Mono- and multivalent cation effects on CO₂ reduction and H₂ evolution

In Chapter 7, we see that layered hydroxides can be deposited on gold upon cycling into hydrogen evolution in a 0.1 M Al₂(SO₄)₃ electrolyte. These materials have various applications, e.g. for: energy storage, dye degradation, organic pollutant degradation, water treatment, photoelectrochemical water splitting and carbon dioxide reduction.³ Conventionally, the synthesis of layered (double) hydroxides is done via co-precipitation (followed by calcination), sol-gel or hydrothermal methods, which are sometimes time consuming and may involve high temperatures and various steps.³ Additionally, the synthesis products may have to be filtered and re-deposited on a support, if the layered hydroxides are to be used as water splitting or CO₂ reduction catalysts. The electrosynthesis of these materials has been reported, but has not yet been well-investigated and understood in detail.⁴ It can present a few advantages for the synthesis of catalysts in comparison to the commonly used methods, as the electrochemically synthesized layered hydroxides can be directly deposited on a conductive support and the synthesis can be done at room temperature.

In Chapter 8 we find that CO₂ reduction to CO does not take place without a metal cation in the electrolyte. We rationalize this with the fact that metal cations explicitly interact with the CO₂⁻ intermediate, thereby stabilizing it. To draw a larger picture on how cations interact with reaction intermediates, it would be interesting to do similar measurements involving other reactions or other CO₂ reduction intermediates. For example, CO₂ or CO reduction to ethylene on copper is proposed to proceed through a CO dimer (negatively charged) intermediate (OCCO⁻).⁵ It is therefore desired to check if ethylene forms from CO/CO₂ reduction in the absence of a metal cation in the electrolyte. As a next step, extending this study to other

reactions, could allow to draw a more general understanding on which reactions/surfaces need a cation to proceed, which do not, and why is that.

Moving on to Chapter 9, we see that 1 mM of multivalent cations as Nd^{3+} added to a Li^+ -containing background electrolyte have an up to 25-fold enhancement effect on the activity for water reduction on gold. Even though these species may deposit on the electrode surface as hydroxides/oxides, the surface is still active and accessible to reactants. It would be interesting to see how this applies to other metal surfaces, as platinum. Also, it will be interesting to test if this strategy can be used to improve the performance of CO_2 or water electrolyzers at larger scale.

Probing cation-surface interactions: Surface X-Ray Diffraction (SXRD)

In Chapter 10, we investigate the effect of alkali cations on the water reduction reaction in alkaline media on platinum and gold electrodes. Previous work from our group has shown that cations and pH play a role in the kinetics of water reduction.^{6,7} The proposed model suggests that increasing the (local) electrolyte pH also increases the concentration of cations near the surface, which promotes water reduction. However, it was also observed that cations start to inhibit H_2 production on gold at too high near-surface cation concentrations (or analogously bulk $\text{pH} \geq 13$), likely by blocking the surface. Despite the many insights gained through cyclic voltammetry experiments, both in Chapter 10 and in the studies of Goyal et al.^{6,7}, we still miss direct experimental evidence on the pH dependence of the cation-surface interactions.

To resolve the structure of the electrochemical interface, we performed *in situ* Surface X-Ray Diffraction (SXRD) experiments at the German Electron Synchrotron (DESY). Several SXRD studies have been performed previously, to determine the electrode-cation distance, as well as cation coverage from specular crystal truncation rod (CTR) measurements.^{8–10} In general, these studies indicate that cations are present at the interface, without being specifically adsorbed. However, the data is far too sparse to obtain a general understanding. Moreover, most measurements were performed at potentials close to the electrode potential of zero charge (PZC). At more negative potentials, the electrode-cation interaction is expected to be stronger, and this potential region is also much more relevant for the electrocatalytic reactions studied in this thesis, and to experimentally confirm the model suggested in the works of Goyal et al.^{6,7} and in Chapter 10. Therefore, we

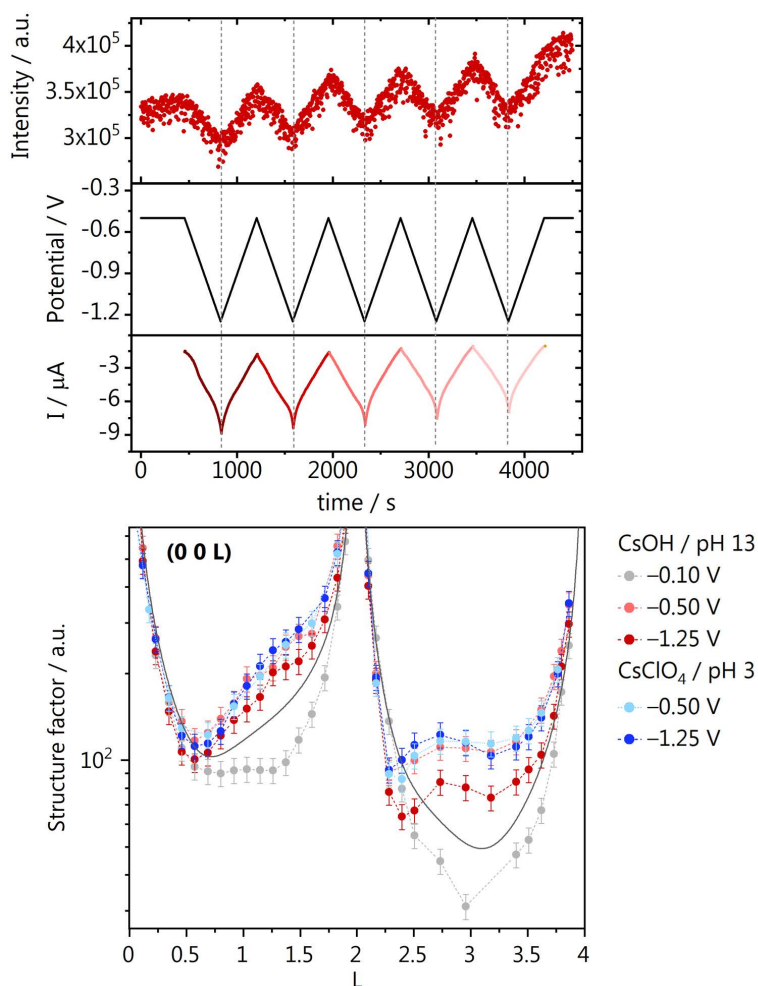


Fig. 1. Specular Crystal Truncation Rods (CTRs) of Au(100) in Cs^+ containing electrolyte: **a)** signal intensity ($L = 0.54$) during a cyclic voltammogram (2 mV s^{-1}) at pH 13; **b)** CTRs measured at different constant potentials (V vs. Ag/AgCl) at pH 3 and 13. The gray line overlapped in the plot represents the simulated CTR of the hexagonally reconstructed Au(100) surface in the absence of cations.

probed the interaction of Cs^+ ions with Au(100) at different negative potentials, both in acidic (CsClO_4 , pH = 3) and alkaline media (CsOH , pH = 13).

From specular CTR measurements during cyclic voltammetry, we see reversible changes in the signal intensity as a function of potential for the hexagonally reconstructed Au(100) in 0.1 M CsOH (pH 13). Such behavior as a function of potential is not present in the absence of cations in the electrolyte, for both the unreconstructed and hexagonally reconstructed Au(100) surface, as

previously shown in the work of Ocko et al. and our own simulations (not shown).¹¹ Furthermore, we observe that Cs^+ interacts stronger with the surface in alkaline than in acidic media (Fig 1b). This is especially visible by the surface-sensitive, low intensity features of the CTRs (at -1.2 V) at $L = 0.5, 1.5, 2.39$. This confirms the model that has been recently proposed⁶, and represents a direct experimental evidence of its validity. We are currently further fitting and analyzing the data, in order to determine the electrode-cation distance as well as cation coverage at the different conditions.

Owing to the success of the SXRD measurements using Au(100), we will soon extend this study to platinum surfaces and other cationic species. Our experimental work shown in Chapter 10 suggests that Pt and Au interact very differently with metal cations in the electrolyte.¹² For both surfaces, weakly hydrated cations (K^+) promote water reduction only at low overpotentials (lower alkalinity) whereas at high overpotentials (higher alkalinity) the higher activity is found using electrolytes containing strongly hydrated cations (Li^+). The difference between Pt and Au is that the inhibition of water reduction on platinum is observed at lower overpotentials and lower pH, suggesting that platinum interacts stronger with metal cations in the electrolyte than gold. The same is also suggested by Density Functional Theory (DFT) calculations, which show that the adsorption potential of alkali cations on Pt(111) and Pt(100) is less negative than on Au(111) and Au(100).¹³ In view of these experimental and theoretical results, we will perform SXRD measurements of Pt(111) and Au(111) in Cs^+ electrolyte, to also compare surface structures (as we previously measured Cs^+ on Au(100), Fig. 1. By systematically defining the experimental conditions, these measurements will enable a direct comparison between the interaction of cations with Au and Pt regarding the electrode-cation distance and cation coverage as a function of cation identity, pH and potential. With these data, we hope to explain the catalytic activity trends from Chapter 10 in more detail and formulate a more general understanding of the role of cations on the electrochemical reactivity of different metal surfaces.

Bridging the gap: assessing the performance of gas diffusion electrodes using scanning probe microscopy techniques

Finally, in Chapter 11, we find that CO_2 reduction to CO can be carried out in acidic media using gold gas diffusion electrodes, with better energy efficiency than in neutral media. It is desired to optimize this process further, by working in more

concentrated electrolytes, and trying to operate at even more acidic pH and higher current densities. Also, assessing the performance of silver catalysts instead of gold, can further help reducing the capital costs. Still regarding gas diffusion electrodes, in Chapter 12 we present a system that allows for systematically probing their local activity using SECM with shear-force positioning. We only looked at the effect of the catalyst loading, but it is desired to also use such a setup to investigate how other parameters define the local GDE performance, by varying for example, the binder composition, and the thickness of the microporous layer. On another hand, shear-forced based SECM alone does not provide accurate topographical resolution, which prevents understanding local GDE structure-activity relationships in detail. This is because the shear-force positioning is very sensitive to disturbances in the reaction environment under technologically relevant operating conditions, such as bubble evolution. Therefore, inspired by the work of Nadappuram et al.¹⁴ it would be interesting to develop a dual-barrel scanning probe microscopy system, combining Scanning Electrochemical Microscopy (SECM) and Scanning Ion Conductance Microscopy (SICM) to simultaneously measure the local GDE activity *in situ*, under *operando* conditions, and obtain the electrode topography with high spatial resolution.

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