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Polycrystalline and single crystal Cu electrodes: influence of experimental conditions on the electrochemical properties in alkaline media

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Abstract

Single- and polycrystalline Cu electrodes serve as model systems for the study of the electroreduction of CO₂, CO and nitrate, or for corrosion studies; even so, there are very few reports combining electrochemical measurements with structural characterization. Herein we investigate both the electrochemical properties of polycrystalline Cu and single crystal Cu(100) electrodes in alkaline solutions (0.1 M KOH and 0.1 M NaOH). We demonstrate that the pre-treatment of the electrodes plays a crucial role in the electrochemical properties of the electrodes. We perform scanning tunneling microscopy, X-ray photo electron spectroscopy and cyclic voltammetry on Cu(100) electrodes prepared under UHV conditions; we show that the electrochemical properties of these atomically well-defined electrodes are distinct from electrodes prepared by other methods. We also highlight the significant role of residual oxygen and electrolyte convection in influencing the electrochemical properties.

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1. Introduction

Over the past half century, fundamental studies of single crystal electrodes have facilitated the investigation of more complex, industrially-relevant high surface area materials.^[1] Monometallic low index (hkl) single crystals (*e.g.*, the face centered cubic (FCC) metal surfaces (111), (110) and (100)) provide atomically flat well-ordered surfaces with a high periodicity of surface atomic structures; they allow the investigation of specific surface sites in a very controlled way.

Electrochemists often deduce the quality of single crystal electrodes on the basis of cyclic voltammetry (CV, which consist of applying a triangular wave potential while recording the current response of the electrode in contact with a supporting electrolyte).^[2] The distinct oxidation and reduction features are characteristic of the experimental conditions, including the pH, electrolyte anions, electrolyte cations, the solvent, the temperature and the presence of defects. As such, electrochemists often use the shape of the CV as a fingerprint of the respective surfaces, acting as a benchmark to compare the quality of different research groups' experiments. They can ultimately be used to explain the electrochemical features observed on more complex three-dimensional catalyst materials.^[1d]

Electrochemists have studied a range of different metal single crystals, including Ag, Au, Pd, Pt, Rh, Ir and Ru.^[3] However, the most intensively studied single crystal system is Pt.^[4] This is partially because nanoparticulate Pt materials constitute the catalyst of choice for the anode and cathode of polymer electrolyte membrane fuel cells.^[5] As far back as 1980, Clavilier demonstrated that Pt single crystals could be prepared by flame annealing in a hydrogen-oxygen flame.^[6] Clavilier's method enabled a whole generation of electrochemists to probe other single crystals than Pt without the need for expensive, ultrahigh vacuum-based equipment for preparing the surface.^[3] Each different Pt surface shows different characteristic peaks, due to the adsorption of hydrogen, $* + \text{H}_2\text{O} + \text{e}^- = *\text{H} + \text{OH}^-$, hydroxyl: $* + \text{OH}^- = *\text{OH} + \text{e}^-$, or oxygen $*\text{OH} + \text{OH}^- = *\text{O} + \text{H}_2\text{O} + \text{e}^-$, or anions such as sulfate $*\text{SO}_4$. Subsequent surface science experiments, based on scanning tunneling microscopy (STM)^[3, 7], low energy electron diffraction (LEED)^[8] and auger electron spectroscopy (AES)^[8c] were able to correlate the CVs to the surface structure. They verified that flame annealing yields highly ordered surfaces. Climent and Feliu have discussed Pt single crystal electrochemistry in detail.^[4] It is not possible to probe adsorbates such as $*\text{H}$, $*\text{OH}$ and $*\text{O}$ on single crystals using in-situ spectroscopy. However, it is possible to conjecture upon the origin of the different voltammetric peaks by comparing the electrochemical data with density functional theory calculations and gas-phase studies of the same adsorbates.^[9] Despite four decades of intense study, the electrochemistry community is still discovering new ways to interpret cyclic voltammograms on Pt single crystals.

In this work, we focus on the electrochemical properties of Cu electrodes under aqueous alkaline conditions. The first fundamental studies in this area date back to the beginning of last century^[10]. This research field has gained an increased importance over the last few decades, due to the potential application of Cu as catalyst material for the electroreduction of nitrate,^[11] carbon dioxide or carbon monoxide.^[12] Scientists have also considered it as a potential candidate as coating material in nuclear waste storage containers.^[13] Experiments show that under alkaline conditions, the oxidation/reduction (including electrode restructuring and corrosion) rate^[14] and the electrocatalytic properties of Cu electrodes^[12d, 15] strongly depend on the crystallographic orientation of the surface. Several other investigations report analogous findings on Cu, albeit in neutral and acidic aqueous environment.^[12a, d, 16]

Despite this apparently pronounced structural dependence, only a few reports are dedicated to the detailed elucidation of the cyclic voltammetry of different Cu single crystal electrodes (Cu(hkl)). Unlike Pt, there are no characteristic peaks for *H formation at any pH. In acid, the current density in the hydrogen evolution region is dependent on the crystal orientation.^[16e] Furthermore, the voltammetric features depend on the anion, such as Cl⁻, Br⁻, I⁻ or SO₄²⁻, in the electrolyte.^[17] Distinct voltammetric features are also observed for metal under potential deposition (upd) on Cu(hkl) electrodes, such as Pb_{upd}^[16e, 18] and Th_{upd}^[19]. In neutral solution, the displacement of phosphate anions by CO yields voltammetric desorption features, which are correlated to the coverage of CO at step sites.^[16b] A great number of Cu single crystal studies have been performed in alkaline solution. In alkaline media, several papers report that the features associated with the oxidation of the surface, i.e., the formation of *O and/or *OH, subsurface oxides, bulk oxides and dissolution, are structure sensitive.^[20] Even so, these features vary significantly between the different studies on Cu (hkl) electrodes. This is exemplarily shown in Fig. 1 for CVs of Cu(100) electrodes recorded in alkaline over the last four decades. While most studies show a distinct redox peak at around -0.15 V, the peak number, shape and size at potentials larger 0.30 V vary significantly. As such — in contrast to the situation on Pt single crystals — it is currently challenging to interpret the CV as a measure of quality of the single crystal preparation. The reasons for these discrepancies between the studies could be due to oxide contamination from exposure to air or water, which cannot be avoided when working under laboratory conditions.^[21] Furthermore, the different preparation procedures employed (see Table 1) do not allow for (i) the complete removal of the native oxide layer^[21a] from the Cu surface and (ii) leveling of the surfaces to atomic flatness. The most common approach to remove the native oxide film is a pre-treatment by mechanical polishing and/or chemical etching in acid solutions. In order to level the surface, the most common approach is electropolishing, originally introduced as a method to smoothen rough metal surface.^[22] Several authors have posited that the electropolishing procedure

requires a pre-treatment step, such as mechanical polishing, to ensure adequate polishing quality.^[22] Whether or not this approach is applicable to obtain well-ordered surfaces on single crystal electrodes has so far not been explored in detail. We anticipate that the different pre-treatments and *in situ* reduction of oxides could lead to the formation of defect sites, which would significantly alter the reactivity of a single crystal electrode. Detailed studies relating the surface structure of Cu(hkl) electrodes with electrochemical properties derived from a CV are scarce. Only a limited number of surface science techniques are available under ambient conditions to determine the structural properties of electrodes. The most commonly employed technique is *in situ* STM^[23] and eventually *in situ* atomic force microscopy (AFM).^[24] Only a limited number of publications show both surface characterization by STM and electrochemical characterization in alkaline in combination with cyclic voltammetry.^[23d, e, 25] This is, however, a prerequisite to assign structural properties to the observed electrochemical response in the CVs, as described above for Pt single crystal electrodes.

The abovementioned issues complicate the interpretation (i) of the CVs of polycrystalline Cu electrodes^[20a, 26] and (ii) more importantly of electrocatalytic tests on Cu single crystals, in particular for CO and CO₂ reduction, where electrodes are typically electropolished. It is unclear whether disparities between single crystal studies are due to (i) different test methods employed, particularly in relation to product detection, or (ii) the quality of the preparation method: studies on polycrystalline Cu show that the CO and CO₂ reduction activity are strongly dependent on the pre-treatment.^[27]

Herein, we present a qualitative description of the electrochemical features of the CVs of polycrystalline and Cu(100) single crystals in 0.1 M KOH or 0.1 M NaOH. We will show and discuss the effect of different pre-treatments available in conventional laboratories. Furthermore, we will report, for the first time, the features observed in the CVs on Cu(100) electrodes in alkaline media, which have been prepared under UHV conditions. We will show that this much less common approach to prepare single crystal electrodes is mandatory to obtain Cu electrodes with a much more defined surface structure. We will discuss these results in the context of the literature on the electrochemical properties of Cu(hkl) electrodes prepared by different pre-treatments, other than UHV. We will characterise the surfaces under UHV conditions, prior to the electrochemical characterization: we shall determine the structural properties with STM and the cleanliness of the samples with XPS. By employing a hanging meniscus cell and a flow cell we were able to elucidate the influence of trace amounts of oxygen in the electrolyte and the experimental conditions. On the basis of our results, we analyse other reports in the literature on Cu electrodes investigated under alkaline conditions without additional anions or cations.

Fig. 1: Cyclic voltammograms of Cu(100) recorded in alkaline media from the literature. Electrolytes and scan rates are indicated in the respective sub-figures. The CVs are adapted from several publications since 1980. The potentials are rescaled to the RHE scale for comparison. The CVs were extracted from the work by a) Droog and Schlenter^[20a], b) Jović and Jović from 2002^[20c] and 2003^[20b], c) Kunze *et al.*^[23d], d) Schouten *et al.*^[20d], e) Huang *et al.*^[28], and f) Le Duff *et al.*^[29]

Ref.	Year	Cu(hkl)	Electrolyte	Preparation procedure
[28]	2017	Cu(111), Cu(110), Cu(100)	0.1 M KOH	1. MP in alumina slurries (0.3 μm , Struers) 2. EP in a solution of $\text{H}_3\text{PO}_4\text{:H}_2\text{SO}_4\text{:H}_2\text{O}$ (130:120:60) at +2 $\text{A}\cdot\text{cm}^{-2}$, $t = 1$ s 3. Rinsed in H_2O and 0.1 M HClO_4
[29]	2017	Cu(111), Cu(100)	0.1 M KOH	1. EP in 66% H_3PO_4 at +2 V. 2. Rinsing with water.
[23g]	2016	Cu(111), Cu(110), Cu(100)	0.1 M KOH	1. MP with suspension of polycrystalline diamond (0.05 μm) 2. EP in 85% H_3PO_4 at 2.0 V for 10 s with a Pt CE 3. Ultrasonicated and rinsed in deaerated water
[23h]	2016	Cu(100)	0.1 M KOH	1. MP (procedure not specified) 2. EP in 85% H_3PO_4 at 2.1 V for 10 s with a 99.8% pure graphite rod as CE 3. Pre-reduction at -0.9 V (SHE) in 0.1 M KOH for 2 h
[14]	2014	Cu(111), Cu(110), Cu(100)	0.1 M KOH	1. MP on a grain paper (<10 μm) 2. MP by water-MgO suspension (<1 μm) on suede. 3. Chemical polishing in a mixture of concentrated nitric, phosphoric, and acetic acids (1:1:1 by volume) 4. Rinsing with water
[20d]	2013	Cu(111), Cu(110), Cu(100), Cu(322), Cu(911)	0.1 M KOH	1. EP in 66% H_3PO_4 at 3 V with a Cu CE for 10 s 2. Rinsed with water
[25]	2003	Cu(111)	0.01 M NaOH	1. MP with Al_2O_3 powder 2. EP in $\text{HNO}_3/\text{CH}_3\text{OH}$ (3:7) at 1.8 $\text{A}\cdot\text{cm}^{-2}$ for 3 min at RT
[20b, c]	2002 & 2003	Cu(111), Cu(100)	0.1 M NaOH	1. MP on fine grade emery papers (1200, 2400 and 4000) 2. MP on polishing clothes with a suspension of polishing alumina (1 μm , 0.3 μm and 0.05 μm) 3. EP in H_3PO_4 (85%) at 1.7 V with a Pt CE until current density dropped to a value of 10 $\text{mA}\cdot\text{cm}^{-2}$ 4. Rinsed with water 5. Cleaned for 30 s in 10 vol% H_2SO_4 and rinsed with water
[30]	2002	Cu(111)	0.1 M NaOH	1. MP with alumina paste 2. EP in 60% H_3PO_4 supersaturated with Cu^{2+} at 1.4 to 1.6 V with a Cu CE at $j = 40\text{--}60$ $\text{mA}\cdot\text{cm}^{-2}$ for 2 min.
[23a-f]	1999 to 2004	Cu(111), Cu(100)	0.1 M NaOH	1. MP with diamond spray 0.25 mm grading 2. EP in 60% H_3PO_4 at 1.80 V with a Cu CE for $t = 5\text{--}10$ min at RT 3. Annealed at 1000 K for 16 h in ultra-pure (6 N) hydrogen
[31]	1995	Cu(111)	0.1 M NaOH	1. MP with 0.5 μm with Al_2O_3 2. EP in mixture of 130 ml H_3PO_4 (85%), 20 ml H_2SO_4 95%, 60 ml H_2O , for 3 min at 2.5 V, with $j = 2.8$ $\text{A}\cdot\text{cm}^{-2}$, $T < 10^\circ\text{C}$, in stirred solution 3. Heating for 3 h at 600°C in a N_2 stream (heating/cooling rates $70^\circ\text{C min}^{-1}$)
[24]	1995	Cu(111), Cu(100)	0.1 M NaOH	1. MP Al_2O_3 powder 2. EP in mixture of $\text{HNO}_3/\text{CH}_3\text{OH}$ (3:7) for 10 min
[20a]	1980	Cu(111), Cu(110), Cu(100)	1 M KOH	1. MP with carborundum paper and polished with diamond pastes (6 - 0.25 μm) 2. EP in a mixture Methanol/ HNO_3 (65%) (ratio 2:1) at 0°C

Table 1: Summary of experimental conditions to prepare Cu(hkl) surface over the last decades for studies in alkaline. MP = mechanical polishing, EP = electropolishing.

2. Results and Discussion

2.1. Influence of pre-treatment

It is well known that different crystallographic orientations of Cu electrodes, show distinctly different redox features in a potential range starting from ca. -0.25 V up to ca. 0.5 V in alkaline.^[20a, 26a, 32] This potential region refers to the initial oxidation of Cu (total transfer of electrons per surface atom is less than or equal to one, *e.g.*, formation of an *OH adlayer). In order to demonstrate the influence of different pre-treatments on the crystallographic orientation of Cu electrodes, we show first results on different polycrystalline Cu (Cu(poly)) and second on Cu(100) electrodes. The CVs of selected Cu(poly) electrodes are depicted in Fig. 2 a) to h), where the preparation procedures and electrode materials are indicated in the respective Figures and the Figure Caption. A description of the preparation procedures can be found in the experimental Section 5. The large number of different peaks observed in this potential region suggests that the crystallographic orientation of each of these samples is to some extent unique. Even two foils with the same specifications and the same supplier, but from different batches, can yield a distinct voltammetric feature, as shown in Fig. 2 a) and b). Both electrodes were pre-treated by electropolishing. Second, pre-treating the Cu foil B by radio frequency heating in a H₂ stream (Fig. 2 c)) changes the crystallographic orientation of the Cu foil B in comparison to the Cu foil B prepared by electro polishing (Fig. 2 b)). Sequential pre-treatment by applying first electro polishing and then radio frequency heating (Fig. 2 d)), and *vice versa* (Fig. 2 e)), also leads to a change in crystallographic orientation compared to the electrode prepared only by electro polishing. However, we observe that on the radio frequency heated and then electropolished sample (Fig. 2 e)) the features of the originally radio frequency heated sample become more pronounced upon electro polishing. This indicates that the electro polishing procedure is sensitive to the initial crystallographic orientation of the electrode surface. Finally, a mechanically polished Cu(poly) electrode cannot be distinguished from a mechanically polished Cu(100) single crystal (compare Fig. 2 g) and h)). We attribute the similar features by the fact that the surfaces have a similar surface structure, obtained by the same polishing agent in both cases.

Fig. 2: CVs of region II (-0.20 to 0.50 V) recorded on various Cu electrodes exposed to different pre-treatments in 0.1 M KOH at a scan rate of 50 mV s⁻¹ in a flow cell set-up under stagnant conditions. The CVs of the following electrodes are shown a) electropolished Cu foil A, b) electropolished Cu foil B, c) radio frequency heated Cu foil B, d) electropolished and subsequently radio frequency heated Cu foil B, e) radio frequency heated and subsequently electropolished Cu foil B, f) Cu(poly) sample prepared under UHV conditions, g) mechanically polished Cu foil B and h) mechanically polished Cu(100).

For Cu(hkl) single crystals also a large number of different pre-treatments were tested and reported in the literature. Table 1 summarizes the preparation procedures for Cu(hkl) surfaces which have been investigated in alkaline. A comparison of representative CVs in alkaline reported since 1980 for Cu(100) electrodes is presented in Fig. 1. We observed that the CVs differ strongly in the potential region > 0.30 V. To compare the influence of different pre-treatments on the voltammetric features in more detail, we pre-treated Cu(100) electrodes by different commonly employed pre-treatments under laboratory conditions. A representative selection of CVs is presented in Fig. 3 (solid lines). These comprise in a) an as received electrode from the supplier that is electropolished for 10 s (pre-treatment according to Reference [20d, 29]), in b) an electrode exposed to air for 30 days that is electropolished for 90 s (EP pre-treatment according to Reference [26b]) and in c) a MP electrode that is subsequently EP for 90 s (pre-treatment based on References [20b, c, 23g, h, 24-25, 28, 30, 32a]). These CVs are compared with the CV of a Cu(001) electrode prepared under UHV conditions (Cu(100)-UHV, dashed line). A more detailed description of the latter is presented in Fig. 4 and described further below. The CVs of all electrodes show redox peaks at around -0.15 V and between 0.35 V and 0.50 V, in agreement with the CVs presented in Fig. 1. The redox peaks at -0.15 V vary slightly in size depending on the pre-treatment. The size, position and number of peaks at higher potentials (0.35 V and 0.50 V), however, depend strongly on the pre-treatment. In detail, Cu(100)-UHV shows a single large peak at around 0.47 V. The mechanically polished and subsequently electropolished electrode also has a single redox

feature at 0.47 V. The reduction peak is, however, shifted to lower potentials compared to the Cu(100)-UHV electrode. The two electrodes which have been electropolished show a broad shoulder/peak between 0.25 V and 0.45 V, which is more pronounced for the electrode kept in air for 30 days. Further CVs that were recorded on Cu(100) electrodes which were electropolished multiple times during one day of measurements, different electropolishing times or on consecutive days, showed similar features compared to those depicted in Fig. 1 and Fig. 3 a) and b) (not shown). It has to be noted that different O_2 concentrations in the cell in the different experiments can influence the absolute current densities of the peak at 0.47 V (see below in Section 2.2).

Fig. 3: Comparison of the CV recorded on a Cu(100) electrode prepared under UHV conditions (dashed line) with a) an electropolished as received Cu(100) electrode from the supplier, b) a 90 s electropolished Cu(100) electrode after storage in air for 30 days and c) a 90 s electropolished Cu(100) electrode after mechanical polishing. All CVs are recorded in 0.1 M KOH and at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$.

Next, we report in detail on the structural and electrochemical properties of Cu(100)-UHV electrodes. In Fig. 4 the XPS survey spectrum as well as an STM image of such an electrode is shown. The XPS indicates that the surface was free of the contamination (inadequate UHV-based preparation yields oxygen, carbon and argon contamination). Recall that XPS measurements were performed on different set-ups than samples investigated by STM experiments (see experimental Section 5). The

surface depicted in the STM image in the inset exhibits large atomically flat terraces extending over several hundred nm, which are separated from other terraces with steps of monoatomic height. The atomically resolved STM image (top left corner of the large scale STM image) shows the quadratic arrangement of the surface Cu atoms for the (100) surface; these images provide no indications of contamination at an atomic scale. The quality of the surface structure of the Cu(100)-UHV electrode, in terms of terrace size and step density, compares favourably with epitaxially grown Cu(hkl) electrodes^[33] and Cu(100) electrodes pre-treated under laboratory conditions and investigated with *in situ* STM.^[23c, d, g]

Fig. 4: Different characterization methods employed to characterize Cu(100)-UHV electrodes. a) XPS survey spectrum recorded and in the inset a large scale and atomically resolved STM image with sizes of 700 nm x 700 nm and 4 nm x 4 nm, respectively (Recorded with $I_T = 1$ nA, $U_T = 0.1$ V and $I_T = 0.6$ nA, $U_T = 0.2$ V, respectively). b) First cyclic voltammograms starting at -0.20 V, after the linear sweep from OCP to -0.20 V, recorded in 0.1 M KOH (labels **1-3**) and 0.1 M NaOH (label **4**) at a scan rate of 50 mV·s⁻¹. The CV labeled **1** was recorded in the hanging meniscus cell, where CVs labeled **2-4** were recorded in the flow cell set-up under stagnant conditions.

Subsequent to the STM or XPS characterization, the electrodes were transferred under well-defined conditions (without exposure to air) to an electrochemical cell (flow or hanging meniscus cell), as described in Section 5. Fig. 4 shows the first CVs starting from -0.20 V of a selection of Cu(100) electrodes recorded in 0.1 M KOH (labels **1-3**) and 0.1 M NaOH (label **4**), between -0.20 V and 0.50 V. All CVs were taken under stagnant conditions. CV **1** has been recorded in the hanging meniscus cell. CVs **2-4** were recorded in the flow cell. CV **2** (recorded in 0.1 M KOH) is also shown with varying upper potential limit. The CVs in both electrolytes show redox peaks at around -0.15 V and 0.47 V. The reduction peak at 0.47 V consists, in most cases, of two peaks, both of which vary in intensity. In the anodic (cathodic) scan, a faint shoulder is observed just negative (positive) of the peak at 0.47 V. We attribute this feature to a small amount of defects on the Cu(100) surface, since we observed a similar feature on polycrystalline electrodes, as shown in Fig. 2. STM is a local probe and XPS measurements

do not provide any structural information; as such, we are unable to quantify the aggregate amount of defects across the entire electrode surface, prior to the electrochemical measurements.

Variation of the upper potential limit (between 0.20 V and 0.50 V in steps of 0.05 V) has no influence on the size and shape of the redox peak at -0.15 V, both in 0.1 M KOH and 0.1 M NaOH (variation of the potential limit is only shown for an electrode investigated in 0.1 M KOH). On the other hand, the intensity of the peak at 0.47 V varies significantly from one experiment to another, which we will discuss in more detail in Section 2.2. Furthermore, we generally observed larger current densities using the hanging meniscus cell, in comparison to the flow cell, especially for the peak at around -0.15 V. One possibility could be that the Cu(100) surface prepared in the UHV-STM set-up is more ordered in comparison to the preparation in the UHV-XPS set-up. A second plausible explanation could, however, be that we overestimate the geometric area for the flow cell set-up, leading to lower apparent current densities in the flow cell system (see experimental part). Finally it is also possible that the rather soft Cu electrodes are prone to mechanical deformation when pressed on the flow cell. Better insights into this observation, could be gained from additional measurements on different cells and eventually different Cu(100) electrodes.

The shape of the CVs recorded in 0.1 M KOH are identical to those reported in 0.1 M NaOH. Consequently, we consider it appropriate to directly compare CVs taken in KOH to those taken in NaOH. Even so, the type of cation may still play a crucial role in catalytic reactions performed on these electrodes.^[34] In total, the main difference between the CVs of Cu(100)-UHV electrodes and Cu(100) electrodes pre-treated under laboratory conditions is, that the Cu(100)-UHV electrodes show less/no features in the potential range between 0.3 V to 0.45 V.

The electrodes prepared by different pre-treatments also show distinct features during the first reduction cycles, which were recorded from the open circuit potential (see Fig. 5). In Fig. 5 a) and b) we compare the Cu(100)-UHV electrodes investigated in the hanging meniscus cell under stagnant conditions and the flow cell under flow conditions, respectively. In the hanging meniscus cell, only a narrow reduction peak at 0.47 V is observed (see Fig. 4 b)). In the flow cell, a single broad reduction peak is observed with a maximum at around 0.30 V. While we have shown above that the CV of Cu(100) shows a reduction peak at 0.47 V, the peak in the first reduction scan is much larger. This is caused by continuous oxidation of the surface while holding the sample at OCP before the measurement is started (see Experimental Section 5), in agreement with literature findings.^[35] In the hanging meniscus cell, the measurement starts almost immediately after the formation of the meniscus, thus surface oxidation is almost not observed at OCP. In the flow cell set-up, the first reduction peak is larger since the time in between flowing electrolyte and starting the measurement

is longer. The first reduction cycles of the electropolished samples investigated in the flow cell are shown in Fig. 5 c). Electrodes which are electropolished without any pre-treatment show two reduction peaks at 0.30 V and 0.10 V. The peak at around 0.30 V has a similar magnitude compared to the one observed on the Cu(100)-UHV electrodes in Fig. 5 b). The additional reduction peak at 0.10 V varies in size. Interestingly, the largest peak at 0.10 V has been observed for the sample left in air for 30 days (see Fig. 3 c)). Both the origin of the reduction peak at 0.10 V as well as the change in size observed on the electropolished Cu electrodes is currently unclear and cannot be determined with CV studies only. On electrodes which are pre-treated prior to the electropolishing, either by mechanical polishing or by electrochemical reduction in alkaline in the flow cell in Fig. 5 d), only the peak at 0.3 V is observed. In few cases a small peak is observed at 0.1 V. For the sake of completeness we show the first reduction cycles of mechanically polished Cu(100) and Cu(poly) electrodes in Fig. 5 e) and f), respectively. In this case a large reduction peak is observed between 0.30 V and 0.20 V, which is much larger in size compared to the otherwise prepared electrodes and is attributed to the larger surface area of these mechanically polished electrodes. In addition some minor features are observed between 0.10 V to 0.00 V.

Fig. 5: First reduction scan in 0.1 M KOH recorded at $50 \text{ mV} \cdot \text{s}^{-1}$ on a) and b) Cu(100)-UHV electrodes, measured in the hanging meniscus cell under stagnant conditions and in the flow cell under flow conditions, respectively and flow cell measurements under flow conditions on c) electropolished Cu(100) electrodes, d) electropolished electrodes which are pre-treated either by mechanical polishing or by electrochemical reduction in alkaline in the flow cell, as well as mechanically polished Cu(100) and Cu(poly) electrodes in e) and f). Each curve represents individual measurements on freshly prepared electrodes.

2.2. Influence of experimental conditions on the initial oxidation of Cu(100) and the HER

Fig. 6: Influence of electrolyte flow and stagnant conditions on the voltammetric features of the CV recorded in 0.1 M KOH at 50 mV s⁻¹ on a Cu(100)-UHV electrode. In a) the full CV is shown including the HER region, b) and c) show the potential region around 0.35 V to 0.50 V for flow and stagnant conditions, respectively. In b) the 1st and 10th cycle is shown and in c) the 1st, 10th and 50th cycle and the so called “restored” cycle. The latter refers to a CV recorded under stagnant conditions after the electrode has been exposed to electrolyte flow after the first 50 cycles. d) and e) show the potential region from -0.30 V to 0.20 V, highlighting the peak at around -0.15 V, for flow and stagnant conditions, respectively. In both cases, the solid (dashed) CV has been recorded in a potential window of -0.20 V to 0.50 V (-0.50 V to 0.50 V).

In a next step we explored the influence of electrolyte flow compared to stagnant electrolyte conditions on the voltammetric features observed in the CV of Cu(100)-UHV electrodes. The CVs were recorded in a potential range between -0.50 V and 0.50 V, which includes the HER and initial oxidation region. Representative CVs of Cu(100) electrodes (marked with “flow” and “stagnant”) recorded at a scan rate of 50 mV·s⁻¹ in 0.1 M KOH are shown in the Fig. 6 a). The CV recorded on Cu(100) under electrolyte flow conditions shows significant reduction currents at potentials < 0.30 V compared to a Cu(100) electrode investigated under stagnant conditions. This is attributed to the reduction of residual O₂ present in the electrolyte. Possible reasons for the presence of O₂ in the electrolyte are described in the experimental Section 5. At the lowest investigated potential (-0.50 V) the HER activity

is almost identical for both experimental situations. We observed that the HER activity differs strongly from one electrode to another, with large variations in current density. Some samples show much higher current densities than those reported in Figure 6a. Especially, in those cases vivid H₂ bubble formation in the flow cell is an issue at more cathodic potentials than -0.50 V. Under stagnant conditions in the flow cell set-up and in the hanging meniscus configuration, the gas bubbles cannot be removed readily from the sample surface due to lacking transport conditions. This leads to loss of potential control. Additional measurements are required to explore in more detail the relationship between the HER activity and the features observed in the CV, as well as the behavior of the CV at potentials smaller -0.5 V of differently structured electrodes.

On the other hand, the experimental conditions, flow vs. stagnant, significantly influence the peak structures and current densities of the peaks around 0.47 and -0.15 V. We focus first on the anodic peak located at 0.47 V. The size of the peak in Fig. 6 b) remains almost constant during electrolyte flow and continuous cycling. When the electrolyte flow is turned off, the current density of the peak decreases by almost 50% (Fig. 6 c). Upon continuous potential cycling (increasing time) the sizes of the peaks decrease further, indicated by the CVs of the first potential cycle compared to the CVs obtained after 10 and 50 potential cycles, respectively. The first assumption is that the surface is poisoned by impurities from the flowing electrolyte.^[36] This causes a decrease of the current density in the voltammetric features, due to irreversible blocking of impurities on certain sites. This effect should in principle be more pronounced during electrolyte flow, where a continuous supply of impurities is supplied by the electrolyte from the supply bottle, *e.g.*, dissolved Si from KOH etching of the glass ware^[26b, 37] and other carbaceous species originating from the PFA tubings connecting the supply bottle and the flow cell. The second possibility would be that the peak observed at 0.47 is caused by oxidation of surface sites by molecular O₂. This is in agreement with the work by Droog *et al.*, where the authors propose that the peak preceding the Cu₂O formation at potentials < 0.5 V is attributed to O₂ electrosorption.^[20a, 32a] Thus the peak remains unchanged when O₂ is continuously supplied to the electrode under flow conditions, where under stagnant conditions the residual O₂ content in the cell is slowly reduced in subsequent potential cycles. Upon flowing fresh electrolyte through the cell when the electrode is almost deactivated and a stagnant situation is again restored, the peak at 0.47 V shows almost identical intensity as the initial CV recorded under stagnant conditions (see Fig. 6 c) CV marked with restored). A similar behavior has also been observed for measurements in the hanging meniscus cell on Cu(100)-UHV electrodes, for Cu(100) electrodes prepared *via* electropolishing, as well as for Cu(poly) electrodes prepared both under UHV conditions and *via* electropolishing (data not shown). A more qualitative evaluation of the peak (peak charge) makes little sense, since it depends strongly

on the residual O₂ content in the electrolyte. This is also the reason for the strong difference in peak size of the CVs shown in Fig. 4.

The influence of the electrolyte flow compared to the stagnant situation on the more cathodic peak around -0.15 V is shown in Fig. 6 d) and e), respectively. The peak is shown for two different lower potential limits, -0.2 V (black solid trace) and -0.5 V (red dashed trace). Under flow conditions (Fig. 6 d)) the peak at -0.15 V remains almost unchanged when the lower potential limit is decreased. Under stagnant conditions (Fig. 6 e)) the oxidation peak is shifted to slightly more positive potentials. Possible reasons for this behavior are discussed further below.

3. Discussion

We demonstrate that the voltammetric features observed in the CV of Cu(poly) electrodes in alkaline in a potential range of -0.30 V to 0.50 V ("fingerprint region"), strongly depend on the crystallographic orientation of the electrode surface (Fig. 2). This in turn depends on the manufacturing process as well as on the pre-treatment of the electrode. In the literature, only very few studies report the fingerprint region of the CV for the initial oxidation of Cu(poly) in alkaline.^[20a, 26, 32a, 38] The CV can be particularly useful for studies of Cu as an electrocatalyst, both to compare different types of electrodes within a single study and to relate reports from different laboratories. For example, some reports show that the CO electroreduction activity depends on the ratio of the different peaks observed in the fingerprint region.^[26] By comparing the CVs of two electropolished Cu foils from the same supplier but different batch number, we show that the voltammetric features do not depend on the pre-treatment but rather on the initial crystallographic orientation of the surface. Therefore it is crucial to report the CVs of the investigated electrodes, in addition to the exact pre-treatment procedures.

In order to deduce the crystallographic orientation from the different features observed in the CV, a more detailed understanding of the electrochemical features observed in the fingerprint region is mandatory. Despite some attempts to attribute these features with those observed in CVs of Cu single crystal electrodes^[20a, 26] a complete picture is still missing. Since the reported CVs for example for Cu(100) differ strongly one from another (see Fig. 1). Therefore a direct comparison of the CVs recorded on complex Cu(poly) materials with literature data of Cu(hkl) is not straight forward.^[26a]

Our CV results for Cu(100)-UHV electrodes (Fig. 4) show similarities to the CVs reported in the literature and electrodes prepared under laboratory conditions in this work (see Fig. 3). However, the CV of the Cu(100)-UHV electrode does not show any distinct features in the potential region from 0.30 V to 0.45 V, which are normally observed for electrodes prepared under laboratory conditions (Fig. 1).

Our STM results show only very few steps on large scale images compared to *in situ* STM images recorded on Cu(100) electrodes prepared under laboratory conditions.^[23c, d, g, 33] We attribute the additional peaks observed in the CVs in the literature to an increased number of different facets/steps on the surface. The most comparable voltammogram to our Cu(100)-UHV electrode is obtained for electrodes that were first mechanical polished and subsequently electropolished, a preparation procedure which is widely used in studies of Cu(hkl) electrodes in acid medium. Interestingly in the work by Huang *et al.* a similar pre-treatment has been employed to prepare Cu(100) single crystals,^[28] but the reported CV (Fig. 1 e)) is very different to the one obtained in the current work. The difference could be caused by the different choice of electropolishing conditions (different electropolishing solution and polishing time).

Distinct differences between the Cu(100) electrodes prepared by different pre-treatments and investigated in different set-ups become apparent from a comparison of the first reduction scans recorded starting from the OCP (Fig. 5). Cu(100)-UHV electrodes, mechanically polished electrodes and electropolished electrodes that were pre-treated by mechanical polishing or electrochemical reduction in alkaline in the flow cell, show a single reduction peak in between 0.20 and 0.50 V. This additional peak could be caused by the reduction of a native Cu oxide layer, resulting from storage in air in between the experiments, *i.e.*, different days of measurement,^[21a] which is not removed from the Cu electrodes during the electropolishing procedure. An indication that this is the case provides the experiment, where the electrode was pre-treated by mechanical polishing before the electropolishing. Such an approach is used in a number of publications listed in Table 1. Mechanical polishing is considered as the most straight forward approach to remove the native oxide layer.^[22] Thus, since the peak at 0.1 V is not apparent on these electrodes and the CVs are rather similar to those obtained on the Cu(100)-UHV electrodes, (which are shown to be free of oxide by XPS and STM), we assume that electropolishing does not remove the native oxide completely. Applying a sequence of mechanical polishing followed by electropolishing, is also consistent with the general procedure to prepare smooth metal surfaces described in detail in the comprehensive reviews for EP of metal surfaces by Landoldt^[22a] and Yang *et al.*^[22b].

The procedures described in the reviews by Landoldt^[22a] and Yang *et al.*^[22b], are, however, primarily addressing leveling of rough polycrystalline surfaces. To the best of our knowledge, the literature lacks any guidelines for producing Cu single crystal electrodes with atomically well-defined crystallographic orientation on a micrometer scale. In addition, there is still a huge debate in the literature whether or not a passivating film or oxide structures are formed during the electropolishing process, which might prevent perfect leveling of the surface.^[22b] Furthermore, we speculate that during the electropolishing of an as received or air stored non-mechanically polished Cu electrode, two processes are competing;

(i) electrochemical oxidation of the surface Cu atoms, where the Cu ions are dissolved by an electrochemical process in the electrolyte (fast) and (ii) chemical dissolution of Cu-oxides, which does not require potential because Cu is already present in its oxidized state (slow).

Further investigations are required to identify the reasons for the different structural and electrochemical properties observed on electrodes pre-treated in different ways other than preparation under UHV conditions. In addition, in order to get a more detailed picture of the actual surface structure formed during the electropolishing procedure of single crystal electrodes more concise and detailed studies are required. It has been discussed that the following effects have an influence on the polishing quality on Cu(poly); influence of etching agent concentration, potential dependence on passive film formation, flattening and pitting,^[22b, 39] polishing time,^[19] photocatalytic effects,^[16c, 40] rotation speeds (electrolyte flow)^[39b, 41] or Cu ion concentration in the etching agent.^[42] To gain a systematic insight on the influence of pre-treatment on the electrode quality only a limited number of pre-treatments reported in the literature were tested in this work. Other pre-treatment procedures described in the literature to prepare Cu single crystal electrodes, summarized in Table 1 for Cu(hkl) surfaces prepared for studies under alkaline conditions, where no CVs were reported to demonstrate the quality of the electrode surface, also have to be revisited and both the structural as well as electrochemical properties have to be compared with existing data.

Another aspect that has to be considered in the interpretation of CVs on Cu electrodes is the residual content of O₂ in the electrolyte. We demonstrate that this has a strong effect on the shape and size of the two main redox peaks at -0.15 V and 0.47 V (Fig. 4), as shown in Fig. 6. The size of the peak at 0.47 V decreases with decreasing amount of O₂. It can be restored upon supplying fresh electrolyte with residual O₂ in the electrolyte to the working electrode. This means that some sites are more easily oxidized by O₂ than by H₂O or OH⁻. The interpretation of the changes in the peak at -0.15 V are more complicated. In almost O₂ free solutions we observe a shift of the peak to more positive potentials, when the lower potential limit is decreased into the HER region (lower potential limit of -0.5 V). In O₂ containing electrolyte such a shift is absent. Matsuoka *et al.* reported a similar shift on a Cu(111) electrode.^[25] In their study, the first oxidation peak shifts by almost 250 mV to more positive potentials when the electrode is cycled into the HER region.^[25] They argue that the position of the oxidation peak depends on the degree of reduction of the oxy-overlayer.^[25] This experimental observation is in agreement with earlier DFT-based calculations.^[43], which suggest *H sorption in this potential range. Further *in situ* STM studies in acidic conditions on Cu(111) and Cu(100) indicate that H can intercalate in the Cu lattice at HER potentials. This process leads to a reversible potential dependent reconstruction of the surface.^[44] Beyond Cu, such a peak shift is observed in cyclic voltammograms on Ru(0001) recorded in 0.1 M HClO₄. According to these results, the “Nernstian”

shape of the peak at -0.15 V on Cu(100) could be the formation of *OH in the negative going scan and the reoxidation to *O in the positive going scan.^[45] Upon excursion to higher overpotentials (HER onset/region), *H is able adsorb on the surface by displacing *OH. This in turn leads to a peak shift in the positive going scan due to kinetic limitations in *OH/*O formation on the surface. Hence, we take the view that hydrogen could also adsorb on Cu(100) at a potential of -0.5 V. The presence of *H shifts the oxidation potential at -0.15 V to more positive potentials. However, when the electrolyte contains significant amounts of residual O₂, the *H is removed at more negative potentials, which is why no shift in peak position is observed in our experiment under flow conditions. This phenomenon could be due to competitive adsorption of *H with *O or *OH derived from O₂.

4. Conclusions

This work comprises a detailed study on the interpretation of CVs of Cu electrodes recorded under alkaline conditions (0.1 M KOH and NaOH). We presented results on various polycrystalline Cu electrodes and Cu(100) single crystal electrodes prepared by different pre-treatments and explored under different experimental conditions. The key findings of this study are the following:

1. According to our CV study, the crystallographic orientation of polycrystalline Cu electrodes depends both on the initial crystallographic orientation and the pre-treatment of an electrode. For example, while electropolishing preserves the crystallographic orientation, radio frequency heating in a H₂ stream changes the crystallographic orientation of the surface.
2. We show the CVs of Cu(100) electrodes recorded in 0.1 M KOH and 0.1 M NaOH. The electrodes were determined free of contaminants by XPS. Atomic flatness has been verified by STM imaging. As such, the CV recorded on Cu(100)-UHV electrodes can be considered as a benchmark for further studies on Cu(100) single crystals.
3. The Cu(100) electrodes prepared under ambient laboratory conditions show additional features in the CV in the potential region from 0.30 V to 0.50 V. We attribute these features are attributed to defect sites and different facets on the surface. We conjecture that the preparation procedures reported in the literature are not optimized to produce atomically flat well defined Cu(100) surfaces. As reported earlier for Cu(poly), removal of the native oxide by mechanical polishing is crucial for a good polishing quality of single crystal electrodes.
4. With flow cell measurements under flow and stagnant conditions we show that the voltammetric features depend on the amount of residual O₂ in the electrolyte. In the

presence of O₂ a pronounced oxidation feature is observed at 0.47 V, which decreases with decreasing amount of O₂ in the cell.

We have thus addressed a number of open questions in our understanding of the electrochemical properties Cu electrodes under alkaline conditions. Further studies, especially with respect to benchmarking the CVs of Cu(hkl) electrodes, are mandatory to compare the results between different research groups. Electrocatalytic reduction reactions, such as CO₂/CO and NO, should be revisited on well-defined Cu(hkl) electrodes in order to determine in how far the quality of the investigated electrodes plays a role in the electrocatalytic activity and product distribution.

5. Experimental

In the present study, we investigated the electrochemical properties of several Cu electrodes, namely Cu(100) single crystals, polycrystalline Cu crystal electrodes and polycrystalline foils. We use (i) an electrochemical flow cell and (ii) a hanging meniscus cell, operated in a load lock chamber. Both are attached to an UHV set-up under inert gas atmosphere. The electrodes have been prepared both *in* UHV and *ex* UHV.

5.1. Materials and electrochemical solutions

Two Cu(100) single crystals were purchased from Mateck GmbH (Purity 99.9999 %, diameter 6 mm and 8 mm, thickness 2 mm). The 6 mm sample was used in the UHV-STM and the 8 mm sample was used in the UHV-XPS set-up (see below). Using two different samples allows us to check the reproducibility of our approach.

The Cu foil was purchased from Alfa Aesar Supratronic® (Purity ≥ 99.9999 %, 0.1 mm thickness) where foil A has the LOT number S29C040 and Foil B has the LOT number M18D049.

The Cu wire (serving as counter electrode during electropolishing and used to mount the Cu foils in the RF heater) were purchased from Goodfellow (Purity ≥ 99.999 %, 0.5 mm diameter).

The ultrapure deionized water (MilliQ) used for rinsing the electrodes and mixing the solutions was obtained from a Millipore MilliQ Integral purification system. The 66% H₃PO₄ (Merck EMSURE, 85%) used for electropolishing was prepared from mixing 85% H₃PO₄ with MilliQ water.

The 0.1 M alkaline electrolytes used for the electrochemical characterization were prepared from MilliQ water and KOH (potassium hydroxide monohydrate, Merck Suprapur®, ≥99.995%) or NaOH (sodium hydroxide monohydrate, Merck Suprapur®, ≥99.995%), respectively.

5.2. UHV set-up

In this work two, UHV set-ups have been employed: (i) the flow cell is attached to an UHV chamber with an XPS setup (UHV-XPS) or (ii) the hanging meniscus cell is attached to UHV chamber with an STM (UHV-STM).

The UHV-XPS set-up consists of three parts, *i.e.*, (i) a UHV chamber dedicated to XPS measurements (details see below) provided by Thermo Fischer ($p_{base} = 1 \cdot 10^{-9}$ mbar), (ii) a UHV preparation chamber ($p_{base} = 1 \cdot 10^{-10}$ mbar) equipped with standard facilities for sample preparation such as a manipulator for sample heating *via* electron bombardment, an Ar⁺ ion sputter gun and several valves serving as gas inlets (O₂, H₂, Ar, etc.) and (iii) a load lock chamber, which allows for lock in or lock out of samples. Furthermore, the load lock chamber serves as a working compartment to mount an electrochemical flow cell. For the electrochemical measurements the samples were transferred from the preparation chamber to the load lock, which is subsequently flooded with N₂ (AGA 5N). XPS measurements after EC were achieved by pumping the N₂ from the transfer chamber until a base pressure of $\sim 5 \cdot 10^{-8}$ mbar was reached, before transferring the electrodes into the main UHV chamber.

The UHV-STM set-up consists of two parts, *i.e.*, (i) a main UHV chamber ($p_{base} = 1 \cdot 10^{-11}$ mbar) containing both an STM (Aarhus Type STM)^[46] and similar facilities for sample preparation as mentioned above and (ii) a similar load lock chamber ($p_{base} = 5 \cdot 10^{-8}$ mbar) for the electrochemical characterization equipped with a newly designed hanging meniscus cell. The procedure for the sample transfer between the different chambers was performed in the same way as described above.

5.3. Sample preparation

Under UHV conditions: Two slightly different preparation procedures were employed. (i) The electrodes were exposed to Ar⁺ ion sputtering ($p_{Ar} = 4 \cdot 10^{-5}$ mbar, $U = 2$ keV) for 1 hour, annealed at 1000 K for 1 hour, Ar⁺ ion sputtered at 1000 K for 1 hour and a final annealing step at 1000 K for 10 minutes. The quality of the samples was either investigated with XPS or STM depending on the used UHV chamber. (ii) The electrodes were exposed to 3-5 cycles of Ar⁺ ion sputtering 5-10 monolayers ($p_{Ar} = 4 \cdot 10^{-5}$ mbar, $U = 2$ keV) and then heating to 1000 K for 300 s. The first cycle is sputtered while the crystal is at room temperature. Subsequent sputter cycles were carried out as the crystal is still cooling down from 1000 K, *i.e.*, to around 800 K.

Mechanical polishing (MP): The electrodes were polished mechanically by hand on a polishing cloth (Struers, MD-Mol) first with 0.1 μ Alumina powder for 10 minutes and further 10 minutes with 0.05 μ Alumina powder (Buehler MicroPolishTM) until a mirror like finish was observed by naked eye and were subsequently thoroughly rinsed with MilliQ water. Residual water had to be removed carefully from

the sample face with a paper tissue, without touching the electrode surface, prior to mounting the sample on the flow cell set-up.

Electropolishing (EP): The electrodes were EP in 66% H_3PO_4 solution at approximately 2 V vs. a Cu wire serving as counter electrode, used as cathode. The potential was controlled with a power supply (EA Elektro-Automatik EA-PS 7016-10 A) and was set at the point just prior to the onset of bubble formation on the electrode, which would be related to the oxygen evolution reaction (OER) on the electrode. Performing the electrolysis at a more positive potential leads to pitting and restructuring of the surface, which can be observed with the naked eye^[22b]. The electrodes were electropolished for 90 s unless otherwise mentioned. After the electropolishing the electrodes were thoroughly rinsed with MilliQ water. Residual water had to be removed according to the procedure described for MP electrodes above.

Radio frequency heating (RF): The Cu foils were attached to a Cu wire and mounted in the RF heater (MTI Corporation SP-15A Portable High Frequency Induction Heating Unit). The samples were heated in a gas mixture of H_2/Ar : 5/95 (AGA, purity: 5.5 H_2 and 6.0 Ar.).

5.4. Electrochemical cells and procedure

In this work two different electrochemical cells have been used: the UHV-XPS chamber is equipped with an electrochemical flow cell and the UHV-STM chamber is equipped with a hanging meniscus cell. Both cells are schematically illustrated in Fig. 7.

The flow cell set-up closely resembles the design reported in an earlier study; however, it has been slightly modified to hold a different type of UHV sample holder.^[36] The potential was controlled with a BioLogic SP-300 potentiostat. The flow cell can be operated either with electrolyte flow or with stagnant electrolyte. In Section 2.2 we show that with electrolyte flow, a reduction current is measured at potentials < 0.3 V, which we attribute to the presence of residual O_2 in the electrolyte. The O_2 likely originates from diffusion through the connectors at the inlets of the flow cell, located between the electrolyte supply bottle and the actual cell.^[36] In principle, complete removal of the oxygen can be achieved by flushing the connectors with inert gases such as Ar or N_2 , as shown elsewhere.^[36] In the current configuration this was, however, technically not possible.

The hanging meniscus cell has been newly designed to investigate the stability of electrodes in electrochemical environment where no electrocatalytic reactions take place. It consists of a cell body made of Kel-F, which contains a tube with an inner diameter of 5 mm (d_4 in Fig. 7), which allows matching the diameter of the meniscus with the diameter of the sample (6 mm, d_3 in Fig. 7). The cylinder has three in-/outlets, where the first inlet is used to mount a Pt wire as counter electrode, the second inlet is used to introduce the electrolyte in the cell from a glass supply bottle, connected

via PFA tubes (high purity plus PFA – IDEX Health & Science) to the cell and the third outlet is leading to the reference electrode and an electrolyte waste container. The potential was controlled with a BioLogic SP-200 potentiostat.

Fig. 7 Schematic illustration of the flow cell and the hanging meniscus cell. Top row: electrode not in contact with cell/electrolyte. Bottom row: sample in contact with cell/electrolyte. The diameters d_2 and d_3 indicate the geometric area, when the electrode is in contact with electrolyte.

In both electrochemical cells a homemade RHE electrode was used and all potentials are given vs. the RHE scale, unless otherwise mentioned. The electrochemical data were collected with the BioLogic EC-Lab V11.12 software.

The glassware (Electrolyte supply bottle) was cleaned with highly concentrated KOH (Merck EMSURE potassium hydroxide 85%) and boiled prior to the experiment in MilliQ water. Prior to each experiment the tubes leading to the flow cell and the hanging meniscus cell were rinsed with deaerated MilliQ water (purged with Ar, AGA 5N) and subsequently with the respective deaerated electrolyte (purged with Ar, AGA 5N).

Procedure to record CVs in the flow cell set-up: First, the electropolished polycrystalline Cu sample was mounted on the cell to test that the set-up is contamination-free (comparison between the CVs for the initial oxidation of an electropolished polycrystalline Cu electrode for each day of measurement). Subsequently, the flow was stopped, the polycrystalline Cu sample removed. During electrochemical tests of the electrodes prepared under UHV conditions, the flow cell was mounted in the load lock chamber. The freshly prepared electrodes (both from UHV or non UHV treatment) were mounted on the cell and electrolyte flow was started. Next, the bubbles were removed from the system with a set of syringes, the working electrode was connected and the measurement was immediately started. The time between the commencement of the electrolyte flow and the measurement was approximately 20 seconds. Ten cycles were recorded between -0.2 and 0.5 V to

stabilize the background pressure of residual O₂ in the cell compartment until a reproducible CV was recorded in this potential range. At this point, CVs were either recorded with electrolyte flow, or the flow was stopped to investigate the surfaces with CVs under stagnant conditions.

Procedure to record the reported CVs in the hanging meniscus set-up: In the hanging meniscus set-up, the cell was raised vertically into the load-lock before the electrolyte cylinder was filled with electrolyte, while the sample was pointing facedown a couple of centimeters above the cell. Finally, a droplet of electrolyte was formed on top of the cylinder before it was aligned with the sample (Fig. 7) The measurement was started approximately two seconds after establishing contact between the sample and the electrolyte.

5.5. Evaluation of the electrochemical surface area (ECSA)

Throughout the article the current is normalized to the geometric surface area. For the single crystal Cu(100) electrodes investigated in the hanging meniscus cell the electrode geometric surface area corresponds to the diameter of the sample (6.0 mm, d_3 in Fig. 7) and in the flow cell the geometric surface area is determined by the inner diameter of the employed O-ring (4.4 mm, d_1 in Fig. 7). In the latter case, the actual surface area can be slightly smaller: when the electrode is pressed against the O-ring, its compression leads to a reduction of the inner diameter, due to its lateral expansion (d_2 in Fig. 7). This can lead to small differences in the absolute currents, when CVs recorded in the different electrochemical cells are compared. For the single crystal Cu(100) electrodes the geometric area corresponds to the actual electrochemical surface area (ECSA). The ECSA of polycrystalline Cu electrodes can be determined by a number of different techniques such as Lead UPD^[16e, 18a], Thallium UPD^[19, 47] or double layer capacitance.^[32c, 48] Due to technical reasons we only explored the latter (if necessary), since this approach allows for monitoring changes in surface area during the measurement.

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