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The effect of dissolved glassware on the structure sensitive part of the Cu(111) voltammogram in KOH

Electrocatalysis with the aim of converting electrical energy from sustainable sources into synthetic fuels or base chemicals for industrial production has become an important field in research.[1–3] One interesting electrochemical reaction in that context is the direct electrochemical hydrogenation of CO_2 that not only allows storing renewable energy but also helps to close the anthropogenic carbon cycle.[4–9] Since the pioneering work of Hori in the 1980s,[10] Cu remains the only pure metal that can convert CO_2 to higher value products like higher hydrocarbons and their alcohols in significant amounts. Despite many years of research, the reason for this unique behaviour is not yet fully understood and considerable effort is therefore devoted to elucidate the fundamental electrochemical properties of various Cu-model systems (see Nitopi *et al.* and references therein[9]).

Whereas there are many results on polycrystalline and amorphous Cu indicating e.g. that product selectivity and activity are strongly structure dependent,[11] not many results are reported on single-crystalline Cu samples with well-defined facets exposed to the electrolyte that could e.g. elucidate the nature of the active site(s).[12–22] This seems partially due to the fact that Cu is difficult to work with due to its oxophilic nature and partly because the electrochemical (EC) response as measured by cyclic voltammetry (CV) is very sensitive to the exact preparation procedure employed.[23] For example, there is not yet any consensus in the literature about the blank CVs of low-index Cu single crystals (SC) in alkaline media, especially in the underpotential region of Cu_2O formation which is known to be structure sensitive.[21,23–27] This region can easily drown when investigating CVs of Cu in wide potential windows.[15,28–30]

The fact that the structure sensitive, intrinsic EC response of low-index Cu facets is not yet unambiguously established hampers the efforts of understanding the special properties of Cu in several ways. Firstly, such blank CVs are needed as benchmarks for theoretical investigations trying to calculate CVs under more complicated reaction conditions.[31,32] Secondly, blank CVs are needed as fingerprints when it comes to establishing whether a model system (e.g. Cu(*hkl*)-oriented films) behaves like a SC electrochemically.[22,33] Thirdly, fingerprint CVs are needed to analyse polycrystalline samples, where the relative abundance of different facets is deduced by a deconvolution of the measured CV into the CVs of the principal facets.[22,34,35] This again hampers ongoing work on investigating structural changes of polycrystalline Cu or Cu nanoparticles under reaction conditions, where the knowledge of the fundamental CVs of the various Cu facets is crucial once more.[36]

This Viewpoint provides insight on the observed discrepancies in such fingerprint CVs. To this end, a combination of STM, EC, ICP-MS and XPS was applied in combination with an ultra-high vacuum (UHV)-EC setup that allows preparation and electrochemical analysis of Cu SCs under very well-controlled conditions.[23] To start with, we compared our CVs to the well-known work by Schouten et al.[27] which reported CVs of different low-index Cu surfaces in the underpotential region of Cu_2O formation. This study is widely used as the benchmark for Cu surfaces as evident from subsequent papers.[18–20,22] Surprisingly, we obtained both contrasting and rapidly changing electrochemical results. While searching for possible explanations, we found two studies by Mayrhofer et al.[37,38] about the impact of glass corrosion on the electrocatalytic properties of platinum electrodes in alkaline media, which turned out to be very inspiring for our investigations.

To simplify the story, we restrict ourselves to report the results of our extensive analysis of the impact of using glassware on the EC response of one Cu facet, namely Cu(111). Several Cu(111) SCs were investigated under various well-defined conditions in order to eliminate possible sample-, preparation- or setup-related artefacts. To this end, we investigated SCs both in the above mentioned dedicated UHV-EC setup and a conventional 3-electrode one compartment EC setup. Both setups consistently show the same influence of glass corrosion on the Cu(111) CVs in the underpotential region of Cu_2O formation, i.e. the region usually used for benchmarking purposes.

Measurement details: As samples we used various Cu(111) single crystals (MaTeck, Jülich; Purity 99.9999 %, typical diameter of the exposed facet 6 mm, thickness 3 mm) which were either cleaned and prepared by sputtering and annealing in the UHV-EC setup or by electropolishing in the case of the conventional setup.

The structure and cleanliness of the UHV prepared SCs were verified in UHV by scanning tunneling microscopy (STM). Afterwards, the SCs were transferred under vacuum to a cube attached to the UHV chamber. The cube was then vented with Ar (6.0, AGA) and an EC cell made of Kel-F was inserted into the cube. EC measurements were carried out under a steady flow of Ar. The electrolyte was a 0.1 M KOH (99.995 Suprapur, Merck) solution made using millipore water (18.2 MΩ cm, Merck Millipore) in volumetric flasks made of either glass (Blau Brand) or PFA (Corning Life Sciences). The electrolyte was bubbled with N_2 (5.0, AGA) in a supply bottle made of glass (for electrolyte prepared in a glass flask) or PFA (for electrolyte prepared in a PFA flask) and connected to the EC cell by PFA tubing (IDEX Health & Science). The experimental method and the UHV-EC setup is shown in Figure S1 and described in more detail in a recent publication.[23]

The setup for conventional EC measurements was a PTFE cell (Pine Research) where the working electrode was a Cu SC housed in a PTFE holder compatible with a Pine Research rotator shaft (shown in Figure S2). Before these measurements, the Cu SC was electropolished against a Cu wire in 66 % H_3PO_4 (85 % EMSURE, Merck) at 2.0 V for 30 s while being rotated at $\sim$ 200 rpm. Finally it was rinsed in deaerated millipore water. The electrolyte was deaerated directly in the cell through a PFA tube (Savillex).

All EC measurements were performed with a Bio-Logic SP200 potentiostat controlled by Bio-Logic's EC-Lab software. A Pt wire was used as counter and a calibrated RHE as reference electrode.

The behaviour of Cu(111) under alkaline conditions: The first measurements were performed on UHV prepared samples. These were exposed to 0.1 M KOH electrolyte prepared in different ways:

(A) freshly prepared KOH in a PFA flask

(B) freshly prepared KOH in a glass flask

(C) KOH stored overnight in a PFA flask

(D) KOH stored overnight in a glass flask

Apart from the different procedures for electrolyte preparation, the rest of the experiment remained the same for all the measurements. All electrolytes were deaerated and then used to measure the base voltammogram of the clean Cu SC sample in the potential range from −0.20 V to +0.45 V vs. RHE at a scan rate of 100 mV/s in Ar atmosphere. The samples were immersed in the electrolyte under potential control at 0.33 V vs. RHE and then swept cathodically to begin the CV. The results obtained for the different variants of electrolyte are summarized in Figure 1.

As clearly seen, the CVs measured using KOH from a PFA flask irrespective of it being fresh or old shows just one relatively sharp

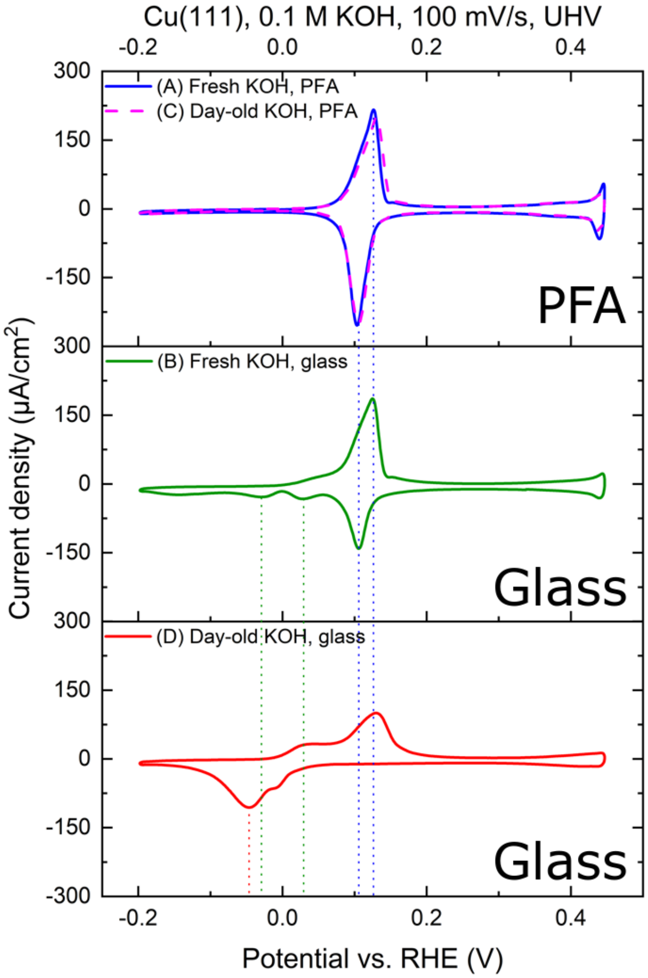

Figure 1: CVs measured on the UHV prepared Cu(111) samples in 0.1 M KOH prepared in different ways, the samples were immersed under potential control at 0.33 V vs. RHE. CVs from electropolished samples are shown in Figure S3, including a measurement in 0.1 M NaOH.

and reversible redox feature at 0.11 V vs. RHE corresponding to a charge of $76.3\,\mu C/cm^2 \pm 2.4\,\mu C/cm^2$, or 0.27 ± 0.01 electrons per surface atom. Contrastingly, for KOH prepared in glass flasks we measured different redox features depending on the contact time of KOH with the glass. The KOH freshly prepared in a glass flask traced a similar redox feature as seen for PFA but with additional cathodic reduction waves negative of the main feature. On the other hand, KOH left overnight in a glass flask had a considerably different redox behaviour resulting in two oxidative and two reductive peaks with a clear peak separation between the anodic and cathodic scan. This very much resembles CVs previously reported in the literature (cf. Figure S5).

After having established a benchmark CV of Cu(111) prepared by sputter/anneal cycles in UHV, we then performed similar measurements on a separate Cu(111) SC prepared by electropolishing in a conventional setup. To do so, we housed the Cu SC in a custom-made PTFE holder that only exposes the crystal face to the electrolyte. The PTFE cell maintained under Ar atmosphere during EC measurements. After electropolishing, CVs were recorded using the same parameters as in the UHV-EC setup. The CVs measured on the electropolished samples are shown in Figure S3 and compare very well to those in Figure 1. This showed that the features measured on Cu(111) SC are consistent across both setups and independent of the crystals used, as long as they are well-defined and clean. We note that the reversible feature in the clean case turns out to be composed of two peaks. The dependence of these two peaks on e.g. the exact potential range used is currently under investigation.

To investigate what constituents of the electrolytes might be the reason for the different features seen when using glass and PFA flasks, electrolyte samples were retrieved from the EC cells after CV measurements (shown in Figure 1) for the four cases of electrolyte explored and analysed using inductively coupled plasma mass spectrometry (ICP-MS). Based on a semi-quantitative analysis of a brief survey of all elements we only identified B, Al and Si as being present in significant amounts in KOH from a glass flask compared to KOH from PFA, thus we performed a thorough analysis of these three elements (see SI for details). Inspired by Mayrhofer's papers,[37,38] we also checked for Pb, but could not detect it in noticeable amounts. The data from this analysis is listed in Table 1 and also shown as a bar graph in Figure 2a. It can clearly be seen that the amounts of these constituents increases significantly with the time that the electrolyte is in contact with glass.

In parallel, we investigated the Cu SC electrode after the EC measurements by trans-

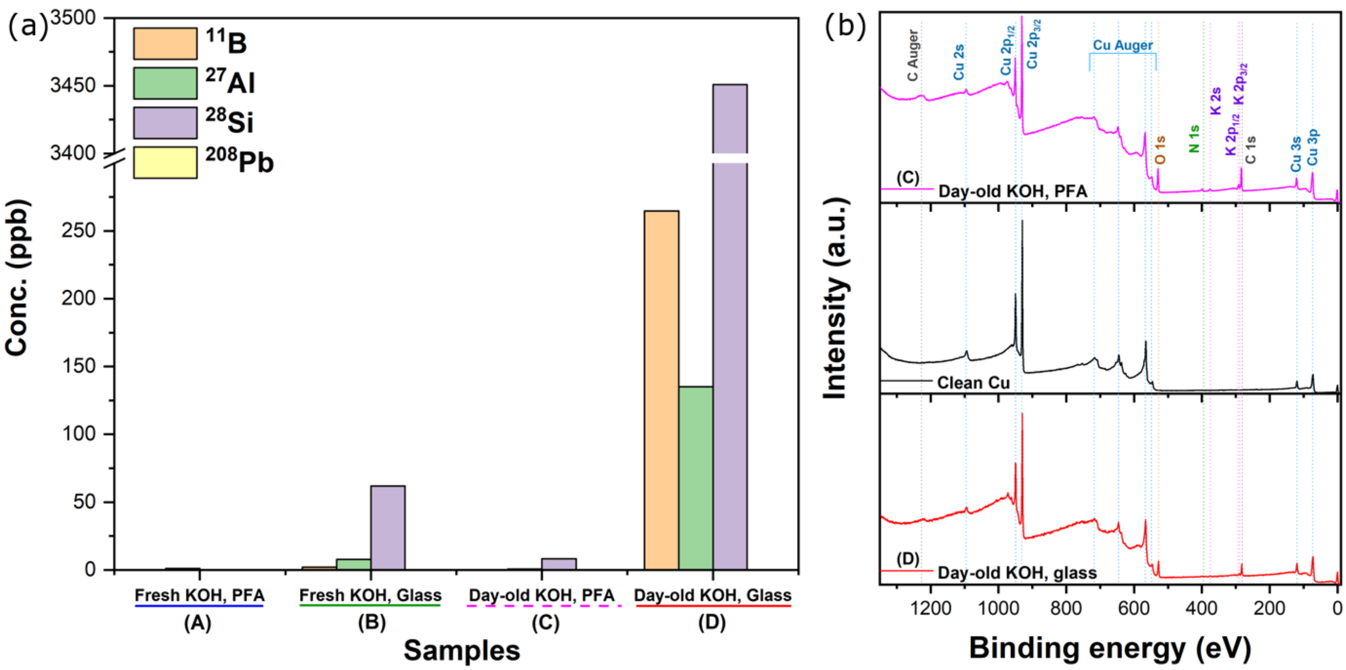

Figure 2: (a) ICP-MS measurements focusing on B, Al, Si and Pb for the different electrolytes used. As can be seen, the KOH left overnight in a glass flask contains large amounts of contaminants compared to those from PFA flasks. (b) XPS surveys measured on the Cu(111) sample after the EC measurement and subsequent rinsing in deaerated millipore.

Table 1: The concentrations of B, Al, Si and Pb detected by ICP-MS in the various electrolytes. The detection limit (DL) is noted as well. The same data is shown in Figure 2a.

Electrolyte	Concentration [ppb]			
	B (DL = 0.229)	Al (DL = 0.191)	Si (DL = 8.927)	Pb (DL = 0.002)
(A) Fresh KOH, PFA	< DL	1.0	< DL	< DL
(B) Fresh KOH, glass	2.1	7.7	61.9	< DL
(C) Day-old KOH, PFA	< DL	0.6	8.3	< DL
(D) Day-old KOH, glass	264.8	135.1	3450.8	0.01

ferring the samples to a separate setup and performing X-ray photoelectron spectroscopy (XPS). Amongst the different samples we performed XPS on those exposed to electrolyte C and D, as these were exposed to the highest concentrations of impurities. Figure 2b shows a comparative survey spectrum for a clean Cu(111) SC prior to exposure to electrolyte and after EC cycling for 100 cycles in the two electrolytes (C and D), respectively. The main Cu peaks are consistent across all the samples but on both the Cu SCs which have seen electrolyte, additional peaks are found for K 2p, O 1s and C 1s. These could be attributed to the electrolyte and adventitious carbon from the atmosphere during sample transfer from the EC-cell into the XPS chamber. Surprisingly we did not observe any of the contaminants seen from ICP at the Cu SC surface even when performing XPS sputter depth-profiling. Additionally, ion scattering spectroscopy (ISS) was performed on separate regions of these samples but even this surface sensitive technique did not indicate any glass contaminants on the surface.

Altogether, this suggests that the contaminants revealed by ICP can possibly influence the CV response by being present in the electrochemical double layer but without getting deposited on to or incorporated into the Cu surface. Interestingly, a recent study by Bertheussen et al.[39] probing polycrystalline Cu (pc-Cu) under reaction conditions observed catalyst deactivation over time that was attributed to poisoning by deposited Si. They were actually able to detect Si on pc-Cu by XPS after performing CO reduction at $-0.5\,\mathrm{V}$ vs. RHE during prolonged EC measurements in a glass cell. To further investigate this aspect, we performed electrolyte exchange going from glass KOH to PFA KOH during EC measurements and observed the glass induced features in the CV disappearing instantly (see Figure S4). Apparently in the case of SCs these contaminants are only loosely bound to the surface or present at the electrode/electrolyte interface.

So far, our data suggest negligible chemical modification of the surface during a typical EC measurement (duration: $\sim 1\,\mathrm{hr}$), but the question still remains whether the surface was structurally altered during the EC measurement or not. In order to answer this, post-EC STM imaging was performed using the UHV-STM-EC setup. After the EC measurements, the samples were transferred back to UHV and STM was performed without any intermediate exposure to air. The sample analysed was the Cu(111) exposed to KOH held overnight in the PFA flask. Figure 3 shows representative pre- and post-EC STM images. In both cases, the Cu(111) shows large terraces separated by monoatomic steps. Furthermore, monoatomic holes induced by the EC measurement are visible. However, no major structural changes like deep etch pits are visible, thus indicating that the overall surface structure remained intact during EC measurements, suggesting that the Cu(111) surface is relatively stable under these conditions.

Summary: We have shown how a combination of STM, EC, ICP-MS and XPS can be used to investigate whether impurities are affecting measurements adversely. In the present case it was shown that dissolved glassware in alkaline electrolyte completely changes the CV of Cu(111) from having one sharply peaked redox feature at $0.11\,\mathrm{V}$ vs. RHE to having two anodic and two cathodic features. Furthermore, these features are separate from each other. Thus we recommend avoiding all glassware in studies involving alkaline media as this can possibly affect the electrochemical behaviour of a given system dramatically.

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Supporting Information Available

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXX

Additional information on the experimental

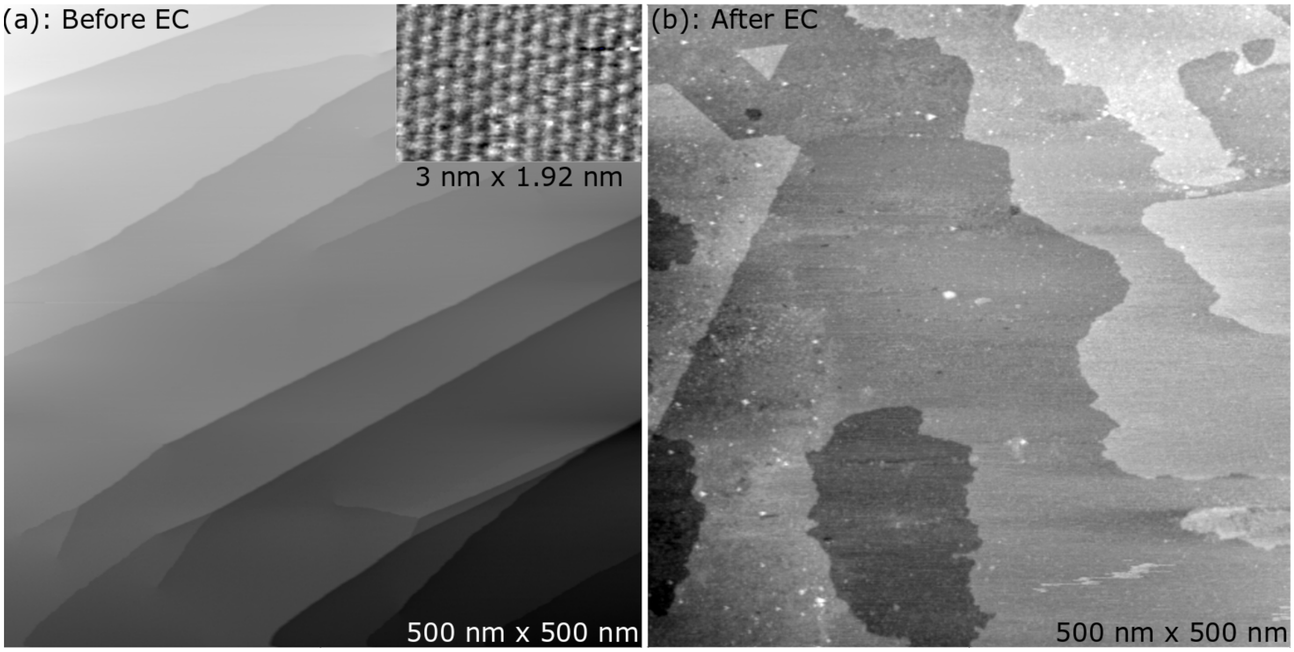

Figure 3: A comparison of the state of the Cu(111) surface before and after being cycled five times electrochemically between −0.2 and 0.45 V vs. RHE in 0.1 M KOH as seen by STM. The inset in (a) shows atomic resolution of the surface.

methods employed including electrochemical results obtained on electropolished Cu(111) samples and a comparison to the literature.

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Notes

Views expressed in this Viewpoint are those of the authors and not necessarily the views of the ACS. The authors declare no competing financial interest.

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