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Fingerprint Voltammograms of Copper Single Crystals under Alkaline Conditions: A Fundamental Mechanistic Analysis

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Abstract

A critical step towards the systematic development of electrocatalysts is the determination of the microscopic structure and processes at the electrified solid/electrolyte interface. The major challenges towards this end for experiment and computations are, respectively, achieving sufficient cleanliness and modelling the complexity of electrochemical systems. In this sense, benchmarks of well-defined model systems are sparse. This work presents a rigorous joint experimental-theoretical study on the single crystal (SC) Cu/aqueous interface. Within typical computational uncertainties, we find quantitative agreement between simulated and experimentally measured voltammograms, which allows to unequivocally identify the $\ast\text{OH}$ adsorption feature in the fingerprint region of Cu (110), (100) and (111) SCs under alkaline conditions. We find the inclusion of hydrogen evolution reaction kinetics in the theoretical model to be crucial for an accurate steady-state description which gives rise to a negligible $\text{H}^\ast$ coverage. A purely thermodynamic description of the $\text{H}^\ast$ coverage through a Pourbaix analysis would incorrectly lead to a $\text{H}^\ast$ adsorption peak. The presented results establish a fundamental benchmark for all electrochemical applications of Cu.

Graphical TOC Entry

Keywords

Copper, Single Crystal, Electrocatalysis, Cyclic Voltammogram, DFT, Microkinetic modelling

In recent years, there has been increasing interest in copper (Cu) due to its electrocatalytic activity towards diverse applications such as nitrate reduction¹ and CO₂ reduction.² The latter is heavily investigated as a possible means to store renewable electricity and to convert CO₂ into valuable chemicals and fuels. Ever since the seminal work of Hori,³ much research has been devoted to elucidate why Cu is the only monometallic catalyst that can facilitate formation of valuable hydrocarbons and alcohols from CO₂ with substantial selectivity and activity (typically in neutral or alkaline electrolytes as Cu is unstable in acid). The majority of these studies are done on polycrystalline, high surface area or thin film systems, whereas results on well-defined single-crystal (SC) Cu electrodes are sparse. Existing SC studies suggest significant variation in activity and selectivity for different Cu facets which –if understood– could help towards rational catalyst design e.g. by optimization of facet distribution.^{4–6}

To this end, a fundamental understanding is required of the electrochemical (EC) response of Cu SCs prior to exposure to reactant(s). In the most extensive experimental work so far, Schouten *et al.*⁷ have investigated the structure-sensitive fingerprint region, i.e. the potential range between hydrogen evolution (HER) and the onset of irreversible Cu oxidation, of various Cu SCs in alkaline media. Their cyclic voltammograms (CV) have since been widely used both for benchmarking and deconvoluting facet distributions of various Cu catalysts.^{8–27} However, recently we have shown that the EC response of at least the Cu(111) is sensitive to contaminants dissolved from glassware in alkaline media.²⁸ This contamination might influence peak position and shape of the CVs which is reflected in the prevailing disagreement in literature on the structure-sensitive part of the CVs of low-index Cu SCs.

The general consensus in literature is that, on bare Cu SCs, the peaks in the fingerprint region arise from *OH adsorption and desorption. This assignment has been suggested by various in-situ EC-STM studies^{29–33} but the inherent lack of chemical resolution in STM hampers this conclusion. In an attempt to identify the adsorbed species, Raman spectroscopy was explored but involved either glass cells or silica-covered particles and may thus

be influenced by silicon contamination.^{34–36}

From the theoretical perspective, *ab initio* simulations can give significant insight into the features of CVs.^{37,38} CVs can be directly simulated via a thermodynamic approximation based on adsorption energies from DFT. These energies depend on the chosen atomic model of the solid/liquid interface and may be significantly affected by e.g. the way solvation effects are included. This sensitivity of results to the model system has been also found for the Cu SC/electrolyte interface, where different studies have shown widely varying H^* and *OH adsorption energies.^{27,39} Resulting simulated CVs deviated significantly from experimental spectra and required *ad hoc* corrections to *ab initio* determined energies to achieve agreement with experimental observations. Further, some of these studies overestimate the degree of H^* adsorption. This overestimation arises from the use of a purely thermodynamic description of the adsorption processes. With the inclusion of hydrogen evolution kinetics, the steady-state H^* coverage is significantly reduced.^{40–42}

In this joint experimental-theoretical work, we present measured benchmark CVs of clean Cu (110), (100) and (111) SCs and interpret them via simulated CVs. To minimize possible influences of the sample preparation, electrochemical measurements were performed on two independent sets of Cu SCs in two different setups, namely an ultra-high vacuum (UHV)-EC setup and a conventional EC setup (details are provided in recent publications^{28,43}). The SC samples for the former are pre-treated by cycles of sputter-annealing whereas the latter are electropolished (SI) before EC measurements. Figure 1 shows CVs from these two different setups using a scan rate of 50 mV/s in deaerated 0.1 M KOH electrolyte under Ar atmosphere. The basic difference is that UHV-EC measurements are on SCs without aerial exposure, while the conventional EC analysis involves a brief transfer through air between electropolishing and recording CVs. However, the EC responses after the first reductive cycle are similar for a given facet under both conditions, as seen in Figure 1.

These CVs clearly indicate that each facet has a distinct EC response. On all facets, oxidation features are observed positive of 0.25 V and it is the region negative of this po-

Figure 1: Cyclic voltammograms for Cu(110), Cu(100) and Cu(111) in the fingerprint region measured using a conventional EC setup (top panel) and a UHV-EC setup (bottom panel) in Ar-saturated 0.1 M KOH, both under Ar-atmosphere at a scan rate of 50 mV/s.

tential that contains structure-sensitive information of the exposed facet. Before discussing these particular features in depth, it is important to note that the potential regions of the measurements in Figure 1 have been chosen to match those considered in recent studies.⁷ This choice avoids both anodic Cu bulk oxidation and cathodic hydrogen evolution that might influence the fingerprint features, which is the subject of an ongoing study.

Concerning the facet-specific features, Cu(111) exhibits a sharp redox feature at 0.12 V vs. RHE which can be attributed to reversible adsorption/desorption of OH. This feature is in stark contrast to asymmetric CVs reported previously on Cu(111), where glass and/or Si was involved, which leads to multiple and asymmetric peaks.²⁸ The Cu(100) exhibits a broad feature centred at -0.13 V vs. RHE. Interestingly, no feature is observed in this potential window on the Cu(110), consistent with previous reports.^{7,18,27}

The trend of the workfunction (Φ) for the different facets, $\Phi(110) < \Phi(100) < \Phi(111)$,⁴⁴ implies the position of the *OH feature on the (110) to be at even more negative potential,

as the binding energy and thus the onset potential of the redox features scale with Φ .⁴⁵ Therefore, we extended the lower bound for Cu(110) to -0.4 V even though this means that HER sets in which was avoided by the traditionally used bounds. Figure 2 shows the resulting CV for Cu(110) (top left panel) and a reversible feature is observed at -0.34 V vs. RHE although convoluted with the onset of HER. Thus a clear trend of the facet-dependent reversible OH adsorption/desorption feature is observed.

Figure 2: (*Left* column) Experimental CVs for Cu(110), Cu(100) and Cu(111) depicting facet-dependent OH adsorption/desorption features in Ar-saturated 0.1 M KOH electrolyte at a scan rate of 50 mV/s; (*center* column) Simulated CVs for a scan rate of 50 mV/s, considering competing contribution from H^* , *OH and HER; and (*right* column) Calculated *OH coverage as a function of potential. Insets illustrate the optimal adsorption geometry of OH under these conditions.

In order to get a deeper understanding of the nature of these features, we simulate CVs using microkinetic modelling in conjunction with *ab initio* reaction energetics that incorporate the impact of solvent and potential. Building on previous developments,^{37,38,40} we unite macroscopic reaction kinetics and adsorption processes in the definition of the simulated CV. This approach allows for an accurate current/potential relationship resulting from electro-

chemical *OH adsorption and the HER processes. The kinetic equations were solved with the CatMap code⁴⁶ (SI Sec. IIIa). The atomic-scale elementary surface processes were modeled by DFT simulations employing the BEEF-vdW⁴⁷ exchange-correlation functional. An appropriate description of the Cu/water interface including the adsorbates considered^{37,48} was obtained with the SCCS continuum solvation model in the Quantum ESPRESSO code⁴⁹ and Environ package^{50,51} (SI Sec. II). Proton-electron transfer processes were described via the computational hydrogen-electrode.⁵² Adsorption sites for H* and *OH were rigorously sampled using ASE⁵³/CatKit⁵⁴ and a first order *OH-*OH interaction model was parameterized to include lateral interactions⁵⁵ (SI Sec. IIIb). Coupled proton-electron barriers for HER were taken from previous work⁵⁶ and adjusted to alkaline conditions via an empirical correction of ≈ 0.10 eV (SI Sec. IIIc).

The simulated electrochemical processes reveal a qualitatively similar atomistic picture for all facets within the investigated potential ranges as evident in Figure 2. At very negative potentials of ≤ -0.4 V, a steady-state HER feature is solely dominant. Since the Volmer step ($=\text{H}^*$ adsorption) is rate limiting, it is only accompanied by marginal H* coverage ($< 1\%$). At more positive potentials, the HER subsides and a bare surface is exposed until *OH adsorption sets in. At the onset of adsorption, the surface is immediately covered by 20 – 30 % *OH at which point repulsive lateral interactions between the adsorbates become limiting. At more positive potentials, *OH surface coverage slowly increases, which results from competition between increasing potential driving force towards adsorption and the increasing lateral interactions. A coverage of $\approx 30 - 50\%$ is reached when Cu oxidation sets in,⁵⁷ which is not included in this model. The Cu facets differ quantitatively in the onset potentials for HER and *OH adsorption which comes from the differences in adsorption and reaction energies (compare table S1 and Figure 2).

We obtain a direct comparison to experiment through simulated CVs (Figure 2, central panel), assuming a scan rate of 50 mV/s. This comparison identifies the reversible redox feature in the fingerprint region to arise from *OH ad-/desorption. A clear qualitative

Table 1: Comparison of OH adsorption-peak charge densities $\mu\text{C}/\text{cm}^2$ for the different Cu facets: (Second column) expected charge density for a full 1 ML coverage for comparison, (third column) experimental values, (fourth column) theoretical values. The measured potential of the OH adsorption-peak E_p [V vs. RHE] is given in the last column. The error for the experimental charge densities was estimated to $5 \mu\text{C}/\text{cm}^2$ (Estimated from the OH adsorption peak)

Cu facet	Charge density			E_p
	1 ML	exp.	theory	
(110)-(1 $\times$ 1)	173.4	25	54	-0.34
(110)-(1 $\times$ 2)	86.7		27	
(100)	245.2	58	59	-0.12
(111)	283.2	78	79	0.12

agreement in the shapes and positions of the *OH peaks, as well as in the HER features on the Cu(110) is seen (see Figure 2). The quantitative deviation between experimental and theoretical *OH adsorption peaks is found in a shift to positive potentials by $0.1 - 0.2 \text{ eV}$. This error is within the uncertainty of DFT. One qualitative difference vs. experiment is seen in the small trailing currents following the *OH adsorption peak, which result from a small and continuous increase in *OH coverage. While this phenomenon is probably present in the experimental signal, but to a negligible extent, it is likely overestimated in the simulation. This deviation may result from the idealized interaction model which neglects entropic barriers due to missing spatial resolution in the mean-field approach employed.⁵⁸

In contrast to the *OH adsorption free energy defining the *OH peak position, the H^* adsorption free energy has little influence on the CV. Since the HER is limited by the Volmer step, essentially all H^* on the surface is immediately consumed to form H_2 (SI Sec. IIId), which prevents a H^* adsorption peak. This behavior agrees with the present experimental data and underlines the importance of including kinetic processes into CV simulations. In the usually applied pure thermodynamic picture (which excludes HER), substantial H^* coverage is predicted from theoretical phase diagrams^{39,59} and simulated CVs.²⁷ This picture would also appear in the present work if the HER processes were excluded (SI Sec. IV).

The area under the *OH adsorption peaks is proportional to the charge transferred during the adsorption processes and thus to the surface coverage. As shown in Table 1, experimental

and theoretical charge densities for the main *OH adsorption peak agree. This result demonstrates an accurate description of the microscopic processes in the simulation. The transferred charge in the case of the assumed pristine Cu(110) suggests a (1×2)-reconstruction because it deviates by a factor of two for the non-reconstructed Cu(110). Coincidentally, the reconstruction does not change peak positions and shapes of the CV, since the atomic *OH adsorption site remains unaffected (SI Sec. II and III). It should be noted, however, that a clear experimental quantification of the charge density is difficult, since the *OH peak of the (110) is convoluted with the onset of HER.

In summary, we present a comprehensive study of the fingerprint CVs of Cu SCs. A facet-dependent *OH feature is observed experimentally and confirmed with *ab initio* simulations. Thus, a clear electrochemical distinction between the facets is established. These features can be used to verify the cleanliness of samples/setup and to deconvolute the facet distribution of nanoparticles, thin-films etc. which will help future rational catalyst design. Furthermore, these results provide understanding of the fundamental EC behavior of these Cu facets and can serve as a starting point for investigation of the CV response in more complex situations, for instance, in the presence of reactants. From a theoretical viewpoint, we illustrate a facile way of simulating faradaic and pseudo capacitive currents in CVs using microkinetic modeling. We demonstrate that kinetics are essential for an accurate description of the Cu/electrolyte interface in regard of (competitive) H* adsorption. The presented approach can be systematically extended to include more complex chemistry and simulate respective CVs.

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Supporting Information Available

Experimental details; full details of the DFT calculations and kinetic mean-field models; methodology for simulating CV-spectra from microkinetic models; detailed discussion of the influence of HER and the atomic model for the Cu/electrolyte interface.

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