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# 4 | The electrochemical characterization of copper single crystal electrodes in alkaline media

**Abstract**

The use of single crystals in electrochemistry requires careful characterization of the surface structure. This paper addresses the characterization of Cu single crystals using blank cyclic voltammetry in alkaline media. The adsorption and desorption of OH species in the underpotential region of $Cu_2O$ formation (-0.25 V - 0.2 V vs. RHE) in alkaline media occur at different potentials on Cu(111) and Cu(100), whereas OH adsorption on Cu(110) is not observed in this potential region. This allows for a direct distinction of the Cu(*hkl*) basal planes. The adsorption of OH on Cu(111) induces a reconstructed adlayer on the surface. On Cu(322), a stepped surface with 5 atom wide (111) terraces, OH adsorption is observed in the same potential range as on Cu(111), but on Cu(322) reconstruction does not seem to take place. This is explained by the fact that the unit cell of the reconstructed layer is much larger than the (111) terrace width of Cu(322) and, therefore, reconstruction cannot take place. Cu(911), having 5 atom wide (100) terraces, exhibits the same voltammetric features as Cu(100), but with a lower intensity. This is explained by the lower amount of (100) terraces present on this surface.

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## 4.1 Introduction

Copper has some unique properties in electrocatalysis, such as a high activity for the electrochemical reduction of nitrate and carbon dioxide. For nitrate reduction, Cu is one of the most active electrode materials.[143] On Cu electrodes, carbon dioxide is converted to hydrocarbons with a relatively high selectivity.[4,5] Therefore, Cu single crystals have been the subject of several recent electrochemical investigations, with the aim to relate the catalytic activity to the atomic surface structure.[87,143–145]

The use of single crystals requires detailed characterization of the atomic surface structure, to allow for the relation between surface structure and (electro-)chemical activity. Single crystal electrodes are usually characterized using blank cyclic voltammetry (CV). For Cu single crystals, the knowledge about the electrochemical characterization of the Cu(*hkl*) surfaces using blank voltammetry is limited. Therefore, we present here a method using blank voltammetry in alkaline media that clearly distinguishes the Cu basal planes, which can also be used to indicate the presence of steps on the surface. Our method builds on previous procedures for the electrochemical characterization of Cu single crystals.

Using blank voltammetry in $H_2SO_4$, only Cu(111) terraces can be distinguished, since on these terraces sulphate adsorption and desorption can be observed in the potential region between hydrogen evolution and Cu oxidation (-0.3 V - 0.3 V vs. RHE).[146,147] However, on Cu(100) the CV is completely featureless in this potential region.[146,147] We have also measured Cu(110) in $H_2SO_4$, which gave a CV very similar to that of Cu(100) (data not shown).

In their work on $CO_2$ reduction, Hori *et al.* present CVs of the Cu basal planes and a number of stepped surfaces in carbon monoxide-saturated phosphate buffers at pH 7.[5,87,148] For Cu(100) and Cu(110) a pair of peaks is observed in the CV, whereas these peaks were not observed in the CV of Cu(111). These peaks, with the peaks observed on Cu(100) at lower potentials compared with Cu(110), have been attributed to charge displacement due to desorption of phosphate during CO adsorption, as was confirmed by IR spectroscopy.[149] For the CVs of several stepped Cu surfaces, with steps of (100) and (111) orientation, similar peaks have been observed. Hori *et al.* have found that the charge of the peaks corresponds to the step density.[87,149] Recently, using voltammetry combined with STM, phosphate ad-

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sorption and desorption has been observed on Cu(111), accompanied with small peaks in the CV of Cu(111).[150] Overall, the characterization of Cu single crystals in CO saturated phosphate buffers can be used to distinguish the various Cu single crystals, but its main drawback is that it requires the use of carbon monoxide.

Another electrochemical characterization could make use of the differences in the CVs for the onset of $Cu_2O$ formation in alkaline media. The formation of $Cu_2O$ is preceded by the adsorption of oxygen species, which has been shown to be surface structure dependent.[151] Although it is possible to identify the Cu basal planes in this way, the differences are rather small, hence this method does not seem suitable for stepped surfaces.

For our characterization method we were inspired by the work of Jović and Jović, who have studied OH adsorption on Cu(111) and Cu(100) in alkaline media using cyclic voltammetry, a potentiostatic pulse technique and electrochemical impedance spectroscopy.[152,153] Their results showed very different CVs for Cu(111) and Cu(100) in the underpotential region of $Cu_2O$ formation (-0.25 V - 0.2 V vs. RHE). It was shown that slow and irreversible reconstruction of Cu(111) occurs as a consequence of OH adsorption/desorption. In the same potential region we have investigated, next to Cu(111) and Cu(100), the CVs of Cu(110) and two stepped surfaces: Cu(911), with the [5(100)x(111)] orientation, and Cu(322), with the [5(111)x(100)] orientation. These CVs all exhibit clear differences, and can therefore be used to characterize Cu single crystals.

## 4.2    Experimental

All experiments were carried out in an electrochemical cell using a three-electrode assembly at room temperature. The cell and glassware were boiled in ultra clean water (Millipore MilliQ gradient A10 system, 18.2 $M\Omega \cdot cm$) before each experiment. A gold wire was used as counter electrode and a reversible hydrogen electrode (RHE) in the same electrolyte was used as reference electrode. All potentials in this paper are referred to this electrode. The potential was controlled using an Ivium A06075 potentiostat.

The single crystal copper electrodes used were bead-type electrodes cut and polished with an accuracy down to 0.5° (icryst). Prior to each experiment the electrode was electropolished in 66% $H_3PO_4$ at 3 V vs. a Cu counter electrode for 10 seconds.[154] After electropolishing, the electrode
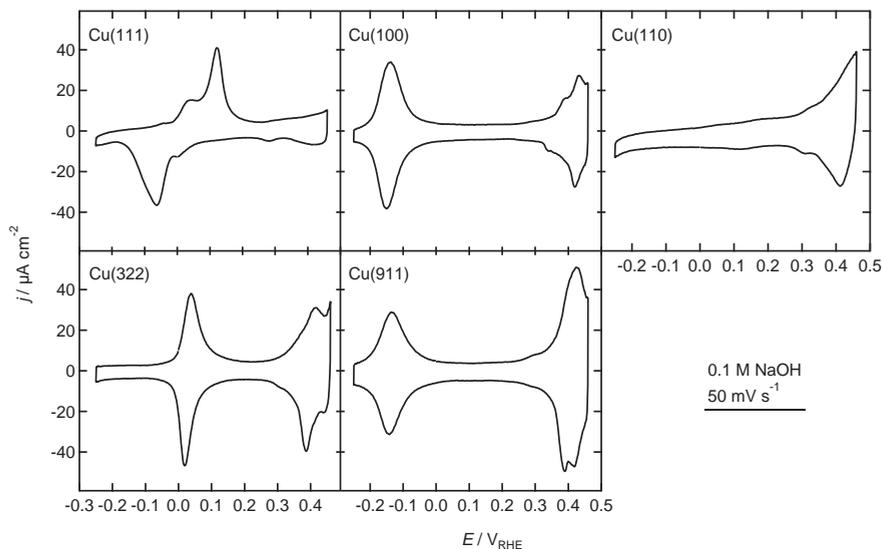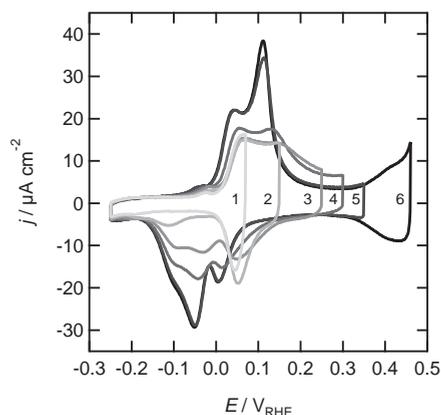
**Figure 4.1** Cyclic voltammograms of five Cu single crystals in 0.1 M NaOH, recorded at 50 mV s$^{-1}$.

was rinsed with water and transferred to the electrochemical cell. The potential of the electrode was 0 V when immersed in the electrolyte. All cyclic voltammograms were recorded until a stable voltammogram was obtained, using a sweep rate of 50 mV s$^{-1}$ .

The experiments were carried out in 0.1 M NaOH (pH 13) prepared from high purity reagents (Sigma-Aldrich TraceSelect) and ultra clean water. Argon (Air Products, 5.0) bubbling was used to deaerate the electrolyte.

## 4.3    Results

The CVs of the three Cu single crystal basal planes, Cu(111), Cu(100), and Cu(110) in 0.1 M NaOH are shown in Fig. 4.1. The CV of Cu(111) exhibits an anodic peak at 0.12 V, a cathodic peak at -0.06 V, and a pair of smaller peaks at 0.02 V. There is only a small oxidation/reduction current above 0.3 V. For Cu(100), a pair of peaks is observed at -0.15 V. The oxidation current

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**Figure 4.2** Cyclic voltammograms of Cu(111) in 0.1 M NaOH, scanned to increasing anodic potentials, recorded at 50 mV s$^{-1}$.

above 0.3 V is larger, with pair of peaks around 0.43 V. For Cu(110) the CV looks again different, no peaks are observed between -0.2 and 0.3 V. The oxidation current at high potentials is the largest of the three basal planes. For most CVs shown in Fig. 4.1, but in particular for Cu(111) and Cu(110), the current is not symmetrical around zero below 0 V, due to the presence of oxygen in the electrolyte which is reduced at the electrode. This oxygen is very hard to remove in alkaline media.

Fig. 4.1 also shows the CVs of the two stepped Cu single crystal surfaces investigated in this work. Cu(322), which has 5 atoms wide (111) terraces with a (100) step, shows a pair of peaks at 0.02 V, at a similar potential at which the small pair of peaks at Cu(111) is observed. The oxidation/reduction current above 0.3 V is significantly higher compared with Cu(111), has a peak at 0.41 V and a corresponding reduction peak at 0.38 V. Cu(911), with 5 atoms wide (100) terraces and a (111) step, exhibits a pair of peaks at the same potentials as observed on Cu(100), but the current density for the peak at -0.15 V is lower. At higher potentials we observe an anodic peak at 0.42 V, and two overlapping cathodic peaks at 0.39 V and 0.42 V.

To investigate the rather complicated CV of Cu(111) in more detail, we performed the measurement shown in Fig. 4.2. We kept the Cu(111) electrode at a standby potential of -0.25 V before and after recording the CV, which is different from the CVs shown in Fig. 4.1, where a standby potential of 0 V was used. Next, we performed a series of CVs in which we stepwise increased the maximum anodic potential. In the first scan (no. 1) a pair of peaks at 0.05 V is observed, which is at a slightly higher potential compared with the pair of peaks at 0.02 V in the CV of Cu(111). With increasing anodic potentials, the peaks at 0.12 V and -0.06 V start growing, until a CV is obtained that looks similar to the CV of Cu(111) shown in Fig. 4.1

## 4.4    Discussion

The underpotential region of $Cu_2O$ formation (-0.25 V - 0.2 V) in alkaline media has not been extensively studied, only a few papers address the CV in this potential region. [152,153,155,156] By comparing surface-enhanced Raman spectra of $H_2O$ and $D_2O$ alkaline electrolytes, Härtinger *et al.* observed Raman bands corresponding to the formation of surface CuOH species on Cu(111). [155] The intensity of these bands was found to depend on potential, and on the time of holding the electrode at a given potential. The intensity of the bands increases when stepping from 0.5 V, a potential where the formation of $Cu_2O$ starts, to a much more negative potential, -0.1 V.

Our CV of Cu(100), shown in Fig. 4.1, is very similar to the CV recorded by Jović and Jović, [153] and, based on the described literature, the pair of peaks observed at -0.15 V is assigned to OH adsorption/desorption. The charge corresponding to these peaks, measured between -0.25 V and 0 V, is ~50 $\mu C\,cm^{-2}$. Since the charge corresponding to a full monolayer is 240 $\mu C\,cm^{-2}$, this charge corresponds to a coverage of 0.2 ML.

The same peaks are observed in the CV of Cu(911), although with a lower intensity: the calculated charge is ~46 $\mu C\,cm^{-2}$. Since these peaks are observed at the same potential as for Cu(100), these peaks can be assigned to OH adsorption/desorption on/from the (100) terraces, and the lower charge corresponds well with the lower amount of (100) terraces present on this surface.

For Cu(111), we observe a more complicated voltammogram. The CV shown in Fig. 4.1 is similar, but not identical to the CV recorded by Jović and Jović. [153] However, as can be concluded from Fig. 4.2, the position and

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intensity of the peaks strongly depends on the maximum anodic potential of the CV, and the CVs in Fig. 4.2 scanned to ∼0.3 V look much more like the CV shown in Ref. 153. From Fig. 4.2 it can also be concluded that the anodic peak at 0.12 V and the cathodic peak at -0.06 V are related, and in between those peaks there is a smaller pair of peaks at 0.02 V. Fig. 4.2 suggests that these peaks are developed only if the electrode is cycled to ∼0.2 V and higher. The total charge corresponding to these peaks, calculated between -0.25 V and 0.2 V, is ∼62 μC cm$^{-2}$. A full monolayer coverage on Cu(111) corresponds to a charge of 302 μC cm$^{-2}$,[157] so the charge of the CV corresponds to a coverage of 0.2 ML of OH species, in agreement with the work of Maurice *et al.* on Cu(111).[156]

Combining cyclic voltammetry with STM, Maurice *et al.* observed a reversible adsorption/desorption process in the underpotential region of $Cu_2O$ formation on Cu(111) in NaOH, with a reversible potential of formation of 0.092 V.[156] Adsorption and desorption were observed to initiate at the step edges on the upper terrace side, causing a lateral growth of the terraces and the formation of Cu adislands having the $Cu_2O(111)$ structure, with a hexagonal lattice having a unit vector of 0.69 ±0.02 nm and two coincidence cells: $(\sqrt{21} \times \sqrt{21})$R.10° and $(\sqrt{49} \times \sqrt{49})$R.20°. Charge transfer measurements indicated adsorption of hydroxide or hydroxyl groups with one adsorbate per unit cell, *i.e.* a coverage of ca. 0.2 ML. In the presence of chlorine, no lateral growth of the terraces was observed, since the strongly adsorbing Cl$^-$ blocks the step edges.[158] Jović and Jović suggested that irreversible surface reconstruction of Cu(111) occurs as a consequence of the adsorption/desorption of OH$^-$ species, and that adsorption of OH$^-$ species takes place in the potential range more negative than -0.17 V only on reconstructed surfaces. They related the large peaks in the CV at 0.12 V and -0.06 V to OH$^-$ adsorption/desorption with a simultaneous lifting of the surface reconstruction. In Fig. 4.2 we observe a reversible CV up to ∼0.2 V, in agreement with the data of Maurice *et al.* When scanning to higher potentials (scan nos. 3-5) the CV becomes irreversible, which we attribute to OH adsorption/desorption on a irreversibly reconstructed surface induced by O or OH species.

Since the total charge in the CV of Cu(111) corresponds to a fifth of a monolayer, it is likely that the other, smaller pair of peaks at 0.02 V is also related to OH adsorption/desorption. These peaks at 0.02 V are also

observed on Cu(322), but with a higher intensity. The calculated charge of the peaks at 0.02 V in the CV of Cu(322) is $\sim$48 $\mu C\,cm^{-2}$, similar to the charge measured on Cu(911), suggesting that the peaks are related to same phenomena: OH adsorption/desorption. Considering that the peaks at 0.02 V at Cu(322) occur at a similar potential on Cu(111), it is therefore likely that these peaks in both CVs are also related to OH adsorption/desorption from (111) terraces. We assign these peaks at 0.02 V, both on Cu(111) and Cu(322), to OH adsorption/desorption on/from unreconstructed (111) terraces. We propose this based on the fact that Cu(322) has only 5-atom wide (111) terraces, while the OH induced reconstruction has the $Cu_2O$(111) structure, with a unit cell that is 29 or 44 times the unit cell of Cu(111),[156,159] which would not fit on the (111) terraces of Cu(322). Hence, the charge of the peaks at 0.02 V is much lower on Cu(111) than on Cu(322), since Cu(111) is mainly reconstructed. Since the adsorption of OH induces a lateral terrace growth,[156,158] this could mean that the average (111) terrace width on Cu(322) increases. However, from our CV we cannot deduce further information on the reconstruction/growth of the (111) terraces.

On Cu(100), OH induced reconstruction has also been reported, but the unit cell is much smaller than the $Cu_2O$(111) reconstruction observed on Cu(111). Kunze *et al.* have reported on the OH induced structural modifications of Cu(100) in the underpotential range of $Cu_2O$ formation.[160] Adsorption of OH induces the formation of dimers of superimposed Cu atoms, presumably in bridging positions. The dimers of superimposed Cu atoms form zig-zag chains, with long range ordering of the zig-zag chains in areas limited in width with $c(2 \times 6)$ and $c(6 \times 2)$ domains.

In the CV of Cu(110) no peaks are observed, suggesting that OH adsorption/desorption does not take place in this potential region. One possibility is that Cu(110) adsorbs OH stronger and, therefore, at more cathodic potentials. However, we did not observe a peak in the CV between the start of the hydrogen evolution (-0.35 V) and -0.2 V.

Comparing the CVs of the three Cu basal planes above 0.3 V, we observe the lowest oxidation/reduction current on Cu(111), a relatively high current on Cu(110), and a peak at 0.45 V on Cu(100). This is similar to the results obtained by Droog *et al.*[151] They observed the highest onset potential for $Cu_2O$ formation on Cu(111) and a sharp peak at the onset of $Cu_2O$

formation on Cu(100). The stepped Cu single crystal surfaces investigated in this paper also have a high oxidation/reduction current in this potential region, and both the CVs of Cu(322) and Cu(911) exhibit a peak at 0.45 V. It seems that step sites, and more open surfaces like Cu(110), are more prone to $Cu_2O$ formation. Our data suggest that the height of the current density in this potential region is at least indicative of the presence of steps on the surface.

## 4.5 Conclusions

We have shown that blank voltammetry in alkaline media is a good way to characterize Cu single crystals. The adsorption and desorption of OH species in alkaline media occur at different potentials on Cu(111) and Cu(100), whereas OH adsorption on Cu(110) is not observed in the same potential region. On Cu(111) this OH adsorption causes a reconstructed adlayer on the surface, leading to a rather complicated voltammetric response. On Cu(322), a stepped surface with 5 atom wide (111) terraces, OH adsorption is observed in the same potential range as on Cu(111), but here reconstruction does not seem to take place, leading to a corresponding simpler voltammetric response. This may be explained by the fact that the unit cell of the reconstructed adlayer is much bigger than the terrace width on Cu(322). The CV of Cu(911), which has 5 atom wide (100) terraces, shows the same voltammetric features as Cu(100) but with a lower intensity, which can be explained by the lower amount of (100) terraces present on this surface. The oxidation/reduction current above 0.3 V is higher on Cu(110) and the stepped surfaces, probably because on open surfaces sites and steps it is easier to form $Cu_2O$. Therefore, the CV in this potential range is indicative of steps on the surface.