SCIENTIFIC WORKSHOP ON THE MECHANISM OF COPPER CANISTER CORROSION IN AQUEOUS ENVIRONMENTS

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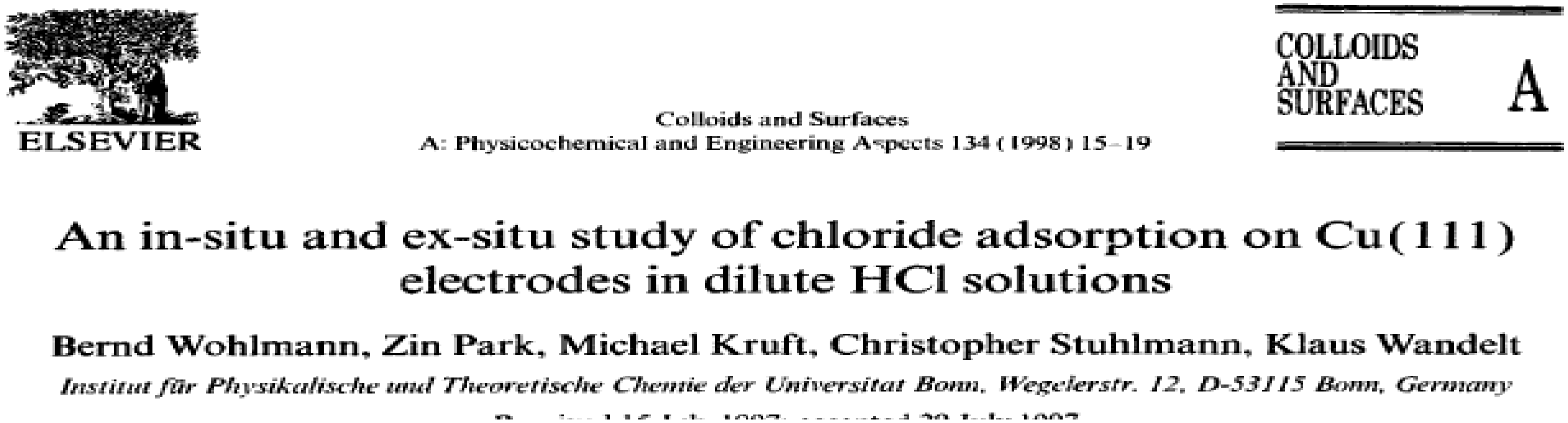
OUTLINE

- **Sub-thermodynamic adsorption of anions on Cu**
- **Sub-thermodynamic formation oxygen and hydroxide species on Cu**
- **The presence of irreducible oxides on Cu**
- **The dominance of sulphide**

LOTS OF ANIONS ADSORB ON COPPER TO PRODUCE SUB-THERMODYNAMIC ADSORBED STATES



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Colloids and Surfaces
A: Physicochemical and Engineering Aspects 134 (1998) 15–19

COLLOIDS AND SURFACES A

An in-situ and ex-situ study of chloride adsorption on Cu(111) electrodes in dilute HCl solutions

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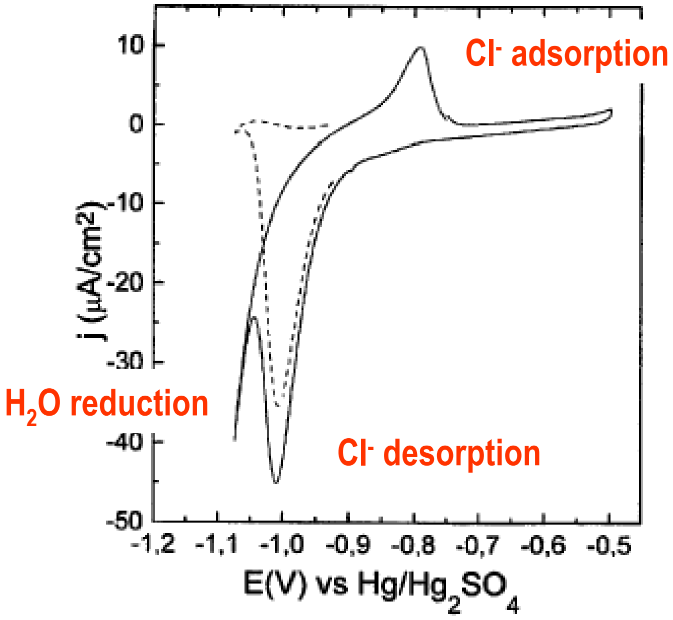
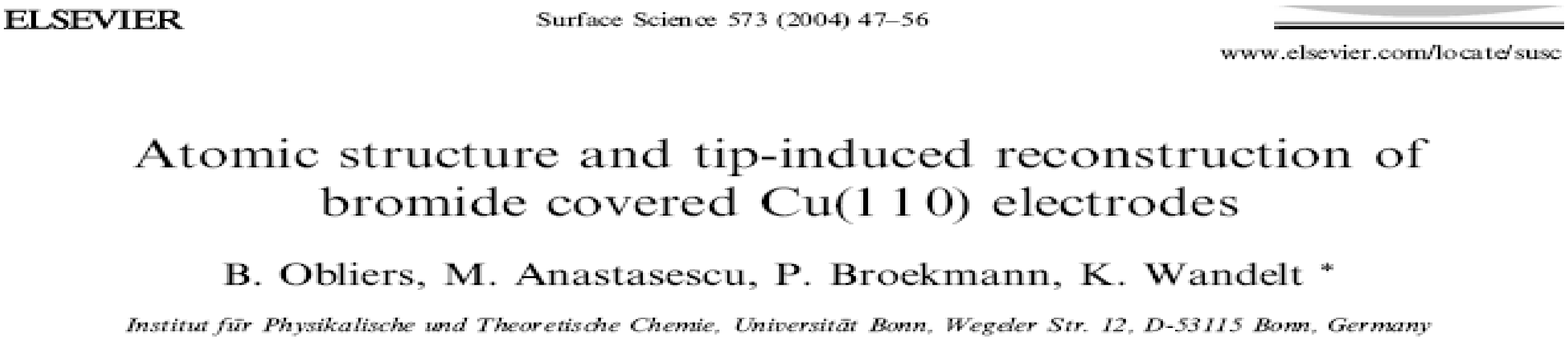


Fig. 1. Cyclic voltammogram of Cu(111) in 10 mM HCl with a scan rate of 10 mV/s. The dashed curve is obtained after correction for the extrapolated hydrogen evolution current on the bare Cu(111) surface (see text for details).

- **Chloride anions strongly interact With Cu surfaces.**
- **Adsorbed chloride can catalyze water reduction**
- **This can be seen in the imbalance in charge between the adsorption and desorption peaks**
- **The pH is ~ 2**
- **Cl^- adsorption destroys surface O adsorbed species**



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Surface Science 573 (2004) 47–56

www.elsevier.com/locate/susc

Atomic structure and tip-induced reconstruction of bromide covered Cu(1 1 0) electrodes

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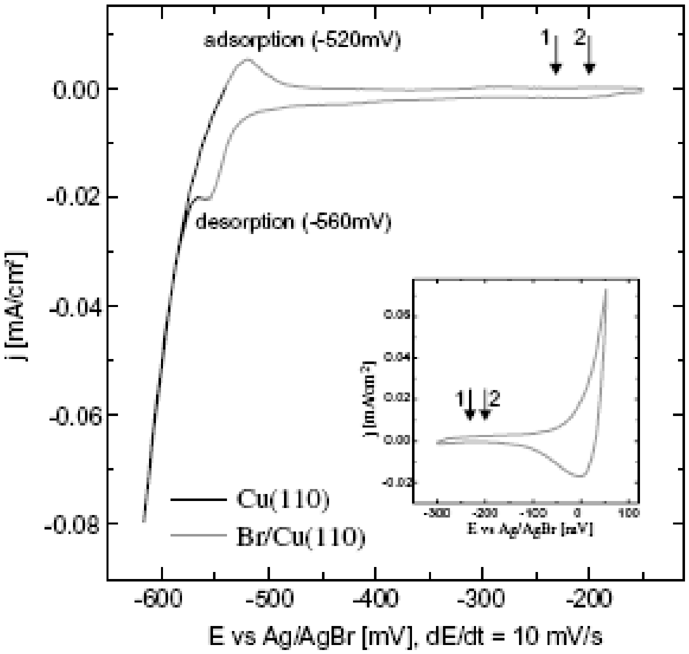

Fig. 1. Representative cyclic voltammogram of Cu(1 1 0) in 10 mM HBr, the inset shows the onset of the anodic copper corrosion followed by the redeposition of copper material in the reverse potential sweep, d*E*/d*t* = 10 mV/s.

- **Bromide adsorption-desorption also occurs close to the H_2O reduction region**
- **The pH is approximately 2**

ELSEVIER Journal of Electroanalytical Chemistry 467 (1999) 307–324

In-situ STM investigation of specific anion adsorption on Cu(111)☆

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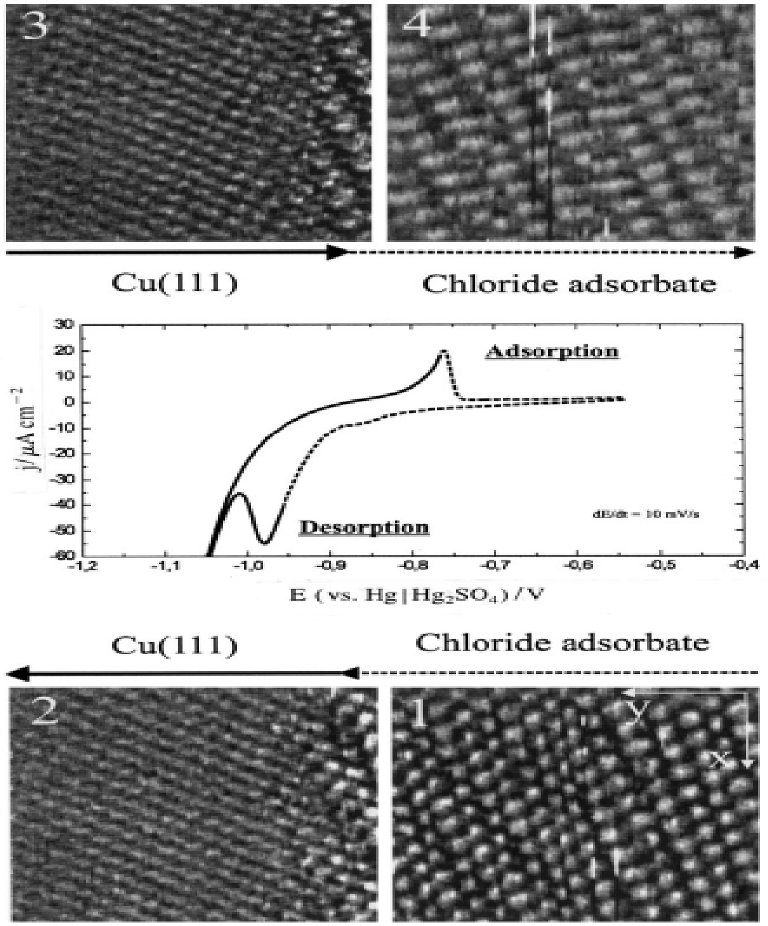

Fig. 2. Cu(111) in 10 mM HCl, potentiodynamic STM measurement: series of high resolution STM images correlated directly with the cyclic voltammogram, 4.5 × 4.5 nm^2, $I_t = 10$ nA.

Cl$^-$ adsorption causes surface restructuring but the original surface is recovered on desorption

FORMATION OF SUB-THERMODYNAMIC $Cu(OH)_{ads}$ AND $Cu_2(O)$ STATES IS COMMONLY OBSERVED ACROSS THE FULL pH RANGE

JOURNAL OF CHEMICAL PHYSICS VOLUME 110, NUMBER 12 22 MARCH 1999

Comparison of aqueous and native oxide formation on Cu(111)

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In-situ X-ray diffractometry

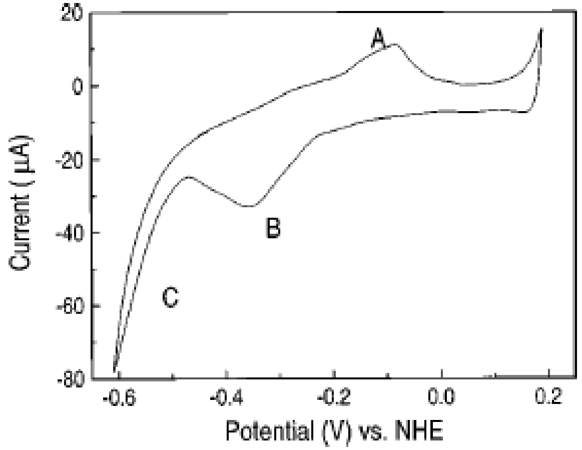

FIG. 6. Cyclic voltammetry of Cu(111) single crystal in 0.1 M $NaClO_4$ at *p*H 4.5 measured at 10 mV/s. Potentials were measured with respect to Ag/AgCl (3 M KCl) and have been converted to the normal hydrogen electrode (NHE) scale. Peak "A" and peak "B" are due to oxidation and reduction of the Cu(111) surface, respectively. Peak "C" is due to reduction of protons (H^+) to hydrogen gas (H_2).

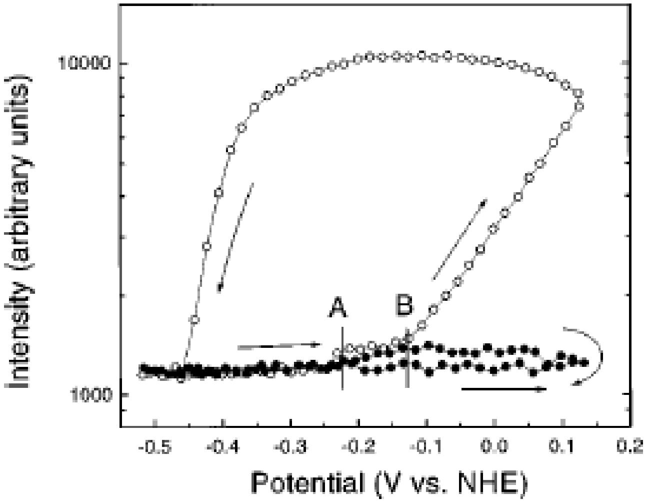

FIG. 7. Diffraction intensity of the reversed (open symbols) and aligned (solid symbols) oxides as a function of potential. Potentials were measured with respect to Ag/AgCl and have been converted to the normal hydrogen electrode (NHE) scale. The arrows indicate the sweep direction.

Oxides grown in air (possibly slightly humid) and electrochemically are both cuprite (Cu_2O)

A – onset of oxidation
B – onset of film thickening for one oxide orientation

Region of sub-thermodynamic stability of monolayer oxide phase

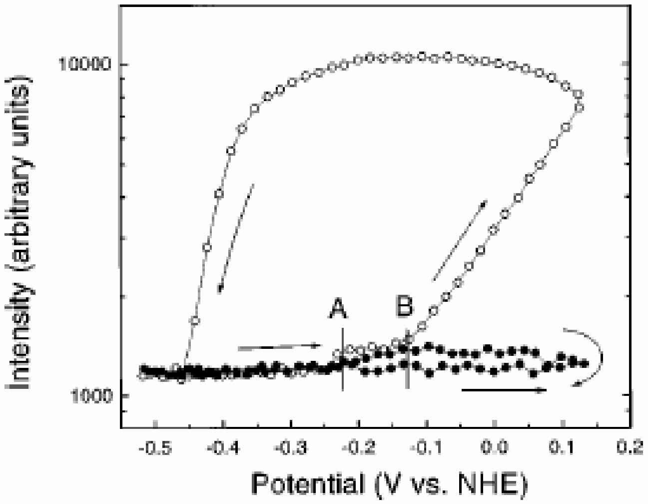

FIG. 7. Diffraction intensity of the reversed (open symbols) and aligned (solid symbols) oxides as a function of potential. Potentials were measured with respect to Ag/AgCl and have been converted to the normal hydrogen electrode (NHE) scale. The arrows indicate the sweep direction.

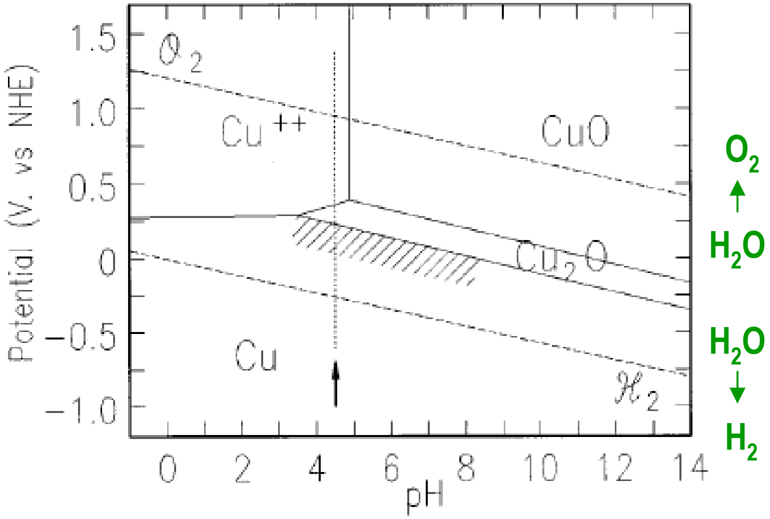

FIG. 12. Modification to the Pourbaix diagram for the copper/water system to include the new monolayer phase identified in this work. This is a phase diagram representing the equilibrium state of Cu as a function of *p*H and potential (Ref. 13). The dashed lines indicate the potential range of stability of H_2O versus formation of H_2 and O_2, as labeled. The Cu^{++} concentration dependence is not shown and is fixed at 10^{-2} M. Potentials are referenced to the normal hydrogen electrode (NHE). The arrow and dotted line shows the *p*H used in these experiments. The shaded region in the center of the figure denotes the range of stability in potential of the *monolayer* oxide at this *p*H.

No oxide present in H_2O reduction region

ELSEVIER Journal of Electroanalytical Chemistry 384 (1995) 105–113

Effect of interfacial pH on the reduction of oxygen on copper in neutral $NaClO_4$ solution

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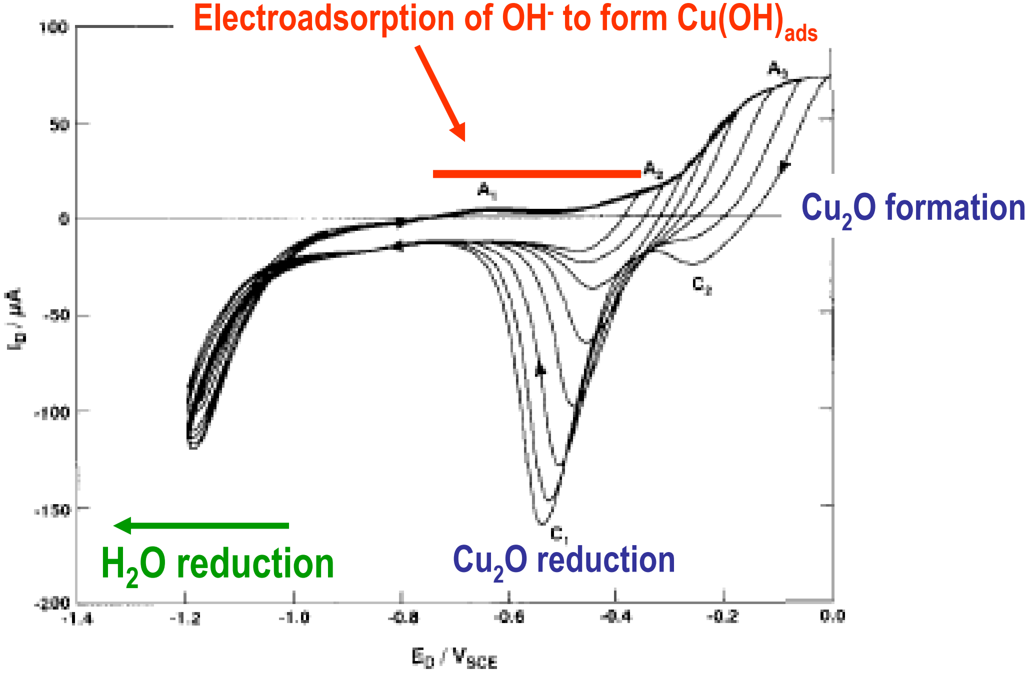


Electroadsorption of OH^- to form $Cu(OH)_{ads}$

Cu$_2$O formation

H_2O reduction

Cu$_2$O reduction

Fig. 6. Voltammograms recorded on a Cu electrode in deaerated pH 10 0.1 mol dm^{-3} $NaClO_4$. pH adjusted with NaOH. Successive scans are shown with upper potential limits between −0.35 and 0.0 V. Disc area, 0.33 cm^2; rotation rate, 14.3 Hz; potential scan rate, 100 mV s^{-1}.

O_2 reduction kinetics influenced
By $Cu(OH)_{ads}/Cu_2O$ layer

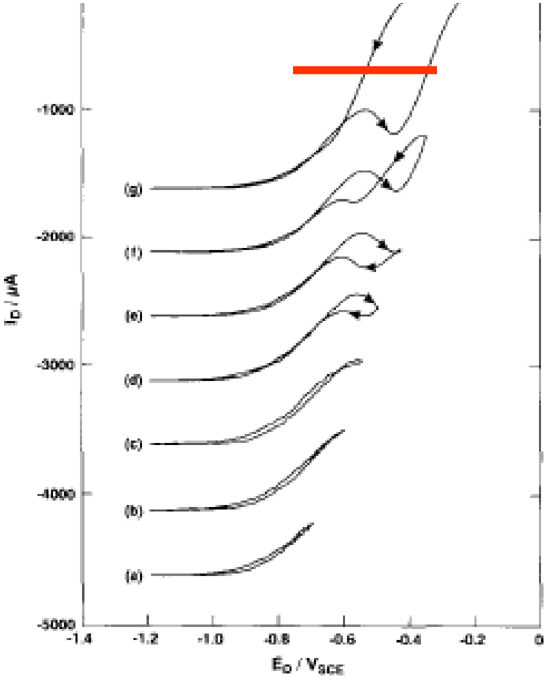
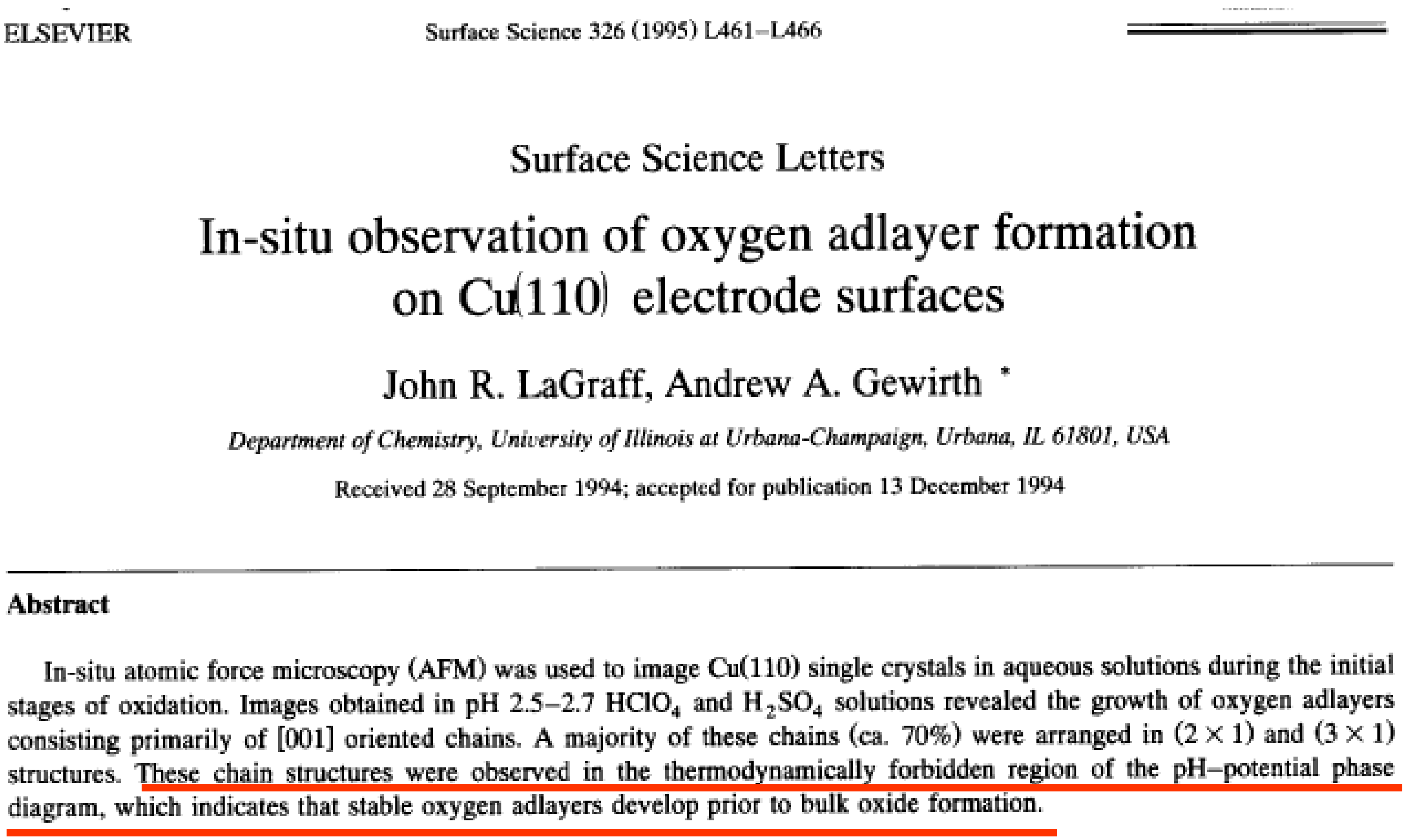


Fig. 5. Cyclic voltammograms for oxygen reduction on Cu in oxygenated unbuffered 0.1 mol dm^{-3} $NaClO_4$. Each successive voltammogram was scanned to a more positive potential limit E_D^U: (a) −0.70 V; (b) −0.60 V; (c) −0.55 V; (d) −0.50 V; (e) −0.425 V; (f) −0.35 V; (g) −0.10 V. The current axis refers to scan (g) with other scans offset by increments of 500 μA for clarity. Disc area, 0.37 cm^2; rotation rate, 14.3 Hz; potential scan rate, 10 mV s^{-1}.

No observable influence of films in the water reduction region



ELSEVIER Surface Science 326 (1995) L461–L466

Surface Science Letters

In-situ observation of oxygen adlayer formation on Cu(110) electrode surfaces

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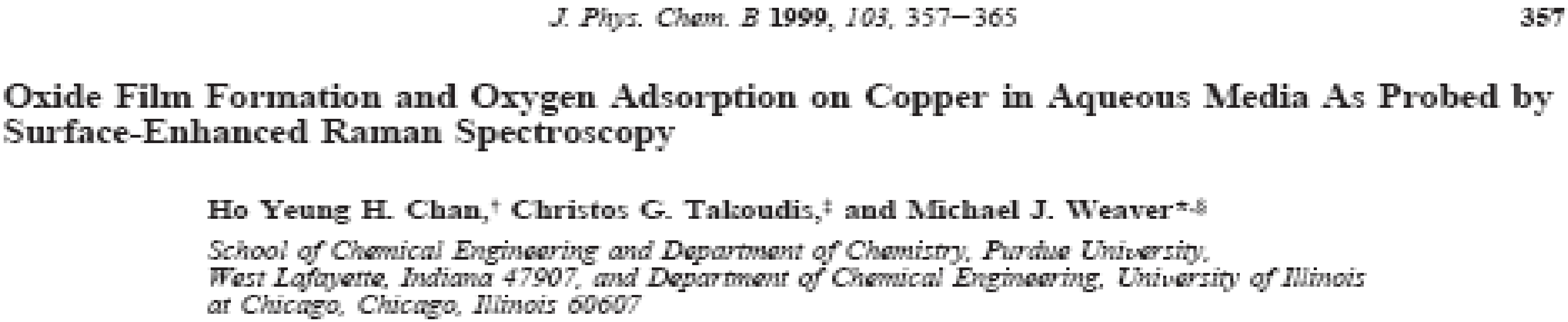
Received 28 September 1994; accepted for publication 13 December 1994

Abstract

In-situ atomic force microscopy (AFM) was used to image Cu(110) single crystals in aqueous solutions during the initial stages of oxidation. Images obtained in pH 2.5–2.7 $HClO_4$ and H_2SO_4 solutions revealed the growth of oxygen adlayers consisting primarily of [001] oriented chains. A majority of these chains (ca. 70%) were arranged in (2 × 1) and (3 × 1) structures. These chain structures were observed in the thermodynamically forbidden region of the pH–potential phase diagram, which indicates that stable oxygen adlayers develop prior to bulk oxide formation.

- Adsorbed O or OH species observed on the Cu surface prior to bulk Cu_2O formation; i.e., in the thermodynamically-forbidden region of the Potential-pH diagram.
- Applying negative potentials removes these species enabling resolution of the Cu (110) surface.
- It was concluded this is in quailitative – but not quantitative – agreement with the potential-pH diagram


J. Phys. Chem. B **1999**, *103*, 357−365 **357**

Oxide Film Formation and Oxygen Adsorption on Copper in Aqueous Media As Probed by Surface-Enhanced Raman Spectroscopy

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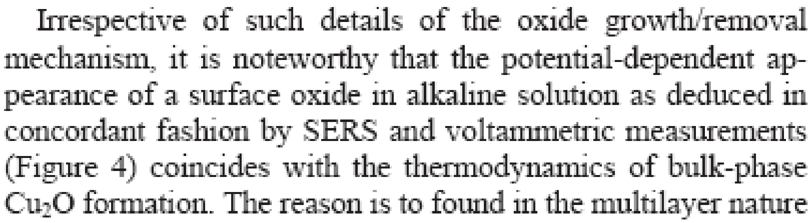
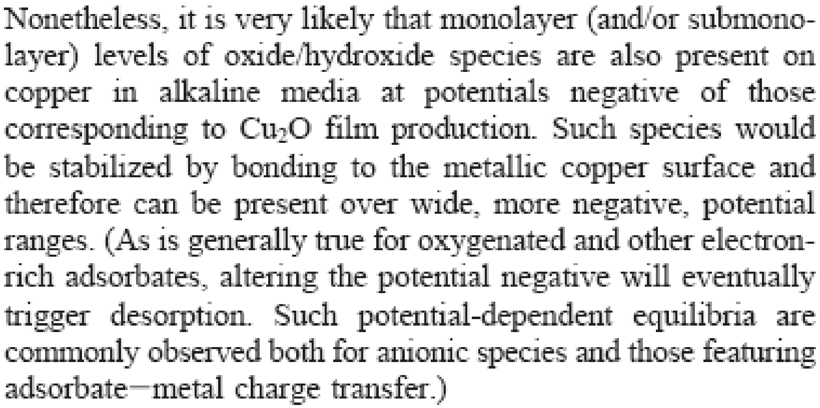
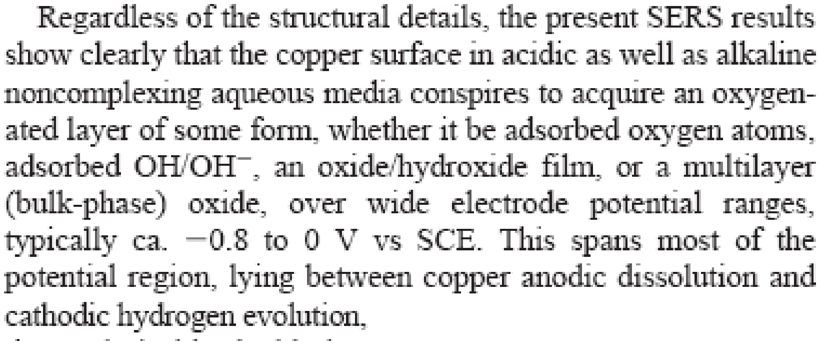

Irrespective of such details of the oxide growth/removal mechanism, it is noteworthy that the potential-dependent appearance of a surface oxide in alkaline solution as deduced in concordant fashion by SERS and voltammetric measurements (Figure 4) coincides with the thermodynamics of bulk-phase Cu_2O formation. The reason is to found in the multilayer nature

Extensive oxidation follows thermodynamic expectations

Monolayers or submonolayers of Adsorbed O and OH are possible sub-thermodynamically


Nonetheless, it is very likely that monolayer (and/or submonolayer) levels of oxide/hydroxide species are also present on copper in alkaline media at potentials negative of those corresponding to Cu_2O film production. Such species would be stabilized by bonding to the metallic copper surface and therefore can be present over wide, more negative, potential ranges. (As is generally true for oxygenated and other electron-rich adsorbates, altering the potential negative will eventually trigger desorption. Such potential-dependent equilibria are commonly observed both for anionic species and those featuring adsorbate−metal charge transfer.)


Regardless of the structural details, the present SERS results show clearly that the copper surface in acidic as well as alkaline noncomplexing aqueous media conspires to acquire an oxygenated layer of some form, whether it be adsorbed oxygen atoms, adsorbed OH/OH^-, an oxide/hydroxide film, or a multilayer (bulk-phase) oxide, over wide electrode potential ranges, typically ca. −0.8 to 0 V vs SCE. This spans most of the potential region, lying between copper anodic dissolution and cathodic hydrogen evolution,

Only formed in the potential region between the equilibrium potentials Cu corrosion in H_2O.

J. Electroanal. Chem., 111 (1980) 61—70

INITIAL STAGES OF ANODIC OXIDATION OF POLYCRYSTALLINE COPPER ELECTRODES IN ALKALINE SOLUTION

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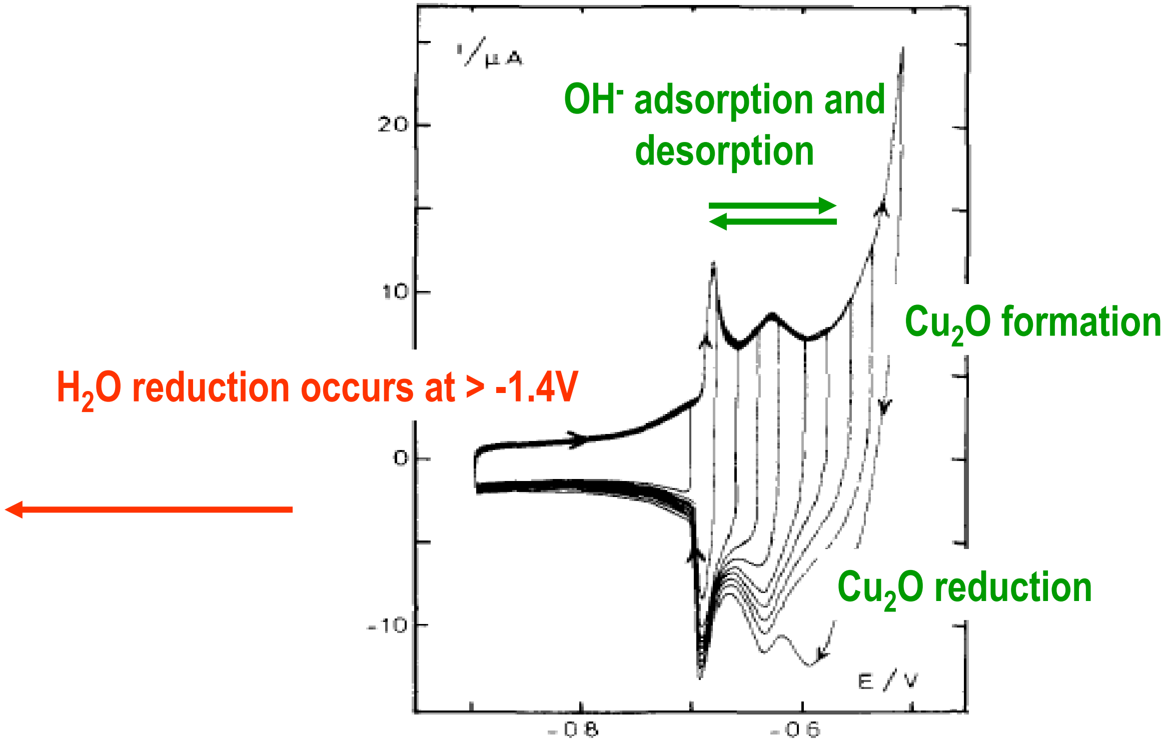


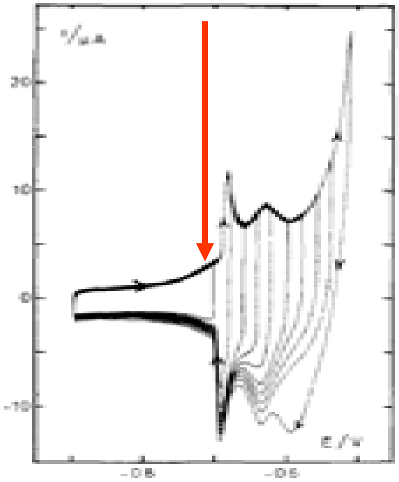
OH^- adsorption and desorption

Cu_2O formation

H_2O reduction occurs at > -1.4V

Cu_2O reduction

Fig. 2. Potentiodynamic charging curves for copper up to various potentials; 1 mol dm^{-3} NaOH, 22°C, dE/dt = 20 mV s^{-1}. Apparent surface area 0.28 cm^2.



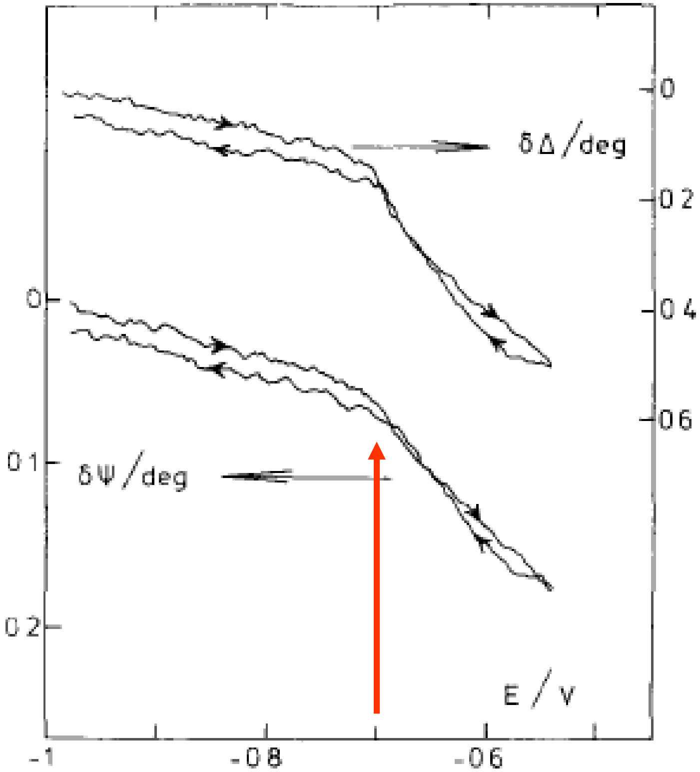


Fig. 5. Change in Δ and ψ during potential scanning up to −540 mV. Cu in 1 mol dm^{-3} NaOH, 22°C, dE/dt = 20 mV s^{-1}.

Potential at which $Cu(OH)_{ads}$ occurs is confirmed by ellipsometry

AIR-FORMED OXIDE FILMS AND FILMS FORMED BY TRACES OF DISSOLVED OXYGEN ARE HARD TO FULLY REDUCE

The electrochemical reduction of hydrogen peroxide on polycrystalline copper in borax buffer

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[b] *INQUIMAE, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Buenos Aires, Pab. II, Ciudad Universitaria, 1428 Buenos Aires (Argentina)*
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(Received 1 November 1993; in revised form 19 January 1994)

Journal of Electroanalytical Chemistry, 374 (1994) 179–187

Ellipsometry shows a monolayer of Cu(I) oxide still exists at -1.1V; i.e., H_2O reduction occurs on this layer

"A thin Cu_2O film is likely to be present owing to incomplete pre-reduction Of the air-formed film. This is known to occur with passive films when their electronic properties lead to the occurrence of the hydrogen evolution reaction in preference to film reduction"

"Even when working with deoxygenated solutions, traces of oxygen…….will lead to the formation of an irreversible attached layer of chemisorbed oxygen that cannot be reduced electrochemically"

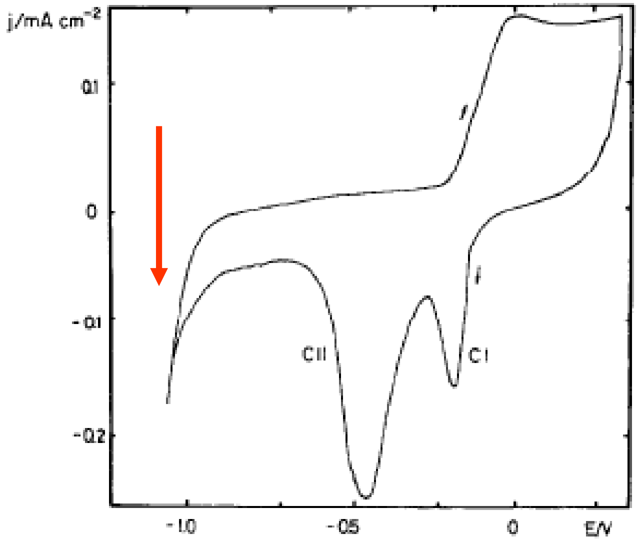
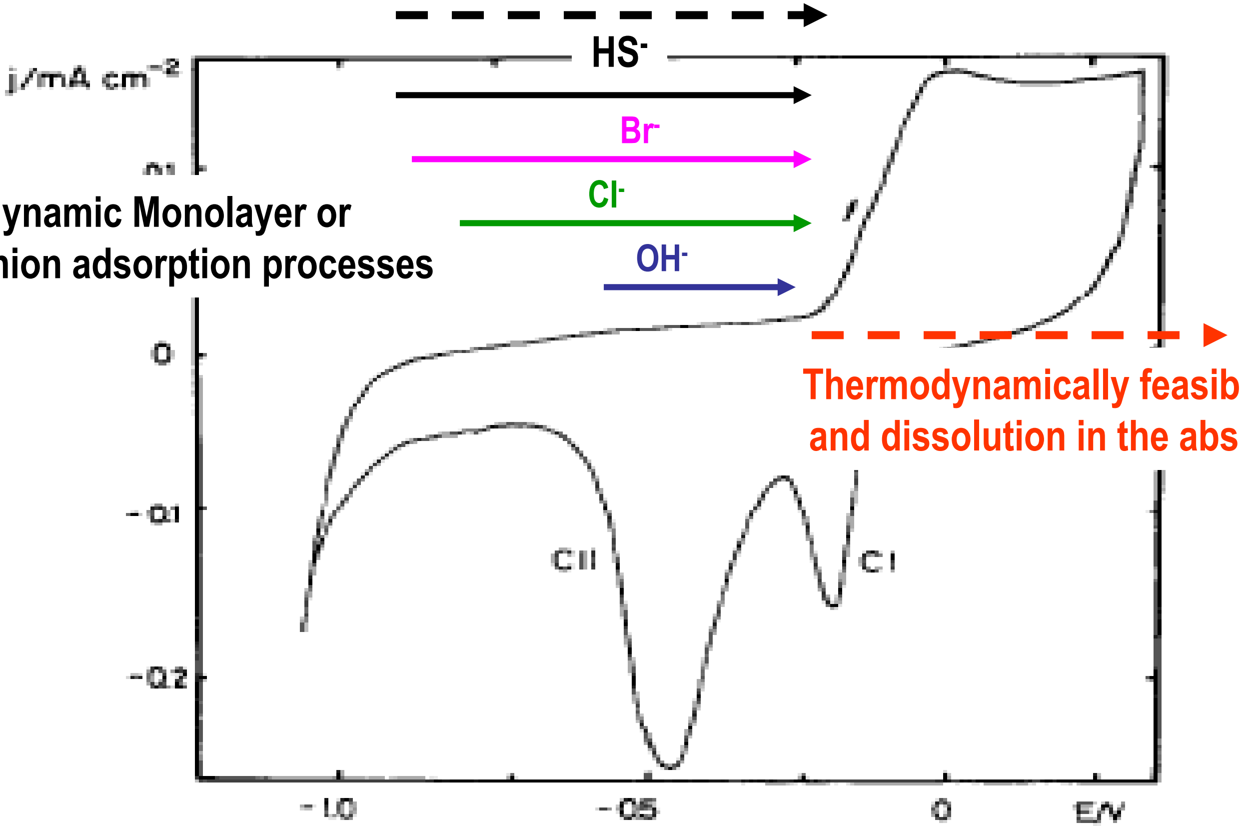


Fig. 1. Cyclic voltammetry of copper in oxygen-free 0.1 M borax buffer (scan rate $\upsilon = 0.02$ V s^{-1}).



Thermodynamically feasible oxidation
In the presence of HS$^-$

HS$^-$

Br$^-$

Cl$^-$

OH$^-$

Sub-thermodynamic Monolayer or
Submonolayer Anion adsorption processes

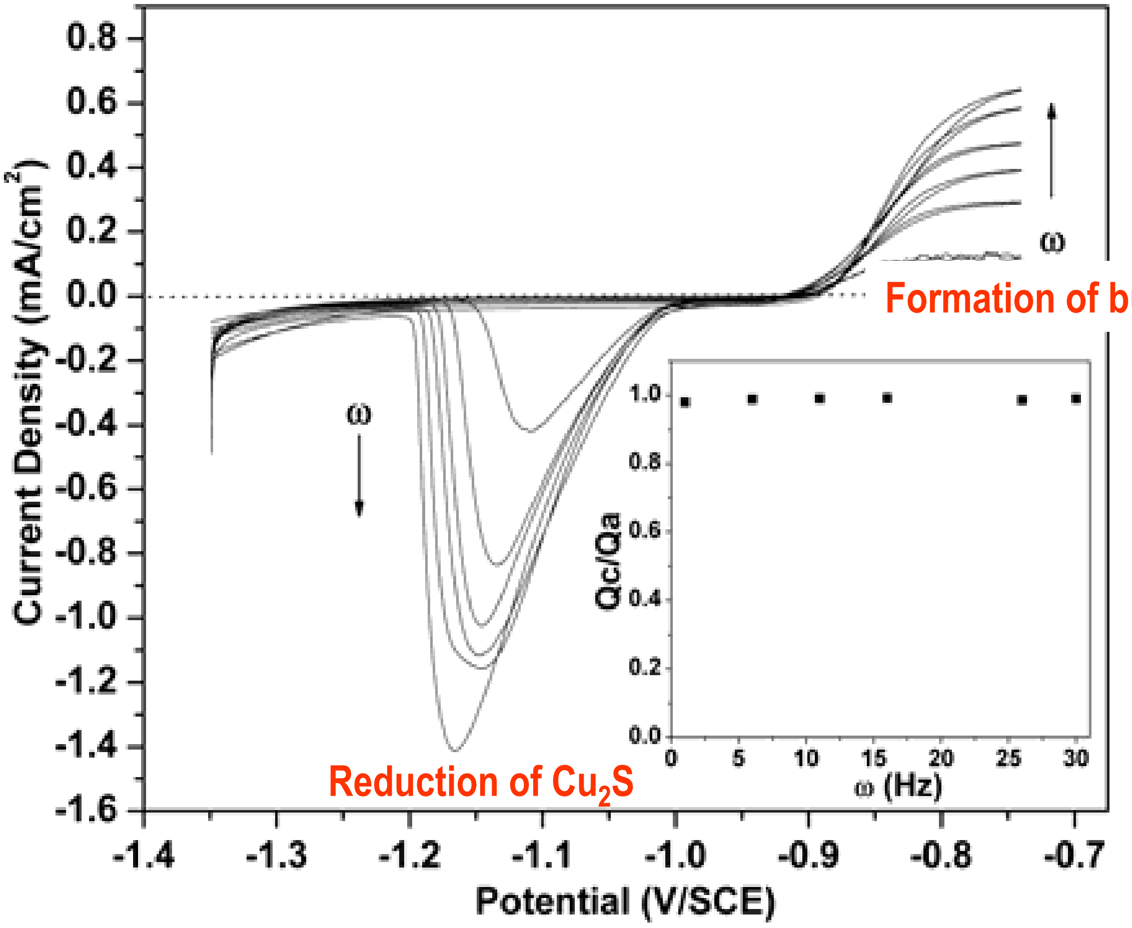
Thermodynamically feasible oxidation
and dissolution in the absence of HS$^-$

Fig. 1. Cyclic voltammetry of copper in oxygen-free 0.1 M borax buffer (scan rate $v = 0.02\ \mathrm{V\ s^{-1}}$).

Sulphide reacts at a diffusion controlled rate
To produce bulk Cu_2S

Cl^- adsorption

OH^- adsorption



Formation of bulk Cu_2S

Reduction of Cu_2S

In the presence of all other anions, sulphide dominates Cu corrosion behaviour