IN SITU X-RAY ABSORPTION SPECTROSCOPY STUDY OF UNDERPOTENTIAL DEPOSITION OF COPPER ON PLATINUM (100)

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Abstract—X-Ray absorption spectroscopy (XAS) spectra have been recorded for the electrochemical adsorption of Cu on Pt(100) in the fluorescence detection mode at grazing incidence, with polarization parallel to the surface During data collection, the Pt(100) surface was under potentiostatic control in a 10^{-4} M Cu^{2+} electrolytic solution, in order to maintain a monolayer coverage The near-edge structure of the copper K-edge resembles that of Cu^{+} The Fourier transform of the EXAFS spectra shows a first peak at 0 15 nm, and a broad unresolved peak with maximum at 0 30 and a shoulder at 0 37 nm The first single peak is associated with oxygen neighbours at 0 197 nm The unresolved peak is built up from contributions of copper first and second neighbours The distance of first copper neighbours is 0 309 nm, and that of second copper neighbours is 0 393 nm, equal to the substrate lattice parameter (0 3929 nm) This suggests that a first copper adlayer of half monolayer density is in registry with the platinum unreconstructed (100) surface net A second copper adlayer of the same density lies over the first adlayer, at a distance of 0 135 nm The copper atoms in this second layer are in the fourfold geometry with respect to the underlying copper half-monolayer These layers form a $c(2 \times 2)$ periodicity on the Pt (100) substrate The copper–oxygen distance is about half the second copper–copper distance The sharing of oxygen between the two copper adlayers is unclear

Key words X-ray absorption, underpotential deposition, Pt(100), copper

INTRODUCTION

Electron spectroscopies are attractive to study the structure and composition of single crystal surfaces modified by electrochemical treatments such as adsorption desorption cycles or underpotential deposition (*upd*)[1] of a monolayer of foreign atoms because they are very surface sensitive (3–10 monolayers) due to the short escape depth of electrons from solids Because the emersion of the crystal out of the electrochemical cell is required, they are qualified as *ex situ* techniques

However, the prerequisite of emersing the electrode from its electrochemical environment before examination is an intrinsic limitation of electron spectroscopies Chemical reactions at constant electric charge may take place after emersion so that the surface investigated by electron spectroscopies is different from what it was in the electrochemical cell Examples were found in the case of lead on platinum[2], silver on platinum[3], and potentially every system is subject to this difficulty

This motivated the development of *in situ* techniques Most of them make use of X-rays, to which electrolytic solutions are transparent for thicknesses less than roughly 1 μm Local atom configuration around an atom absorbing an X-ray photon is studied by X-ray absorption spectroscopy (XAS), and long range crystallographic order by X-ray diffraction

These techniques have not yet been very widely used, because they are at the very limit of sensitivity of X-ray spectroscopies They require both an intense X-ray beam (synchrotron radiation), and special devices to increase surface sensitivity XAS is used in the fluorescence detection mode, sensitive to the adsorbate only, and X-ray diffraction is used in the grazing incidence mode to reduce X-ray penetration in the sample

Electrochemically induced phase transitions on Au(111) were demonstrated using X-ray diffraction[4]

A few *upd* were investigated with X-ray diffraction

Tl and Pb on Ag and Au electrodes[5],

Ag and Pb on Au(111)[6]

XAS was used to study a few *upd* systems

Pb/Ag(111)[7], Cu/Au(111)[8], I/Pt(111)[9],

Cu/(I/Pt(111))[10], Cu/Au(111)[11],

and Cu/Au(100)[12]

In the present paper, we describe the structure resulting from the *upd* of copper on a naked (*ie* not pretreated with iodine) Pt(100) electrode determined with XAS in the fluorescence detection mode The electrochemical study of that system was

previously performed by Kolb et al.[13], Scortichini and Reilley[14] and Andricacos and Ross[15]

EXPERIMENTAL

The experiment was performed at LURE (Orsay), using the synchrotron radiation of the DCI storage ring The experimental set-up and working conditions were identical to that described in [12], for the study of the upd of copper on Au(100) and Au(111), except for the single crystal substrate and the chemical composition of the electrolytic solution

The 99 999% pure Pt(100) single crystal was 11 mm in diameter, 3 mm in thickness Cleaning of the surface prior to copper upd was performed in the flame of a H_2–O_2 blow pipe, and then covered with a droplet of high purity (18 MOhm cm) water, as described in [16]

The electrochemical cell used in this work was made of KEL-F®, and was designed by Tadjeddine et al [12] The chemical composition of the electrolytic solution was 1 M $NaClO_4$, 10^{-3} M $HClO_4$, 10^{-4} M Cu^{2+} This low concentration in Cu^{2+} ions is necessary to keep negligible their contribution to the fluorescence signal The high concentration in sodium perchlorate reduces the ohmic drop in the thin electrolyte layer, and keeps the anion coadsorption moderate

Spectra were recorded at the Cu K edge, located close to 8980 eV, at an energy depending on the electronic state of the copper absorbing atom The small number of absorbing atoms required a long accumulation time 20 XANES spectra, 200 eV wide by steps of 0 5 eV, and 28 EXAFS spectra, 600 eV wide by steps of 2 eV were recorded at a time rate of 4 s per step

RESULTS

Electrochemistry

Due to the low concentration of Cu^{2+} ions in the solution, the voltammetric deposition of Cu/Pt is diffusion limited, in a standard electrochemical cell with dipping geometry (Fig 1a) as well as in the XAS cell (Fig 1b) In both configurations, the anodic peaks are well defined, but in the XAS cell, the lateral parts of the crystal, associated with its thickness, are immersed in the electrolyte, and thus contribute to the cell current To minimize this contribution, the crystal is put into a PTFE ring Unfortunately, this induces a deformation of the voltammograms, related to the corresponding increase of ohmic resistance, and correlatively an uncertainty in measuring the amount of electric charge under the upd peak on the Pt(100) surface (Fig 1a) This amount is about 420 μC cm^{-2}

Assuming 2 e$^-$ per Cu atom, it means 1 Cu/Pt Comparison with Fig 1b shows that roughly 1 Cu/Pt was also deposited during the upd process in the XAS cell After holding the electrode potential at 0 1 V (sce) for hours during data collection, the voltammetric dissolution shows that the Cu layer was still present on the surface at the end of the experiment
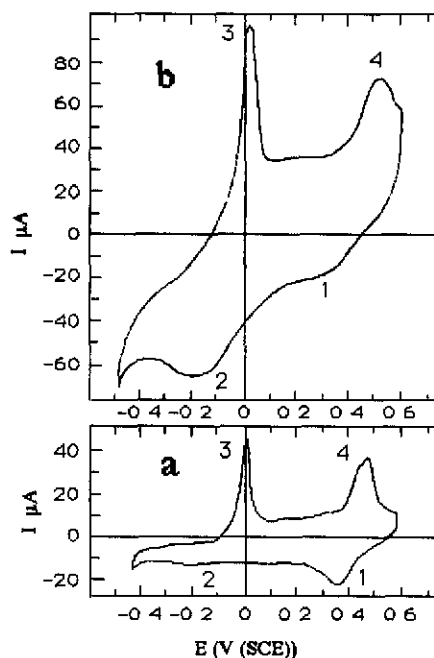

Fig 1 Voltammograms of Cu adsorption on a Pt(100) electrode of geometric area 1 12 cm², in a 10^{-4} M Cu^{2+}, 10^{-3} M H⁺, 1 M $NaClO_4$ solution (a) dipping technique, scan rate 10 mV s⁻¹ (b) XAS cell, scan rate 20 mV s⁻¹ 1 copper under potential deposition, 2 copper bulk deposition Both are displaced and broadened by the slow diffusion rate of copper 3 Dissolution of copper bulk deposit, 4 dissolution of copper underpotential deposit

Platinum is more sensitive than gold to contamination by organic compounds, and is an efficient catalyst for the reduction of molecular oxygen This required a careful cleaning of the cell and degassing of the solutions In spite of these precautions, voltammograms are not perfect A glass cell, easier to clean, has been designed for further experiments

XANES information

Threshold position and near edge structures are sensitive to the electronic state of the absorbing atom Figure 2 is a comparison of the Cu K edge shape
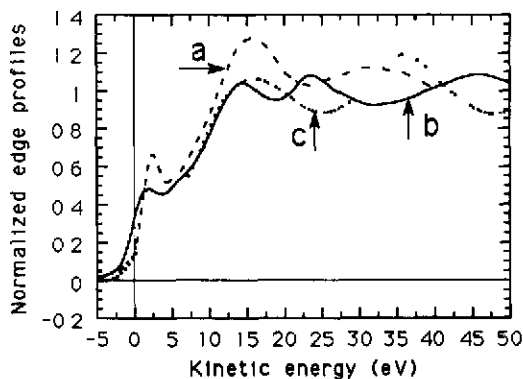

Fig 2 A comparison of near-edge profile shapes for Cu/Pt(100) K-edge (a) Cu⁺ from Cu_2O, redrawn from Ref [12], (b) metallic Cu, measured in the present experiment, (c) Cu/Pt(100), measured in the present experiment

recorded on Cu/Pt(100) to that of copper in known oxidation states[11] The edge profile for metallic copper contains a pre-peak located about 1 5 eV above threshold, and two structures at about 14 and 23 eV above threshold In the Cu^+ edge profile, the pre-peak is enhanced and shifted to higher energy by about 1 eV The first structure is also shifted upwards by roughly 2 eV, whereas the second structure is flattened and much more shifted, from 23 to 32–36 eV above threshold

The threshold position for Cu/Pt(100) is 8983 3 eV, about 1 eV above that of metallic copper, located at 8982 3 eV This shift is not measured very accurately because the data are rather noisy, but is similar to that observed from Cu to Cu^+ The structures observed for Cu/Pt(100) agree well with those for Cu^+ except for the pre-peak which is reduced to a bump in the profile The oxidation state of copper electrochemically adsorbed on Pt(100) thus resembles that of Cu^+ However, the difference in the shape of the pre-peak indicates that the two states are not identical A possible origin for that difference might be, as explained below, that all copper are not equivalent in the present system

EXAFS analysis

Standard analysis of the data consists of background substraction, normalization, conversion of the energy E-scale to wave-number k-scale, and weighting by k to get the $k X(k)$ function A Fourier filtering of the various shell contributions to the EXAFS signal is performed to fit these contributions with calculated models Atom scattering properties, necessary ingredients for the model calculations, are taken from McKale tables[17] The energy range of the processed data is not very large, about 450 eV Consequently, the Fourier transform of the k-weighted, normalized, $k X(k)$ function are somewhat broadened

Main peaks in the Fourier transform of $k X(k)$, not corrected for atom phase-shifts, are located at 0 15 and 0 30 nm (Fig 3) The latter is the superposition of unresolved contributions, with a shoulder located roughly at 0 37 nm These unresolved contributions must be Fourier filtered as a whole
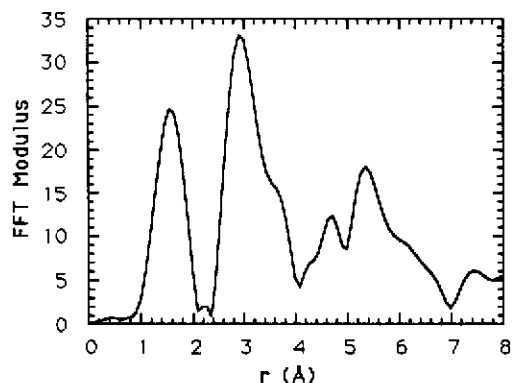

Fig 3 Raw Fourier transform of $k X(k)$ Peak at 0 15 nm is assigned to oxygen neighbours Peak at 0 30 nm is the unresolved combination of contributions of first and second copper neighbours
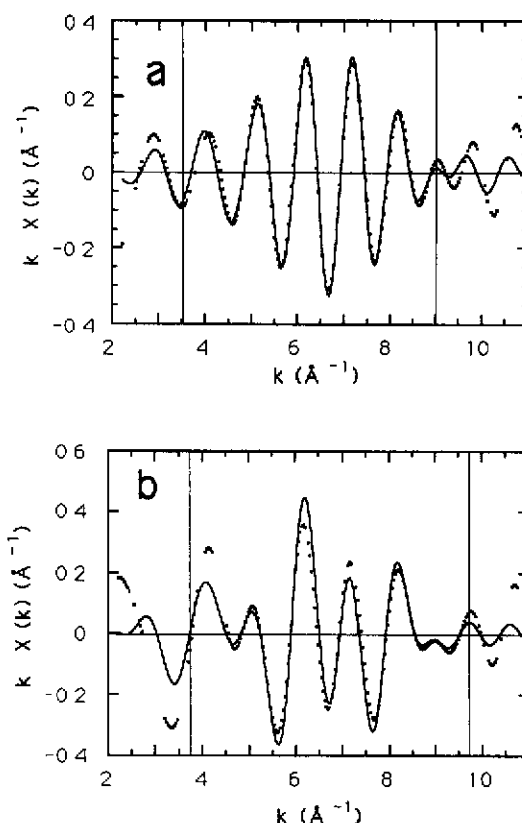

Fig 4 (a) Solid line Fourier filtered EXAFS contributions of Cu neighbours, dotted line calculated EXAFS with Cu at 0 309 and 0 393 nm (b) Solid line Fourier filtered EXAFS contributions of O and Cu neighbours, dotted line calculated EXAFS with O at 0 197 nm, and Cu as in curve a

The first peak is safely assigned to the contribution of a first neighbour shell of oxygen atoms, located at a distance of 0 197 nm of the absorbing copper atom This distance agrees well with known copper oxygen distances in various copper–oxygen compounds[18]

Fourier filtering of the second composite peak shows a sharp beat node, from which it is concluded that this peak is built up from the contributions of two shells of neighbours at well defined distances, or, at least, with gaussian distance distributions These contributions are assigned to copper–copper first and second neighbours, no platinum contribution being able to fit the data (Fig 4) The Cu–Cu first neighbour distance is 0 309 nm This is larger than both the Pt–Pt first neighbour distance and the Cu–Cu first neighbour in copper oxides[18] The Cu–Cu second neighbour distance (0 393 nm) is equal to the cell parameter of bulk platinum No significant contribution of platinum is found, which may be an indication that the Cu–Pt first neighbour bond is perpendicular to the electric vector of the X-ray beam, that is perpendicular to the surface Cu atoms may thus be located on top of the platinum atoms

The following model, sketched in Fig 5, rationalizes these results

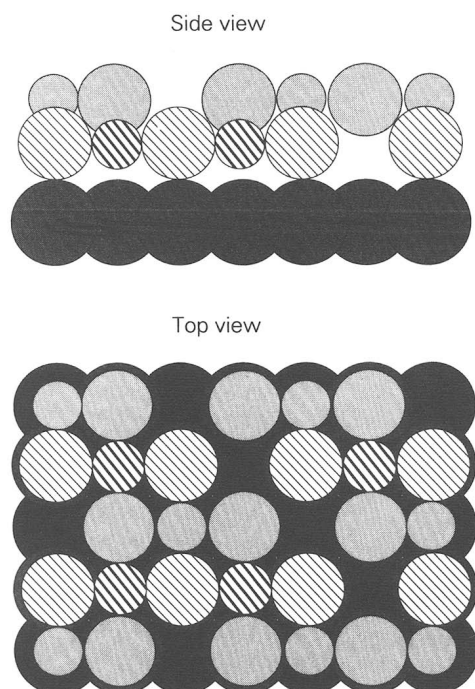(i) A square array of Cu atoms sits in registry on the unreconstructed Pt(100) surface, with half-mono-

Side view

Top view

Fig 5 Schematic drawing of the model Large black circles
Pt surface and subsurface layers Middle hatched circles Cu
inner sublayer Middle light grey circles Cu outer sublayer
Small hatched circles inner sublayer Small light grey
circles outer sublayer The inner adlayer sits on top of Pt
atoms

layer density (1 Cu/2 Pt), thus forming an adlayer
with a $c(2 \times 2)$ surface mesh periodicity

(ii) A second adlayer of copper of the same
density sits in registry over the first one, at a distance
normal to the surface of 0 135 nm Parallel to the
surface, the two copper adlayers are shifted by a
Pt–Pt first neighbour vector, of length 0 278 nm, so
that the Cu–Cu first neighbours are not in the same
adlayer, and are 0 309 nm apart The angle of the
Cu–Cu first neighbours vector with the surface plane
is 26 deg The total copper coverage in this model
is 1 Cu atom per Pt atom, as expected from the
upd process

The potential of the electrode during the exper-
iment was maintained at 0 1 V (*sce*) This potential
is about 0 1 V above the Nernst potential for the
Cu^{2+}/Cu system No oxygen is expected to adsorb
on pure platinum at this potential, but in the con-
ditions of the experiment, the adsorption of copper
may allow the coadsorption of oxygen, that is
the formation of a stable copper–oxygen adlayer
Consequently, oxygen found in the EXAFS exper-
iment is assumed to sit in both copper adlayers,
midway between copper atoms, because (i) the Cu–O
distance (0 197 nm) is half the in-plane Cu–Cu dis-
tance (0 393 nm), and (ii) the strong contribution of
oxygen neighbours is possible only if they lie in (or
close to) the plane of copper atoms, the electric vector
of the X-ray beam being parallel to the surface

In principle, this geometry requires that the for-
ward scattering of the electron wave by oxygen atoms
on its path from the Cu absorber to the Cu second
neighbour (and conversely) be taken into account

Doing this proved to produce a little change in the
least mean square fit between the calculated and the
Fourier filtered EXAFS The quality of the raw data
is not good enough to justify the addition of the
required additional parameters

The number of neighbours in the different co-
ordination shells is more difficult to get from the
EXAFS analysis than distances They are sensitive
to parameters describing phenomenologically in-
elastic processes, and their accurate determination
requires very good raw data This is not precisely the
case here, so that the numbers given below must be
given an uncertainty of 20%, much larger than
the standard deviation resulting from the least-mean-
square fit

To get the actual number N of neighbours from
the effective number N^* resulting from the fitting
procedure, it is necessary to take into account the
relative directions of the interatomic vector and the
electric vector of the X-ray beam The results are not
sensitive to the azimuth of the E-vector thanks to the
symmetry of the model The electron inelastic-mean-
free-paths (IMFP) where not allowed to vary during
the fitting procedure They have been determined
according to the recipes described by Seah and
Dench[19]

The effective number of in-plane oxygen neigh-
bours is $N^* = 1\,8$, corresponding to an actual
mean number $N = 1\,2$ This is between the value
expected on the basis of the stoichiometric compound
Cu_2O ($N = 1$) and that for CuO ($N = 2$) This is
to be related with the observed oxidation state
of copper However, we have no information relative
to how oxygen is shared between the two copper
adlayers All copper are not necessarily equivalent
in the model, and therefore definite conclusions
relative to the oxidation state of copper are difficult
to draw

The effective number of out-of-plane first Cu
neighbours is $N^* = 4\,7$, corresponding to an actual
number $N = 3\,87$, the angle between the bond and
the surface plane being 26° The actual number of
first copper neighbours is thus close to the expected
value $N = 4$

The effective number of the in-plane second
Cu neighbours in both adlayers is $N^* = 6\,3$, corre-
sponding to an actual number $N = 4\,2$ The differ-
ence with the expected value $N = 4$ is much less than
the uncertainty

DISCUSSION

In this study, copper appears to be in an electronic
state which resembles that of Cu^+ Other authors
have made similar observations for copper on gold
surfaces[11, 12] In the present case, however, it must
be noted that copper atoms might be in non equival-
ent electronic states Some are directly bound to
platinum, others are not Some are probably bound
to oxygen, others are not The shape of the near-edge
profile may thus be a complicated superposition of
differently shaped profiles, resulting in a global simi-
larity with the Cu^+ edge shape

A particularity of the present model is the splitting
of the copper layer into two sublayers of half

the monolayer density The inner adlayer forms a $c(2 \times 2)$ structure with the platinum substrate, and the gathering of the two adlayers still maintains this $c(2 \times 2)$ periodicity The formation of a $c(2 \times 2)$ structure has been suggested by Kolb *et al* [13] from electro-reflectance measurements Recent first principle calculations by Kramar *et al* [20] show a very strong Cu-Pt bond strength, with a very short Cu-Pt layer spacing The present model agrees well with these earlier suggestions However, no significant contribution of Pt atoms to the EXAFS is found This might be interpreted as an *atop* adsorption geometry, as suggested for the *upd* of copper on gold(100)[13]

Both these results, (i) the relative similarity of the Cu edge shape with that of Cu^+, suggesting an oxidation state close to one for the adsorbed copper, whereas an exchange of two electrons between a Cu^{2+} ion and a surface Pt atom is expected from voltammetry and (ii) the atop geometry of the inner adlayer found by EXAFS, are related to the presence of oxygen in the adlayers These adlayers constitute the stable configuration in our experimental conditions

A Cu^+ oxidation state might be due simply to the use of a polymer film (kapton®) to cover the cell, through which a slow diffusion of oxygen molecules occurs Other authors have worked with this type of polymer film in previous XAS copper *upd* experiments, on gold[11, 12] and on polycrystalline platinum[22]

The proposed structure then results from a mechanism working at the potential of the experiment, and described by the following schematic equations, where two electrons are transferred and the end-product is copper in Cu^+ form

$$2\,Cu^{2+} + 4\,e^- \rightarrow 2\,Cu_{ad}$$

$$2\,Cu_{ad} + \tfrac{1}{2}O_2 \rightarrow Cu_2O_{ad}$$
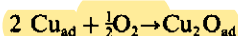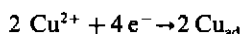
But a Cu^+ oxidation state might also be related to more fundamental processes implying the concept of electrosorption valency[21] In effect, measuring an electrosorption valency $n_e \approx 2$ does not necessarily means a charge transfer of two electrons, because various parameters contribute to n_e, namely the position of the adsorbate atoms with respect to the double layer, the position of water molecules, and the rearrangement of the double layer itself due to the geometry of the adlayers This is still an open question

The model assumes that oxygen lies within the planes of the copper adlayers This is because of the strong contribution of oxygen to the EXAFs, which requires a nearly in-plane bond, and because of the copper-oxygen distance which is half the copper-copper distance In-plane oxygen may stabilize the configuration of the adsorbed copper in two distinct adlayers In the absence of further information relative to the sharing of oxygen between the two copper adlayers, equipartition was assumed to calculate a mean number of neighbours $N = 1\,2$, giving a density of about 0 6 O atom per Cu atom Depending on the distribution of oxygen, assuming a tendency to ordering, the surface periodicity remains $c(2 \times 2)$ for the limiting case of CuO surface composition, or steps

up to a $p(2 \times 2)$ for the limiting case of Cu_2O surface composition

The distance between the two copper adlayers, 0 135 nm, is quite short This must be related to the very low density of the two adlayers (half the monolayer) Large interlayer contractions of low density planes are not uncommon in solid-vacuum interfaces

CONCLUSION

The model proposed for the structure of copper electrochemically adsorbed on Pt(100) has the particularity of splitting the copper into two layers of half the monolayer density, 0 13 m apart, and expanded parallel to the surface to match very closely the underlying platinum surface net The outer one is shifted by a Pt-Pt first neighbour vector Oxygen is present in the copper deposit, probably in both adlayers with an approximate density of 0 6 O atom per Cu atom In this model the total coverage in copper is one monolayer The inner copper adlayer, in direct contact with platinum, sits on top of Pt atoms This configuration may be stabilized by the presence of oxygen

Uncertainties remain relative to the actual number of neighbours in the various shells This is partly due to a relatively poor quality of the XAS data In spite of this, XAS in the fluorescence mode has proved to be very useful for the *in situ* structural determination of underpotential deposition of Cu on Pt(100)

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