Supplementary Material

Oscillatory patterns in Redox gradient materials through wireless bipolar electrochemistry. The dynamic wave-like case of copper bipolar oxidation

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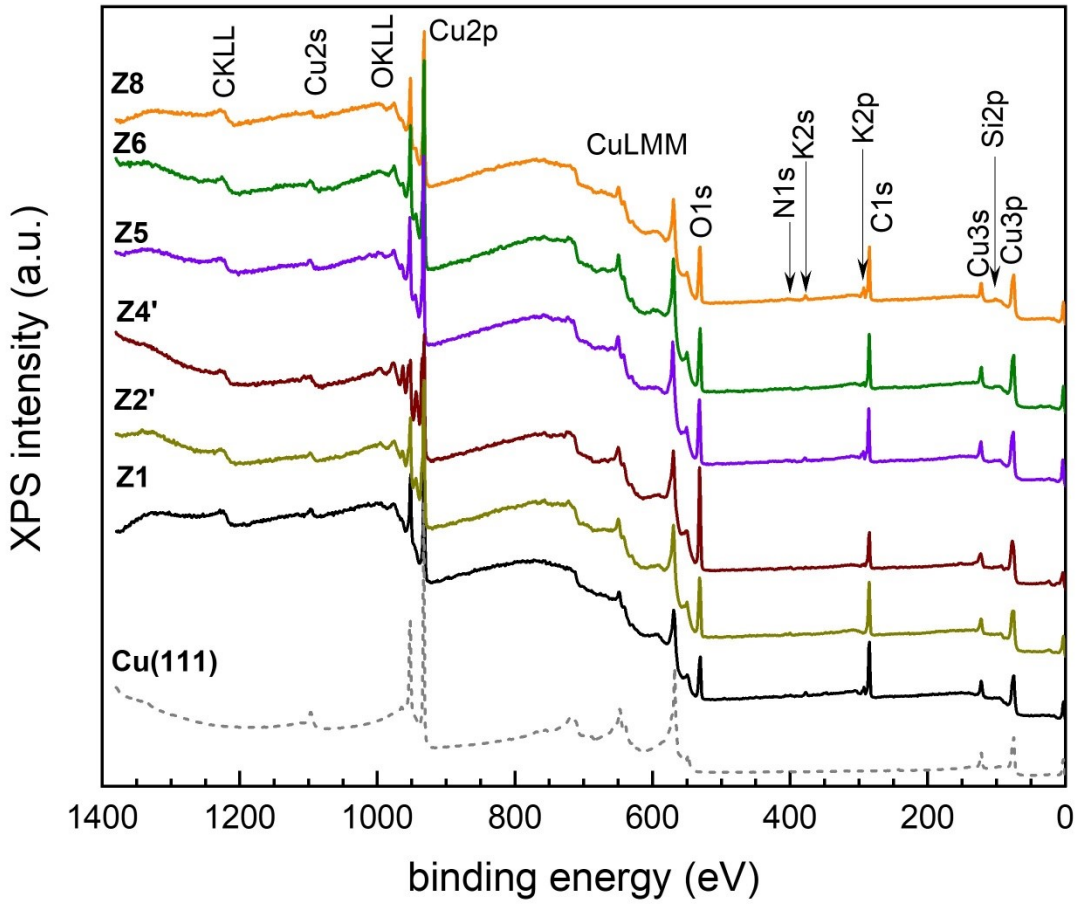

Figure S1. Survey XPS spectra of regions Z1, Z2', Z4', Z5, Z6 and Z8 and of an atomically clean Cu(111) single crystal surface reference. The main XPS and Auger lines are identified in the spectra. In addition to the lines associated to copper, the presence of carbon, oxygen, potassium as well as of small traces of silicon and nitrogen is indicated.

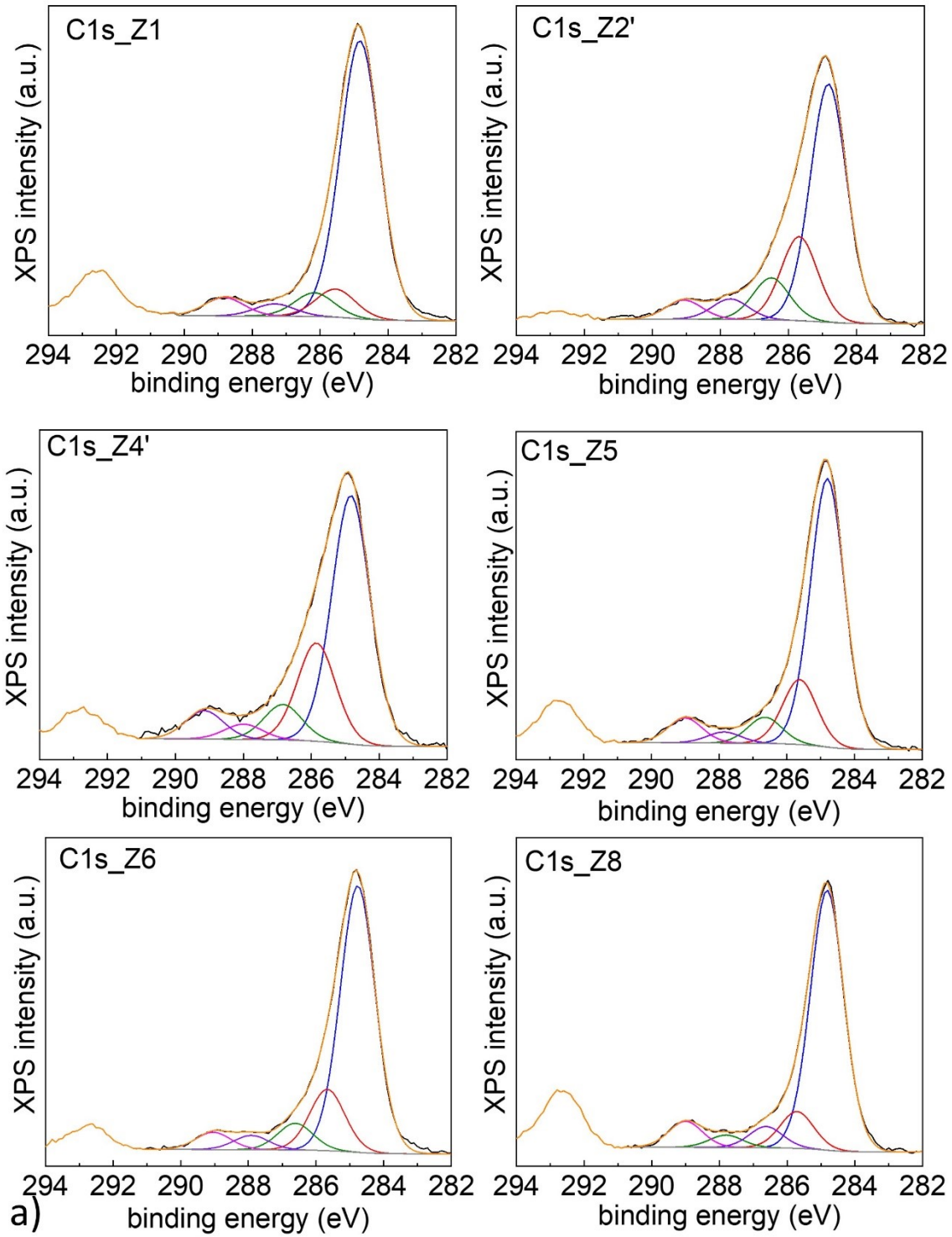
C1s_Z1
C1s_Z2'
C1s_Z4'
C1s_Z5
C1s_Z6
C1s_Z8
XPS intensity (a.u.)
binding energy (eV)
294 292 290 288 286 284 282
a)

Figure S2a.

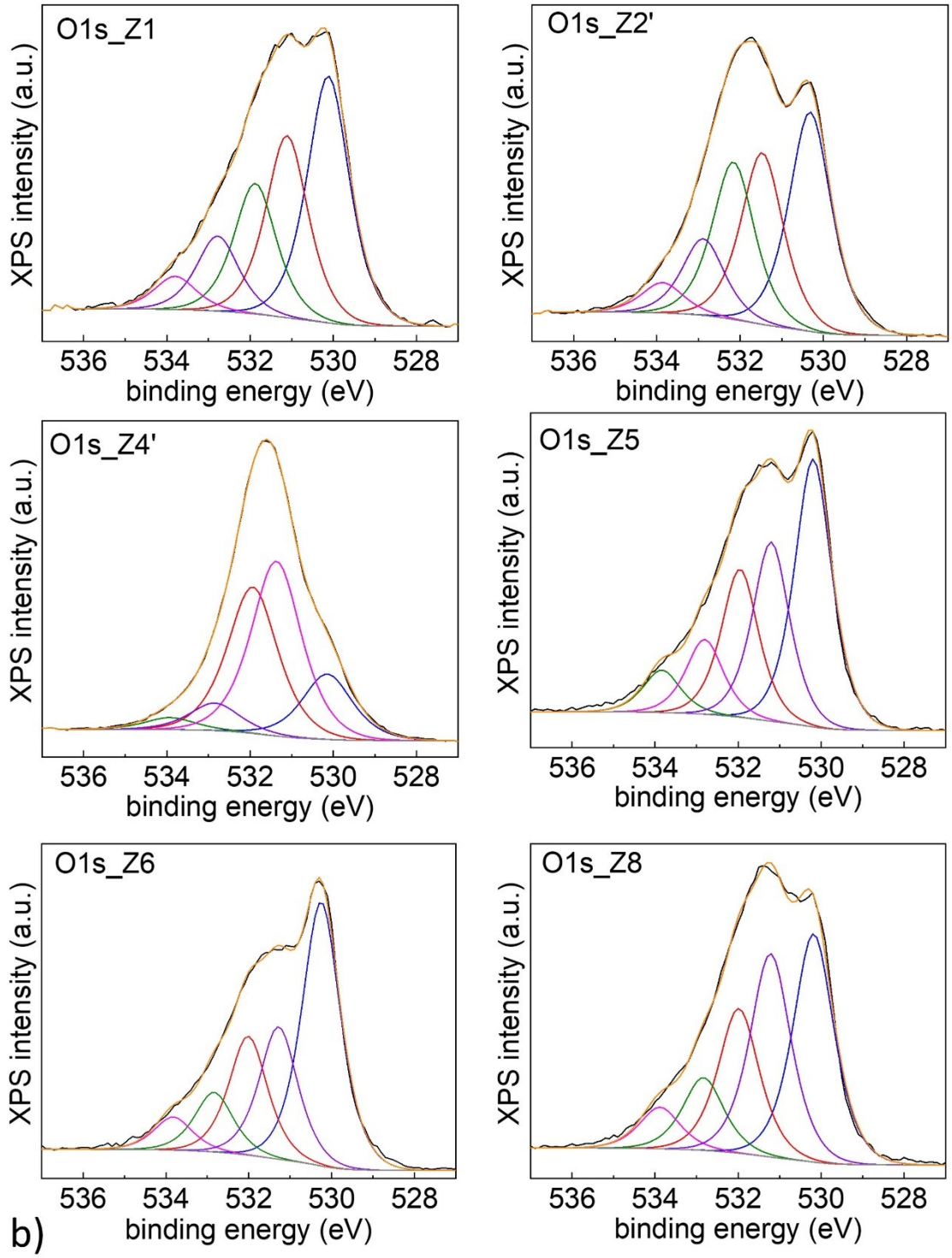

Figure S2b

Figure S2. High-resolution XPS spectra corresponding to the (a) C1s and (b) O1s core levels of regions Z1, Z2', Z4', Z5, Z6 and Z8. Least-squares fits of the experimental data (black line) after a Shirley-type background subtraction (grey line) are shown using a combination of Gaussians and Lorentzian functions under the constraint of identical full width at half maximum(FWHM) for all components. The envelop of the fit is represented by an orange line and the five components by blue, red, olive, violet and magenta lines, respectively.

COMMENTS on DECONVOLUTION

Apart from data in the main manuscript, additional studies with deconvoluted peaks are given in the Figure S2. Least-squares fits of the C1s and O1s lines using the CasaXPS software[30] after a Shirley-type background subtraction using a combination of Gaussian and Lorentzian functions under the constraint of identical full width at half maximum (FWHM) for all components are shown in Figure S2. The deconvolution shows that the C1s region exhibits five components at 284.8 (used as reference), 285.7, 286.6, 287.8 and 289.0 eV, respectively, which are assigned mainly to graphitic carbon (284.8 eV), C-C/C-H (sp3) carbon (285.7 eV), C-O(H) bonding (286.6 eV), adsorbed CO_2 and formate (287.8 eV) or carbonates (289.0 eV), respectively [49-51] in all zones. The feature located at 292.6 eV in Figure 5a corresponds to the $K2p_{3/2}$ core level line. We have selected five components since this is the minimum number of lines that provide a satisfactory fit with realistic FWHM (1.2-1.4 eV) (see Figure S2).

From the O1s region we obtain the following (five) components: 530.2, 531.2, 531.9, 532.8 and 533.8 eV, respectively, with FWHM values between 1.1 and 1.4 eV. The 530.2 eV component can be assigned to lattice (Cu-O) oxygen and is in agreement with the accepted value corresponding to the Cu_2O phase [48,49] while the 531.2 and 531.9 eV lines contain contributions from hydroxides, formates and adsorbed CO_2 and to C-O bonding and carbonates, respectively [49,50]. The presence of molecularly physisorbed water is highly improbable at room temperature and under UHV [51] but its eventual presence would be revealed by the 532 eV feature. Contributions from silicon oxide (around 533 eV) probably arising from the used glassware cannot be discarded but should be minor given the small amount of silicon detected in the survey spectra (Fig. S1). Contributions of defective oxides may be discarded in most zones, since O 1s would appear at 531 eV, but not in Z4, with a signal in that energy region [52]. Non stoichiometric paramelaconite, Cu_4O_3, or CuO_x o K_xCuO_2, could have signals in that zone, all with expected black color.

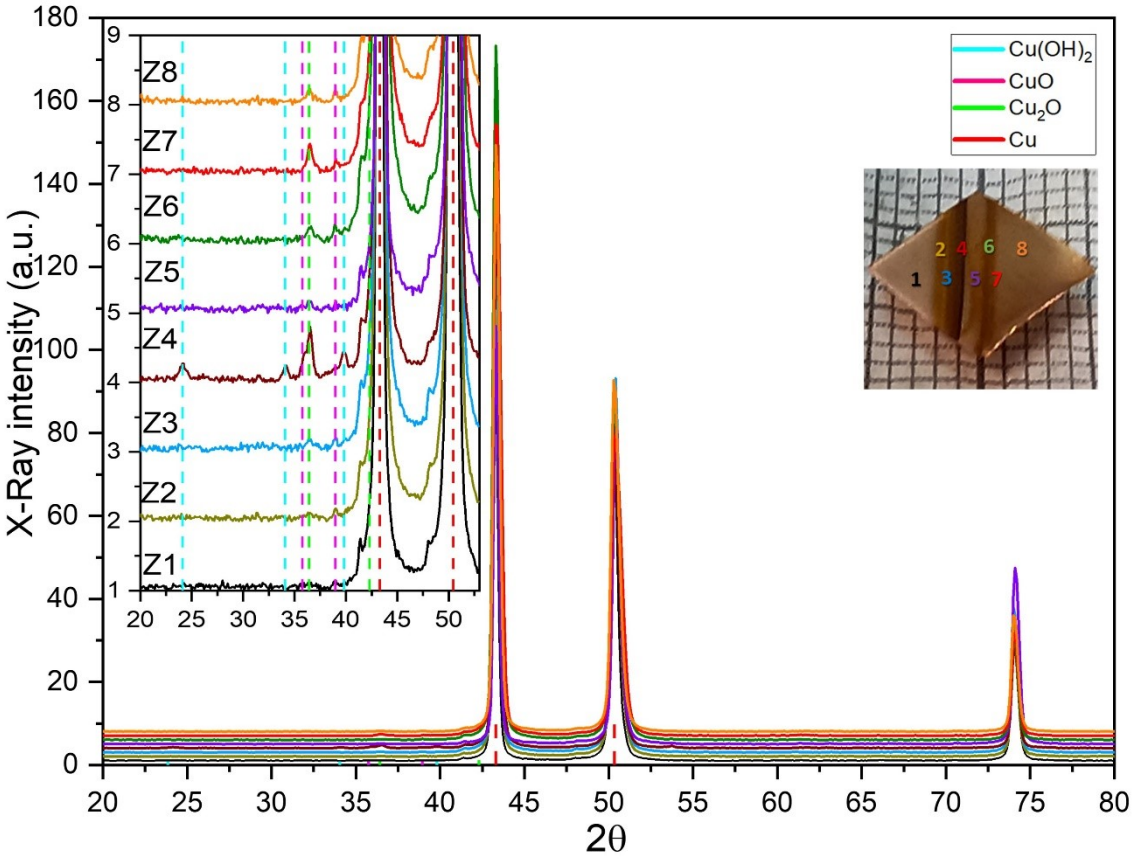

Fig S3. General diffraction pattern extracted from bidimensional detector for each zone labelled in inset picture

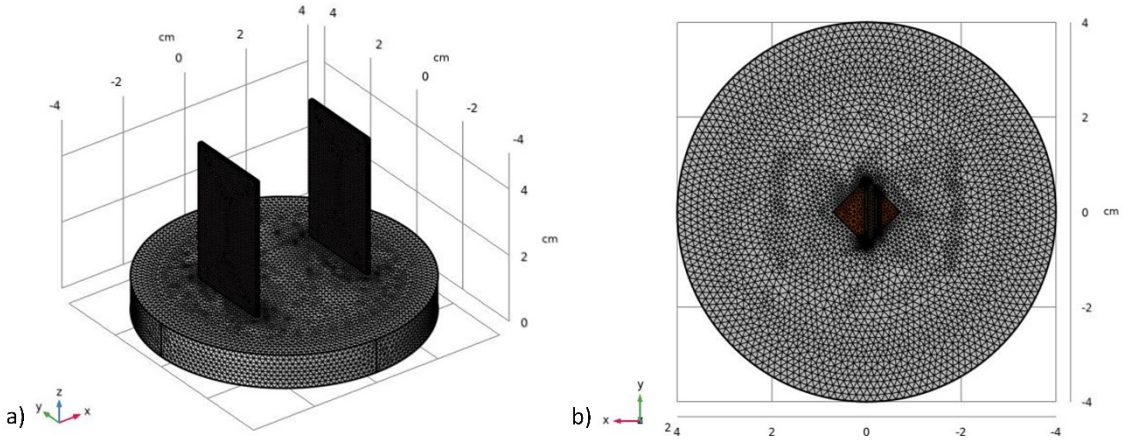

Figure S4. Finite element mapping in COMSOL main cell configuration according to the two mesh sizes described in Table S1. A) general cell, b) immersed copper piece within the cell

Table S1. Comsol parameters used in calculations. Please note that Comsol Electrostatics module uses classical electromagnetism equations, including contorn conditions

Mesh values	
Mesh1	
Maximum element size	0.16 (cm)
Minimum element size	1.6E-3 (cm)
Maximum growth rate of element	1.3
Curvature factor	0.2
Resolution narrow regions	1
Mesh2	
Maximum element size	0.016 (cm)
Minimum element size	1.6E-4 (cm)
Maximum growth rate of element	1.2
Curvature factor	0.2
Resolution narrow regions	1
Materials values	
Electrolyte KOH 1M	
Electric conductivity (S/m)	17.8 (S/m)
Relative permittivity	5
Platinum	
Electric conductivity (S/m)	8.9E6 (S/m)
Relative permittivity	1
Copper	
Electric conductivity (S/m)	58.1E6 (S/m)
Relative permittivity	1
Copper – Brown	
Electric conductivity (S/m)	1E-5 (S/m)
Relative permittivity	1
Copper – Black	
Electric conductivity (S/m)	1E-10 (S/m)
Relative permittivity	1

Mesh1 is for all the geometry and the Mesh2 is for the pieces.