Supplementary information

The role of the copper oxidation state in the electrocatalytic reduction of CO_2 into valuable hydrocarbons

Juan-Jesús Velasco-Vélez[1,2]*, Travis Jones[2], Dunfeng Gao[3,4], Emilia Carbonio[2], Rosa Arrigo[5,6], Cheng-Jhih Hsu[7], Yu-Cheng Huang[7,8], Chung-Li Dong[7], Jin-Ming Chen[8], Jyh-Fu Lee[8], Peter Strasser[9], Beatriz Roldan Cuenya[3,4], Robert Schlögl[1,2], Axel Knop-Gericke[1,2], Cheng-Hao Chuang[7]*

[1]Department of Heterogeneous Reactions, Max Planck Institute for Chemical Energy Conversion, Stiftstraße 34-36, Mülheim an der Ruhr 45470, Germany
[2]Department of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, Berlin 14195, Germany
[3] Department of Physics, Ruhr-University Bochum, Universitätstraße 150, 44780 Bochum, Germany
[4]Department of Interface Science, Fritz-Haber-Institute of the Max-Planck Society, Faradayweg 4-6, 14195 Berlin, Germany
[5]Diamond Light source Ltd., Harwell Science & Innovation Campus, Didcot, Oxfordshire OX 11 0DE, UK
[6]School of Environment and Life Sciencesm, University of Salford, Cockcroft building, M5 4WT, Manchester, UK
[7]Department of Physics, Tamkang University, No. 151 ,Yingzhuan Rd., Danshui Dist, New Taipei City 25137, Taiwan.
[8]National Synchrotron Radiation Research Center, No. 101, Hsin Ann Rr., East District., Hsinchu 30076, Taiwan
[9]Department of Chemistry, Chemical Engineering Division, Technical University Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany

*Corresponding authors: velasco@fhi-berlin.mpg.de, chchuang@mail.tku.edu.tw

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***In situ* flow cell for X-ray spectroscopy**

The *in situ* EC flow liquid cell was operated on the main chamber of the beamline 20A1 end station of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu (Taiwan) with a background pressure of ~10^{-8} mbar while the aqueous electrolyte circulated on the back side of a SiN_x membrane 100 nm thick (from the company Norcada, Edmonton, Canada). Theeffective area of the working electrode was ~2 mm^2. This membrane is used as working electrode and membrane to separate the liquid form the vacuum side. Hard X-ray absorption measurements at the Cu K-edge were performed at the beamline BL17C1 of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu (Taiwan). The photon source consists of a 25 poles wiggler (W20) with 20 cm period length and a focus spot size of 2 mm x 6 mm. The excitation energy ranges from 4.8 keV up to 14.2 keV. The signal was collected in fluorescence yield mode using an ionization chamber detector. A similar cell to the used in beamline 20A1 was located in the BL17C hutch at 1 bar in air with an effective area of the working electrode of ~36 mm^2. The flow of liquid was assured with a peristaltic micro pump, flowing continually around 1 ml/min of electrolyte. In the Si_3N_4 membrane a thin Au/Ti thin film was deposited by sputtering using a Cressington 208HR sputter-deposition system. First of all, 3 nm-thick adhesion layer of Ti (99.99%, Elektronen-Optik-Service GmbH, Dortmund, Germany) was deposited in a 0.1 mbar Ar atmosphere at a current of 40 mA during 30 s. After that, a 20 nm-film of Au (99.99%, Elektronen-Optik-Service GmbH, Dortmund, Germany) was deposited in a 0.1 mbar Ar atmosphere at a current of 40 mA during 140 s. It yields the formation of a homogenous polycrystalline thin film used as working electrode20 nm thick on a SiN_x membrane (100 nm), which yields a total signal transmission of ~74% of the incoming X-ray photons. The X-ray transmission through this membrane is estimated to be approximately equal to 80% of the incoming X-ray. The main body of the cell is made of polyether ether ketone (PEEK) which is electrically insulator and chemically inert.

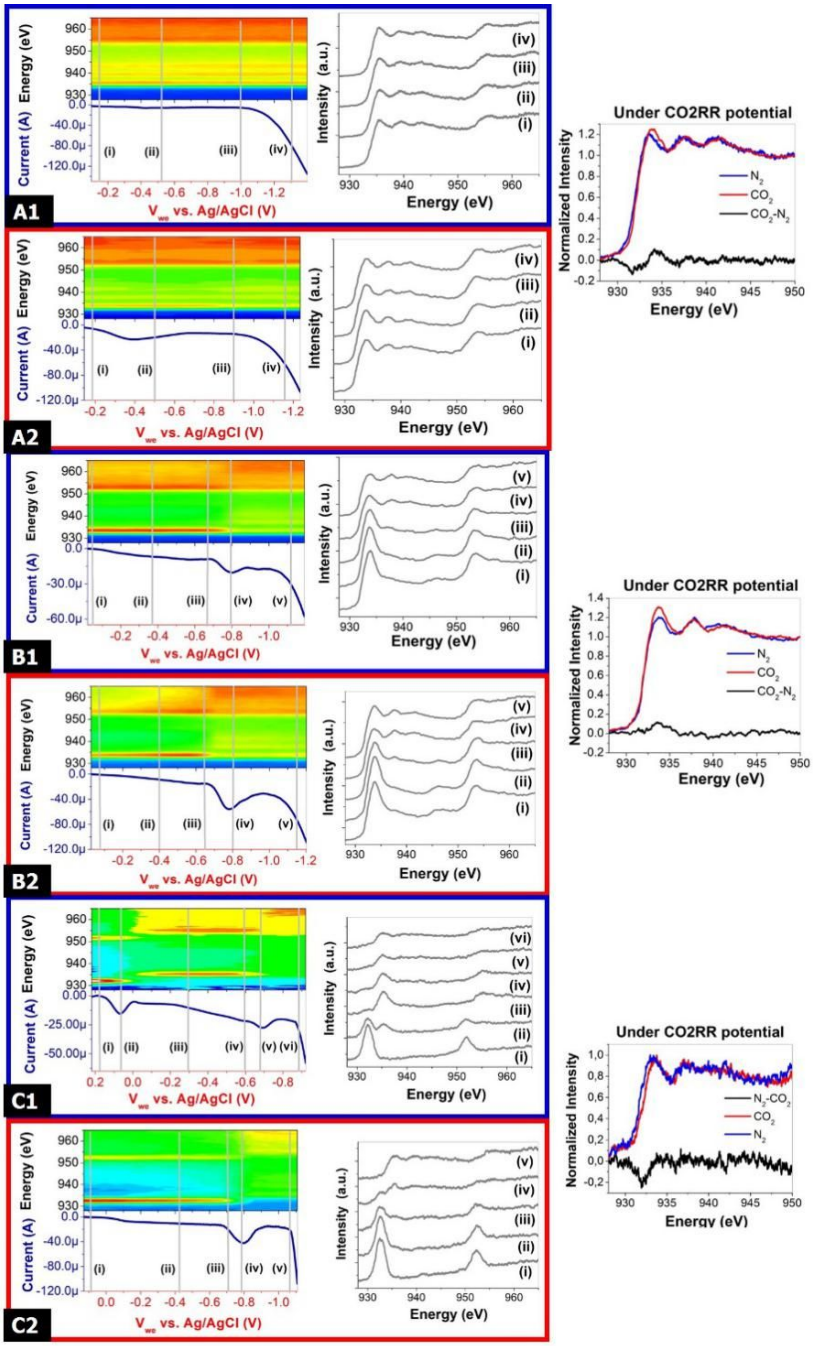

Figure S1: Cu $L_{2,3}$-edges spectra depending on the cathodic polarization in the presence of different electrolytes and initial oxidation state: **A** Cu^0 catalyst **A1** 5 mM $KClO_4$ saturated with N_2(gas) and **A2** 5 mM $KHCO_3$ saturated with CO_2(gas). **B** Cu^+ catalyst **B1** 5 mM $KClO_4$ saturated with N_2(gas) and **B2** 5 mM $KHCO_3$ saturated with CO_2(gas). **C** Cu^{2+} catalyst **C1** 5 mM $KClO_4$ saturated with N_2(gas) and **C2** 5 mM $KHCO_3$ saturated with CO_2(gas). Side graphics are the Cu L-edge spectra under the highest cathodic polarization with the different electrolytes in order to compare the formation of surface/sub-surface oxygen species.

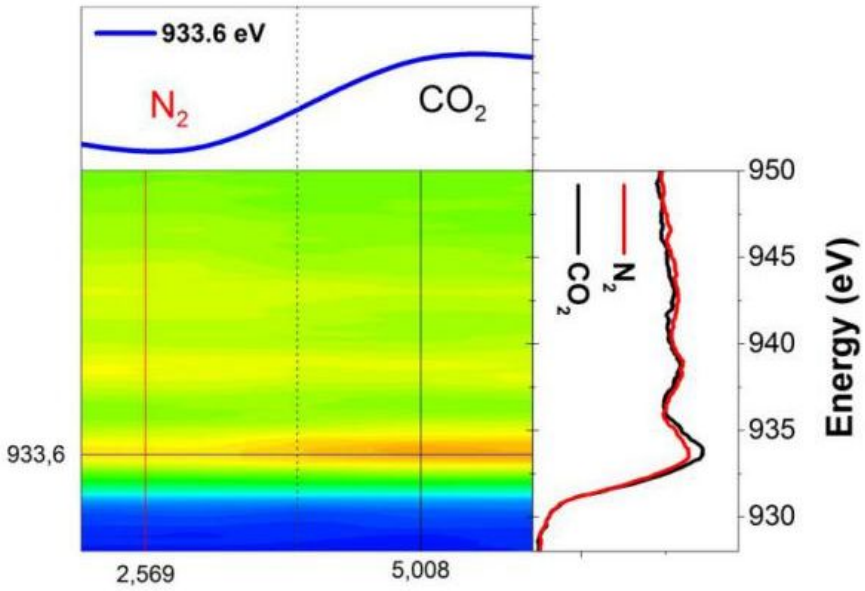

Figure S2: Cu L_3-edge of Cu^0 catalyst in presence of N_2 and CO_2 shows the existence of a slightly increase of Cu^+ species in presence of CO_2 ascribed to the existence of dissociative proton-consuming reactive adsorption of CO_2 on copper yielding chemisorbed CO.

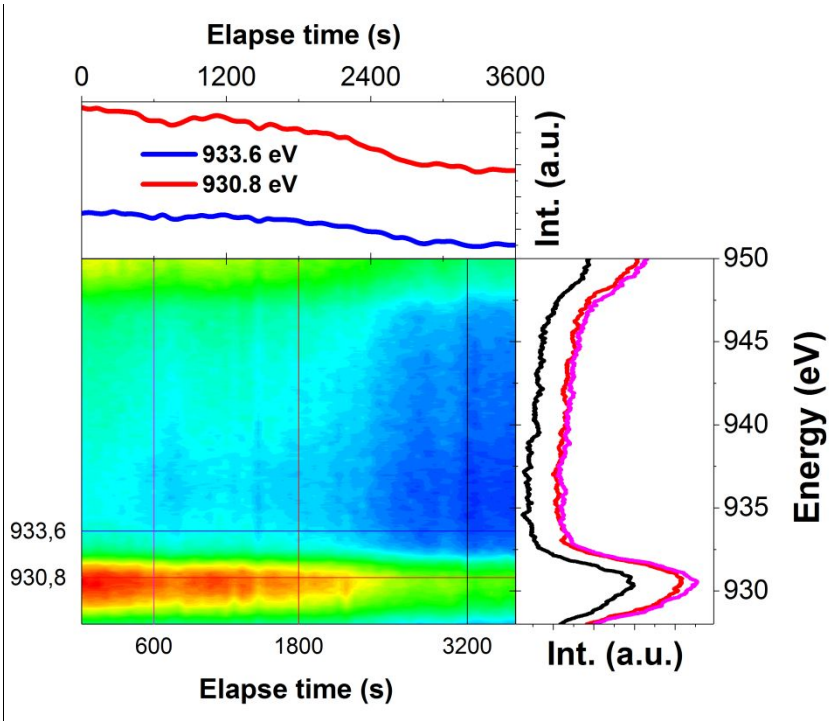

Figure S3: Cu L_3-edge depending on elapse time of copper carbonates species in presence of 100 mM $HClO_4$ acidic media.

Calculation of the Faradaic efficiency of gas products:

$$f_{gas} = \frac{f_{flow} \times c_{gas} / V_m \times n \times F}{I \times 60} \times 100$$

f_{gas}: Faradaic efficiency of gas product, %;

f_{flow}: flow rate of CO_2, mL min^{-1};

I: electrolysis current at 60 min, A;

c_{gas}: volume ratio of gas product, determined by online GC;

V_m: the molar volume of an ideal gas at 1 atmosphere of pressure, 22400 mL mol^{-1};

n: number of transferred electrons for certain product;

F: Faradaic constant, 96485 C mol^{-1}.

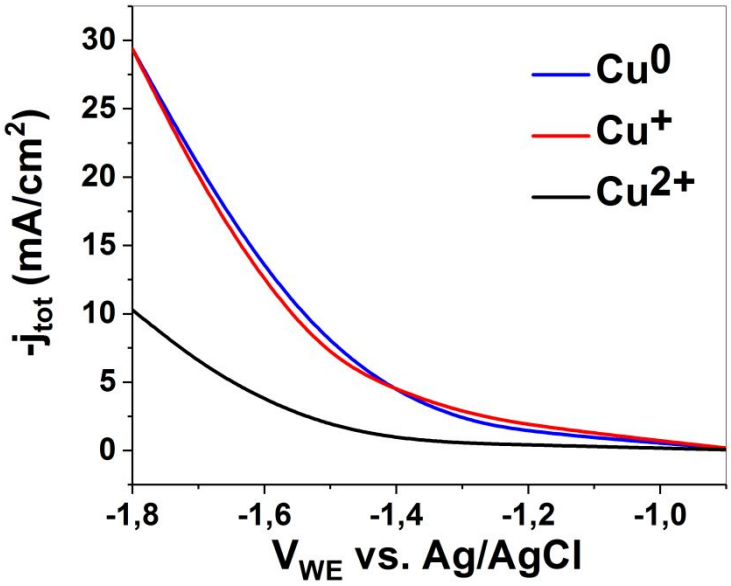

Figure S4: Density of current for Cu^0, Cu^+ and Cu^{2+} depending on the applied potential in 100 mM $KHCO_3$ saturated in CO_2.