

## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:  
<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

#### Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

### Deadlines for submitting a report supporting a new proposal

- 1<sup>st</sup> March Proposal Round - **5<sup>th</sup> March**
- 10<sup>th</sup> September Proposal Round - **13<sup>th</sup> September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

#### Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

#### Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### Instructions for preparing your Report

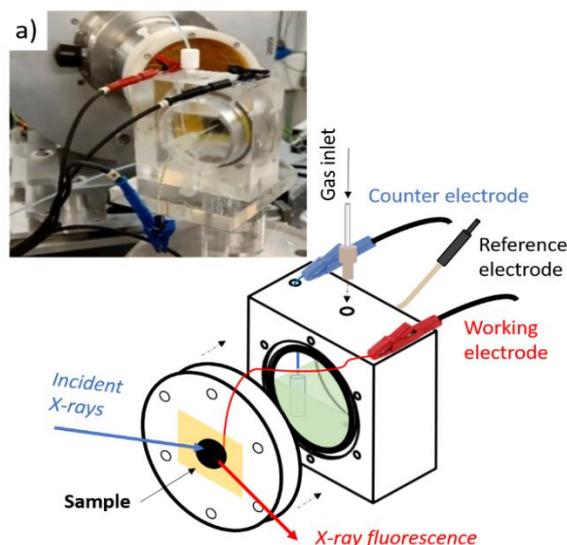
- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> Operando XES and XRS investigation of Cu <sub>2</sub> O-derived nanocatalysts for pulsed CO <sub>2</sub> electroreduction reaction	<b>Experiment number:</b> CH6324
<b>Beamline:</b> ID20	<b>Date of experiment:</b> from: 28/06/2022 to: 04/10/2022	<b>Date of report:</b> 20/09/2022
<b>Shifts:</b> 18	<b>Local contact(s):</b> Dr. Alessandro Longo	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Dr. Janis Timoshenko, Dr. Andrea Martini, Dr. Hyo Sang Jeon, Martina Rüscher		

### Report:

For this experiment we used a single compartment electrochemical, similarly to the ones commonly used by us for in situ XAS measurements<sup>1</sup>. In particular, it features a typical three electrode setup, represented by a reference electrode (Ag/AgCl electrode), counter electrode (Pt mesh) and working electrode (sample spray-coated on a carbon-based electrode).



**Figure 1:** Schematics of the electrochemical setup used for our measurements. It is worth noting that this picture shows the cell in the typical configuration used for the XAS measurements, while, in our case we tilted it by 165° in order to maximise the amount of scattered photons directed towards the detectors.

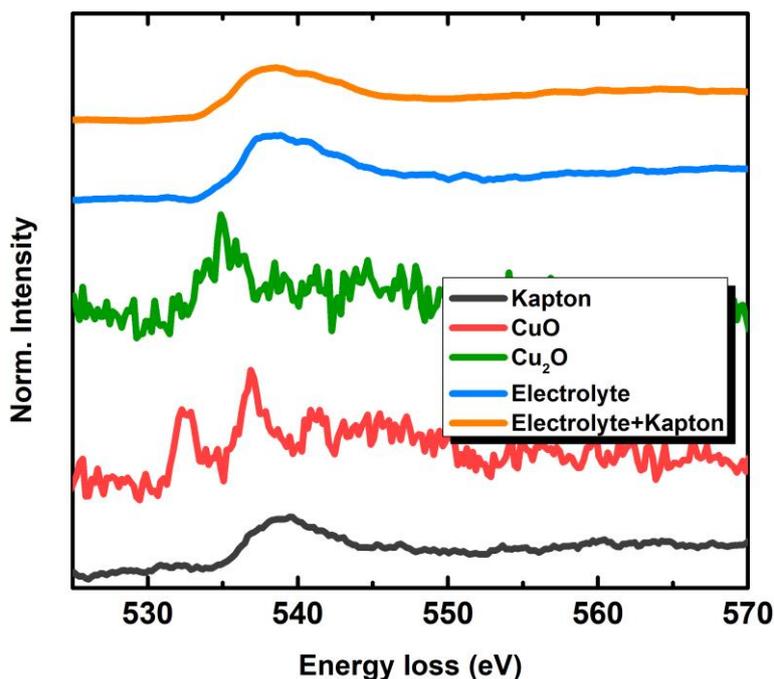
For this experiment, the sample was copper oxide-derived catalyst (Cu<sub>2</sub>O nanocubes with sizes ca. 20 nm), which we investigated under CO<sub>2</sub>RR conditions. During the operando experiments, the CO<sub>2</sub> (20 ml/min) was flowing inside the cell through a gas inlet connection while a peristaltic pump guaranteed the recycling of the electrolyte (0.1 M solution of KHCO<sub>3</sub>). Finally, the applied potential was controlled by a *BioLogic* potentiostat.

The pink beam from four U26 undulators was monochromatized using a cryogenically cooled Si(111) monochromator and focused to a spot size of approximately 10 μm × 20 μm (V × H) at the sample position using a mirror system in Kirkpatrick–Baez geometry. The cell was placed on the beamline stage tilted by ca. 165° in order to maximize the amount of scattering photons arriving to a large solid angle detector composed by with 36 spherically bent Si(660) analyzer crystals. At the same time an additional XES detector with a von Hamos geometry was located at 45° with respect to the sample beam direction, in order to acquire the emission signal.

All measurements were collected at room temperature. The acquisition scans lasted around 6 h per sample. We collected several XRS spectra at the oxygen K-edge by scanning the incident beam energy between 10.22–10.26 keV to create energy losses in the vicinity of the oxygen K-edge by using the Si(660) analyzer reflection at 9.7 keV (elastic line). All

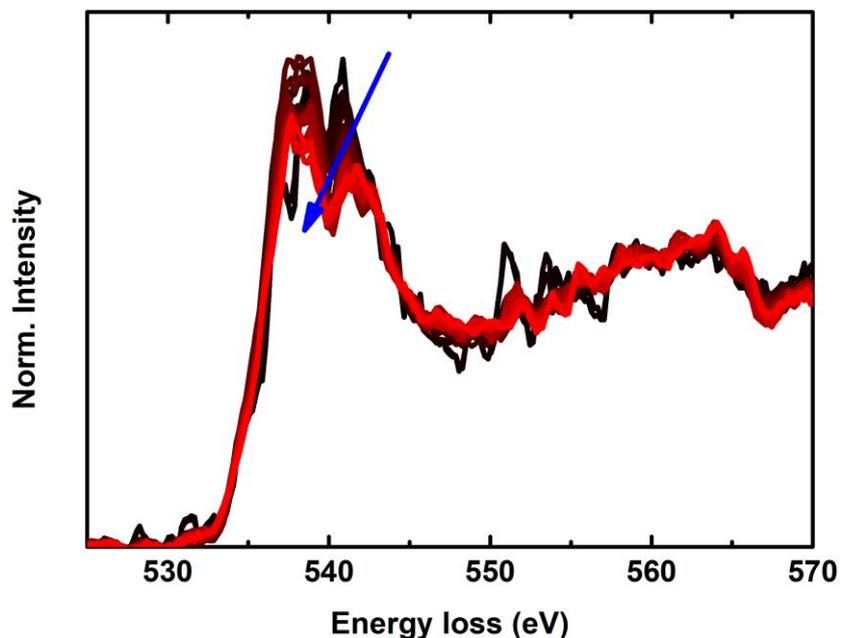
scans were checked for consistency and signals from different analyzer crystals were averaged. The mean momentum transfer was of ca.  $6.2 \pm 0.4 \text{ \AA}^{-1}$  while the overall energy resolution was of 1 eV as estimated from the full width at half maximum of elastic scattering from a piece of adhesive tape. All the measured profiles have been treated by removing the pre-edge background through a third order victoreen curve. the same type of polynomial profile was used to fit the post-edge region and estrapolating the intensity value in correpondece of the energy edge. The latter term was used to normalize the spectra for their jump of absorption.

Concerning the XRS measurements at O K-edge, reported in this **first, preliminary** report, we focused, initially, on a set of O K-edge references fundamental to extract quantitative, structural information from the spectra corresponding to the  $\text{Cu}_2\text{O}$  nanocubes under reaction conditions. In particular, we collected the O K edge XRS spectra of the CuO and  $\text{Cu}_2\text{O}$  reference materials and from the bare electrolyte (without any sample). Afterwards, we noted that a strong contribution to the measured O K-edge signal was stemming also from the kapton tape, that acted as X-ray window in our setup.. For this reason, we collected then the spectrum also for the bare kapton tape and from the system composed by the kapton tape plus the electrolyte (without sample but with the carbon paper electrode). All these references have been used to extract quantitative structural information from the single XANES measurements involving the  $\text{Cu}_2\text{O}$  nanocubes<sup>2,3</sup> during reaction condition. In particular the fraction of each reference spectrum was derived recurring to the linear combination analysis (LCA).

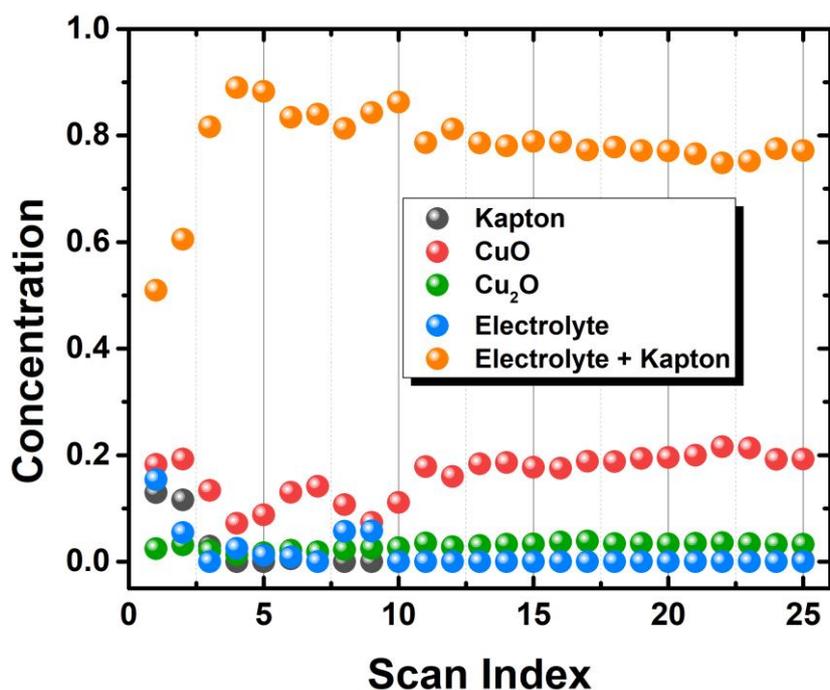


**Figure 2:** Set of XRS spectra at O K-edge used for the linear combination analysis

In the following some basic results are shown for the  $\text{CO}_2\text{RR}$  process involving  $\text{Cu}_2\text{O}$  nanocubes under a static potential:  $-1.9 \text{ V vs Ag/AgCl}$ .



**Figure 3:** Set of 25 XRS spectra collected at O K-edge under static potential  $-1.9$  V vs Ag/AgCl V for the  $\text{Cu}_2\text{O}$  nanocubes during the  $\text{CO}_2\text{RR}$ . The blue arrow indicates the trend of the white line intensity of the spectra as a function of the scan number. Each spectrum is collected approximately every 30 minutes. Different spectra correspond to different spatial regions within our cell (1<sup>st</sup> scan corresponds to Kapton window, the last scan - to electrolyte inside the cell).



**Figure 4:** Results of linear combination analysis of XRS spectra, using as standards the O K edges of the: i) Kapton tape, ii)  $\text{CuO}$ , iii)  $\text{Cu}_2\text{O}$ , iv) Electrolyte and (v) the Electrolyte plus Kapton.

The LCA shows that all the states collected at a fixed potential of  $-1.9$  V vs Ag/AgCl show a major contribution represented by the spectrum of the electrolyte plus the one of the kapton spectrum. No particular differences are present between this last profile and the one proper of the electrolyte (collected in presence of the carbon paper without any deposited sample) or just the kapton one, although small variation in the concentration profiles is visible for the first scan of the dataset. However, we suppose that these small changes can be attributed to the strong noise contribution affecting every spectrum of the dataset and the chosen references. An intriguing phenomenon is instead represented by the increase of the  $\text{CuO}$  phase, which remains stable around the 20% while the contribution coming from the O K edge of the  $\text{Cu}_2\text{O}$  phase is almost negligible.

## References

- (1) Timoshenko, J.; Cuenya, B. R. *Chem. Rev.* **2021**, *121*, 882.

- (2) Aran-Ais, R. M.; Gao, D. F.; Roldan Cuenya, B. *Accounts Chem. Res.* **2018**, *51*, 2906.
- (3) Aran-Ais, R. M.; Rizo, R.; Grosse, P.; Algara-Siller, G.; Dembel, K.; Plodinec, M.; Lunkenbein, T.; Chee, S. W.; Roldan Cuenya, B. *Nat. Commun.* **2020**, *11*, 8.