



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

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th 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.



	Experiment title: Relation between the catalytic efficiency, morphology and chemical state of Cu catalyst in high-rate CO ₂ conversion devices for low-carbon economy	Experiment number: MA – 4791
Beamline: ID31	Date of experiment: from: 14/6 - 2021 to: 21/6 - 2021	Date of report: 10/09/2021
Shifts: 9	Local contact(s): Marta Miroló	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Jakub Dreñec - ESRF Prof. Ib Chorkendorff - Technical University of Denmark, Department of Physics Brian Seger - Technical University of Denmark, Department of Physics *Sahil Garg - Technical University of Denmark, Department of Physics *Asger B. Moss - Technical University of Denmark, Department of Physics *Carlos A. Giron Rodríguez - Technical University of Denmark, Department of Physics *Roosa Ilvonen - ESRF		

Report:

The aim of beamtime MA-4791 (and the following in-house time) was to investigate multiple aspects of membrane electrode assembly (MEA) based CO₂ electrolysis (CO₂E). The results obtained from this work will be used to understand the mechanisms behind changes in product selectivity over time. For this purpose, a special electrolysis cell was developed in a collaboration between ESRF ID31 staff and DTU Physics. The cell was thoroughly tested at DTU for electrochemical performance. The first step during the beam was to familiarize, align, and calibrate the cell along with the different components from an X-ray imaging and diffraction perspective. Hereafter, a series of in-operando experiments were performed in order to investigate the following:

1. Initial native copper oxide (CuO) reduction to Cu
2. Variation in water content of the cathode catalyst and gas diffusion layer during electrolysis operation
3. Transformation in catalyst morphology

Cell testing:

The cell is an MEA type electrolysis cell designed with a casing sufficiently X-ray transparent to execute in-operando investigations of the MEA itself. The MEA is an assembly of two gas diffusion electrodes (GDEs) directly in contact with each side of an anion exchange membrane (AEM). In all experiments, the cathode GDE contained a 150 nm sputtered copper catalyst layer, and the anode was a commercial IrO₂ coated GDE. Figure 1 shows a completely assembled CO₂ electrolyzer so that the cathode flow channel was parallel to the beam axis (i.e. in-plane axis), which allowed for the quantification of the transient catalyst morphology (and oxidation) cathode GDE water content. We used the first two shifts for initial alignments of the cell and took reference XRD patterns to identify the different parts of the cell in the absence of current. The cell performance was good and from the diffraction patterns, it was easy to differentiate the different components of the cell, including flow-fields, catalysts, membrane, etc.

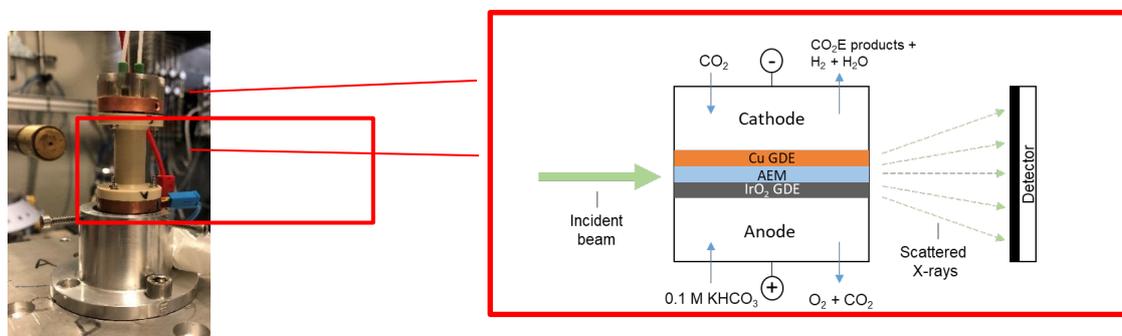


Figure 1. The actual cell (CO_2 electrolyzer) was mounted on the stage before starting the experiments. The red box shows the schematic of the cell for an in operando synchrotron X-ray imaging of MEA-based CO_2 electrolyzer highlighting Cu cathode GDE, anion exchange membrane (AEM), IrO_2 anode GDE, reactants, and products.

CuO reduction:

The surface of the Cu catalyst will unavoidably oxidize during the manufacturing and handling in an air/oxygen environment, and it has been discussed¹ if this oxide layer was important to the performance of the catalyst. Therefore, the first thing investigated was the reduction of the initial native copper oxide (Cu_2O) layer. As the crystal structure of Cu_2O and Cu is different, the reduction process can be observed as a change in the diffracted pattern. Figure 2 shows the integrated WAXS patterns and the time when the potential was turned on or when CO_2E was started. Most notably, the Cu_2O peak around 4.2 degrees visibly diminishes within the first 20-30 s. A similar fast reduction of the initial Cu_2O was observed for multiple experiments.

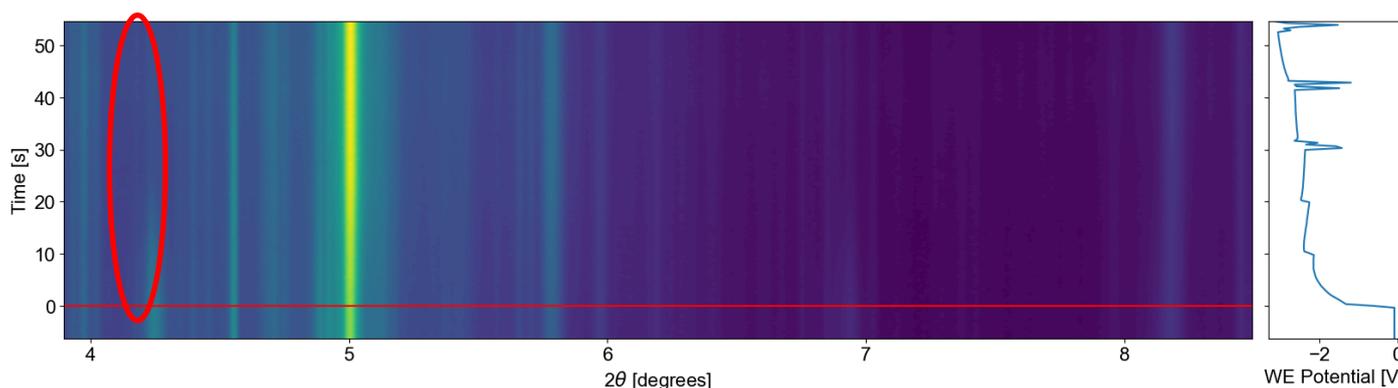


Figure 2. The figure shows the diffraction pattern of the Cu catalyst layer vs. time as well as the applied cell potential. The horizontal red line indicates the time where the potential is turned on and the red circle indicates the major Cu_2O peak. It is clearly observed how the Cu_2O peak diminishes fast. It can also be seen that the major Cu peak at 5° is intensifying.

Water management:

It is expected that water (electrolyte) flooding of the catalyst layer and the GDE impacts cell performance significantly, therefore, a series of in-operando experiments were performed at varying current densities. A total of 9 (3 h) experiments were successfully performed, and the preliminary data analysis indicates a correlation between cell potential and water content in the cathode gas diffusion layer. Figure 2 shows one example where the water content has been estimated by integrating the scattered X-rays in an appropriate section of q-values where only a few Bragg peaks (mainly Cu) are present. The y-axis is the position normal to the MEA plane, ranging from the membrane at 0 and far into the GDE at position 50. The high-intensity strip around 2θ position 10-20 is the Cu catalyst layer. It can be seen that at the top of GDE, the intensity of the signal increases with time, and towards the end of the experiment, the signal, i.e. water content, fluctuates. Furthermore, it was observed that these fluctuations correlate with potential changes. The gas analysis data from the gas chromatograph (GC) and mass spectrometer (MS) shows a similar fluctuation in selectivity, with hydrogen evolution reaction (HER) being the primary reaction when the cell is flooded.

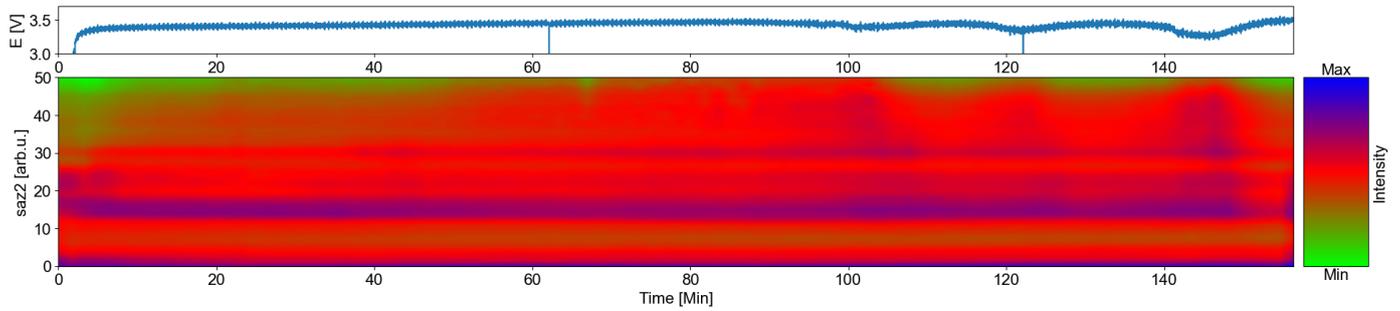


Figure 2. The figure shows the increased water intensity signal (content) as a function of time (in the GDE) and the fluctuations in the cell potentials correlate well with the change in water content in the GDE. The plot is constructed by integrating the diffraction patterns.

Catalyst morphology

The morphology of the catalysts layer was continuously investigated using SAXS, but our preliminary analysis of the data does not show any indication of changes. As the catalyst used was sputtered Cu, we did not expect to observe any significant change in morphology.

Conclusion:

Our experiments clarified the timeframe in which the initial Cu_2O layer reduces during CO_2E . Additionally, a large amount of experiments shows the correlation between water content in the cathode GDE and the cell potential of the CO_2 electrolyzer. An increase in water content at the cathode GDE also correlates with the increase in hydrogen evolution reaction. Additionally, the catalyst morphology was analyzed and did not show any significant change. In general, the results from the beamtime are highly satisfactory and the quality of our data is excellent. We expect to publish at least two scientific articles based on the obtained results and hope that the work can be continued in the future.

References:

1. S. Nitopi, E. Bertheussen, S. B. Scott, X. Liu, A. K. Engstfeld, S. Horch, B. Seger, I. E. L. Stephens, K. Chan, C. Hahn, J. K. Nørskov, T. F. Jaramillo and I. Chorkendorff, *Chemical Reviews*, 2019, **119**, 7610-7672.