



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: Linking catalytic selectivity and water management in Cu based gas diffusion electrodes for high-rate CO electrolysis

Experiment number:
MA-5226

Beamline:	Date of experiment: from: 04/04/2022 to: 11/04/2022	Date of report:
Shifts:	Local contact(s): Marta Mirolo	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Sahil Garg - Technical University of Denmark, Department of Physics *Qiucheng Xu - Technical University of Denmark, Department of Physics *Asger B. Moss - Technical University of Denmark, Department of Physics Prof. Ib Chorkendorff - Technical University of Denmark, Department of Physics Brian Seger - Technical University of Denmark, Department of Physics *Jakub Drenc - ESRF		

Report:

The aim of beamtime MA-5226 (including the following in-house time) was to investigate water management and salt precipitation in membrane electrode assembly (MEA) electrolyzers for CO₂/CO electrolysis. For CO₂ electrolysis (CO₂E), we focused specifically on understanding how different alkali cations (Li, Na, K, and Cs) and their concentration could affect the occurrence of salt precipitation in the gas diffusion electrode (GDE) and thus affect the CO₂ reduction reactions (CO₂RR) selectivity. As for the CO electrolysis (COE), we investigated how water management changes in cathode GDEs with different PTFE contents. The results obtained from this work: (1) for CO₂E, will be used to identify cations that can replace the existing alkali cations but without having to sacrifice the CO₂RR selectivity and to develop membranes that are selective enough to prevent excessive cation crossover to the cathode; (2) for COE, will be used to identify the suitable GDE substrate for loading cathode catalyst as well as developing stable anode catalyst in alkaline conditions.

Setup used:

We used an MEA-based cell which has earlier shown successful results during our last visit to ESRF in June 2021 (MA-4791). To explore the water and salt precipitation distribution in the GDE, we used wide-angle X-ray scattering for all our experiments. The product measurement was done using an inline mass spectrometer (MS) and gas chromatograph (GC).

Cation effect on salt precipitation in the GDE during CO₂E:

First, we investigated the salt formation with different alkali cations in the GDE during CO₂E. As expected, we found that lithium, sodium, and potassium cations allow salt formation in the GDE while no signs of salt formation were observed with the cesium cations (Figure 1). This is attributed to the high solubility of cesium salts as compared to other alkali cation salts. Surprisingly, with the lithium cations, we found that the lithium cations formed a salt layer right at the top of the catalyst layer (Figure 1a), while in the case of sodium cations, the salts seem to move from the interior to the exterior of the GDE (Figure 1b). With the potassium cations, the salt layer remains relatively stable at the interface of the micro and the macroporous layer of the GDE (Figure 1c).

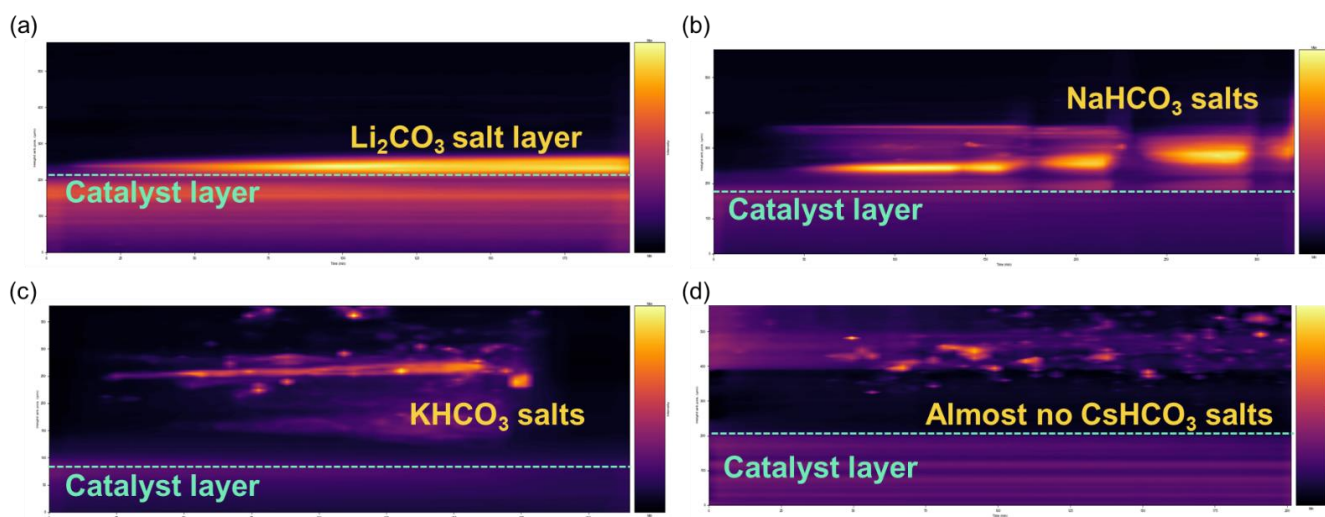


Figure 1. The figure shows the salt intensity as a function of CO₂E time in the GDE with anolyte having 0.1 M (a) LiHCO₃, (b) NaHCO₃, (c) KHCO₃, and (d) CsHCO₃ at 200 mA/cm². On all plots, Y-axis shows the arbitrary height of the MEA being scanned while the X-axis shows the electrolysis time. The plots are constructed by integrating the diffraction patterns obtained from X-ray data.

Modulating potassium concentration affects salt precipitation during CO₂E:

Secondly, we investigated how salt precipitation in the GDE changes by modulating K⁺ concentration in the anolyte. In principle, we should see less precipitation with reducing K⁺ concentration given that diffusion should decrease. As expectedly, we observe a delay in the formation of salt precipitation with reduced concentration (0.001M) and significantly stable CO₂R selectivity (see Figure 2c).

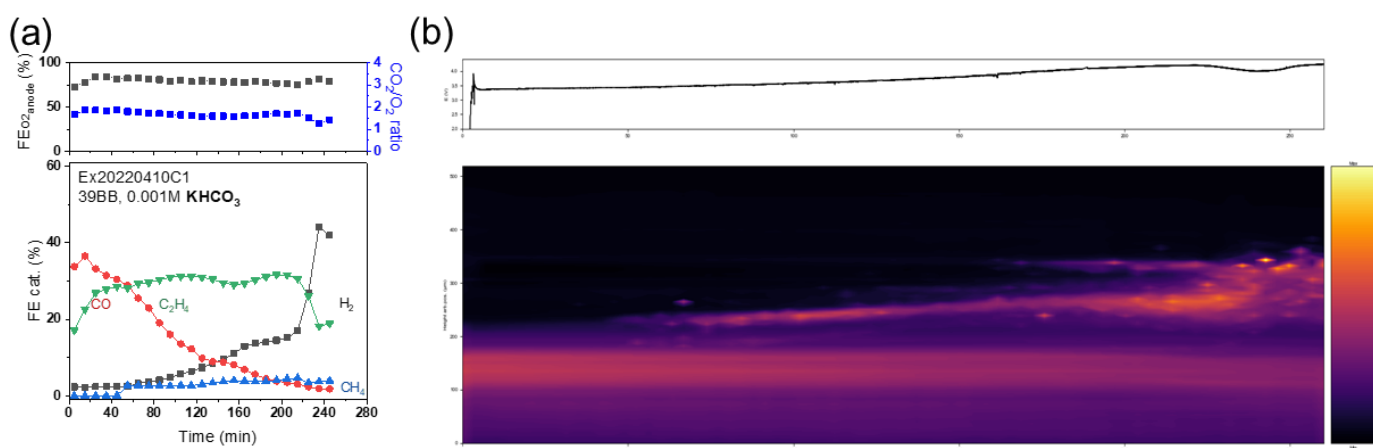


Figure 2. (a) Change in CO₂RR and HER selectivity at the cathode and OER selectivity and CO₂/O₂ ratio at the anode with electrolysis time; and salt intensity as a function of time in the GDE. The experiment was done at 200 mA/cm² and with 0.001 M KHCO₃ anolyte.

Water management over different Cu GDE substrates in COE:

With CO electrolysis, we were expecting a vastly different water flux due to the transfer of hydroxyl groups being the dominant anion species crossing over the membrane rather than carbonates in CO₂E. Figure 3 shows the increase in electrolyte intensity (which could also be termed flooding) in the GDE correlates well with an increase in HER in both 28BC and 39BC GDEs. However, in 39BC, the maximum intensity of electrolyte flooding was slightly lower than in 28BC, and that could very well explain why 39BC has slightly better CORR selectivity than 28BC. The reason for increased electrolyte flooding in 28BC could be its lower thickness than 39BC (235 vs 325 μm).

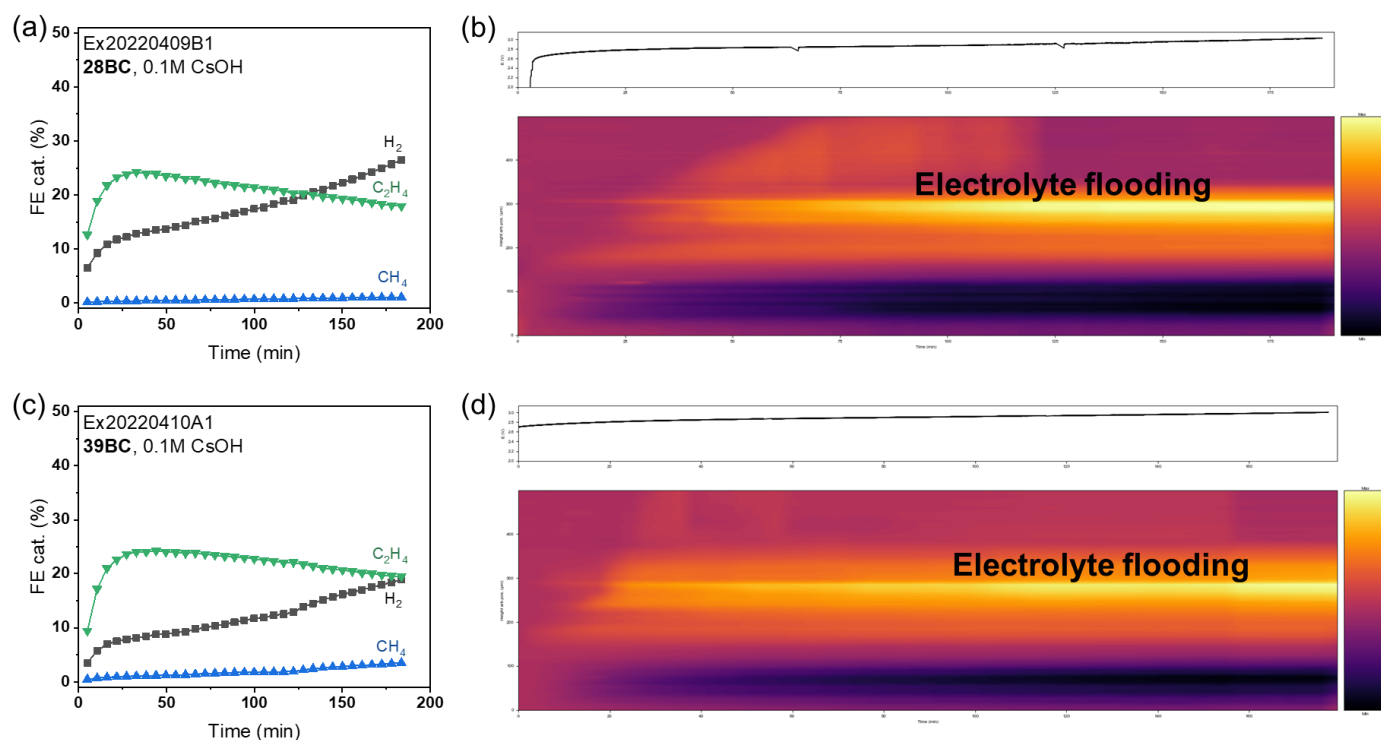


Figure 3. Change in CORR and HER selectivity at the cathode (a, c) with electrolysis time; and electrolyte intensity as a function of time in (b) 28BC and (d) 39BC. All experiments were done at 200 mA/cm² and in 0.1 M CsOH anolyte.

Conclusion:

Our CO₂E experiment with different alkali cations clearly shows that using a more soluble salt (e.g. cesium bicarbonates) could help prevent the salt formation in the cathode GDEs. Also, reducing the cation concentration in the anolyte could delay the salt precipitation phenomenon. Moreover, the COE experiment shows an increase in electrolyte content in the cathode GDE which correlates well with an increase in HER. In principle, the results obtained from the beamtime are excellent and we aim to publish at least two high-impact publications and hope to put a new proposal to continue investigating existing hurdles in the CO₂/CO electrolysis field. The knowledge and techniques used by our group could also be helpful for other researchers working with different electrochemical devices such as fuel cells, water splitting, N₂ reduction, etc.