EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: **Understanding the iron center anion interaction in FeNCs catalysts for the oxygenreduction reaction**	**Experiment number**: A08-1-1075
Beamline: BM08	**Date of experiment**: from: 07/06/21 to: 15/06/21	**Date of report**: 12/02/23
Shifts: 21	**Local contact(s)**: Francesco D'Acapito	*Received at ESRF:*

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Report:

We tested two different series of Fe-N-C cataysts (based on Fe phthalocyanine or FePc) toward the dendrimental effect of anions such as nitride (NO_2^-) and sulphide (S^{2-}) By sampling them by XAS ath Fe k edge. The two anions were chosen because they were renown for their capacity to fastly worsen the electrochemical performances toward the Oxygen Reduction Reaction (ORR). Along the various standards, we tested two series of samples;

- An **ex-situ** series, produced in our lab by immersing the catalyst in the polluting electrolyte (using different pullutant concentrations) for different times (from 3 h to 2-3 days). All the produced catalysts were electrochemically characterized after the immersion period to assess the loss in performance. This series of data was acquired in transmission mode.
- An **in-situ** series, in which the pristine catalyst is left in contact with the polluted solutions for different times, eventually appliyng a potential to the electrode, in order to follow changes at the Fe centre. This series of data was acquired in Fluorescence mode.

A schematic of the series can be found in Figure 1. The initial part of the experiment was devoted to the definition of the best acquisistion conditions for the ex-situ and in-situ samples, due to the low concentration of Fe (1% wt approx). We were able to acquire good data just before 9 in k-space, making it difficult to elaborate the spectra for EXAFS.

Ex-situ (different exp. Times & Potential)	**In-situ** (different exp. Times & Potential)
FeNC	FeNC
FeNC + 1mM NO2-	FeNC in PBS
FeNC + 10mM NO2-	FeNC in PBS + 1mM NO2-
FeNC + 1µM NO2-	FeNC in PBS + 10mM NO2-
FeNC + 1mM S2-	FeNC in HClO4
FeNC + 10mM S2-	FeNC in HClO4 + 1mM S2-
FeNC + 1µM S2-	FeNC in HClO4 + 10mM S2-

Figure 1 – Measurement series

The ex-situ data for the NO_2^- showed no major change in the XANES region between the pristine FePc sample and the poisoned ones, despite the contact time and the pollutant concentration. It was interesting however to observe a decrease of electrochemical performance with the addition of the pollutant for the tested samples. On the contrary, the S_2^- polluted samples showed minor changes in XANES after long (> 48h) immersion in the pollutant solution (Figure 2).

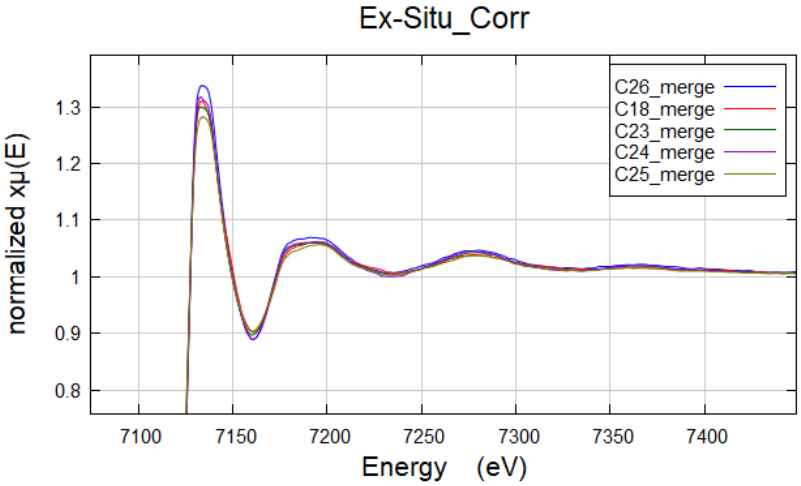

Figure 2 -Ex-Situ FePc in S_2^- after different immersion times

Similar trend was seen for in-situ. The particular experimental geometry permitted also to assess absence of Fe leaking in the solution, during the various contamination tests.

Actually, part of the data acquired during the turn has been used for an article on FeNC catalyst for ORR, alongside with the data acquired from EXP A08-1 1084.