ESRF	**Experiment title:** **Temperature dependant iron speciation by in-situ XAS during pyrolysis: Unravelling the formation of the active sites in FeNCs catalysts for the oxygen reduction reaction**	**Experiment number:** A08-1-1084
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Shifts: 18	**Local contact(s):** Baroni Tommaso	*Received at ESRF:*

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Report:

The aim of the experiment was to acquire XAS spectra of a Fe-N-C catalyst based on Fe Phtalocyanine (FePC) during pyrolisis at Fe k-edge. The objective was to unravel Fe-N-C evolution during the heat treatment, and to correlate it with changes in electrocatalyst performances. The experiment was divided in two series of measurements:

1) In-situ XAS acquisitions of the sample during pyrolisis (performed during daytime);
2) Ex-situ XAS acquisitions of Fe-N-C samples previoulsy heat-treated in our labs (performed during nighttime).

To perform in-situ heating, we used the Microtomo gas flow cell designed and produced by the experimental pool. The cell was able to reach 900°C by specifications. A first part of the experiment was devoted to the definition of the best conditions do achieve highter temperature using an Ar/H2 gas mixture (95%/5%). A fter a series of tests in which we changed the heating conditions, fluxes and loadings, we managed to reach a maximum temperature of about 650°C. which was partly insufficient for the full definition of the changes on the FeNC centers (we had to reach at least 800°C,

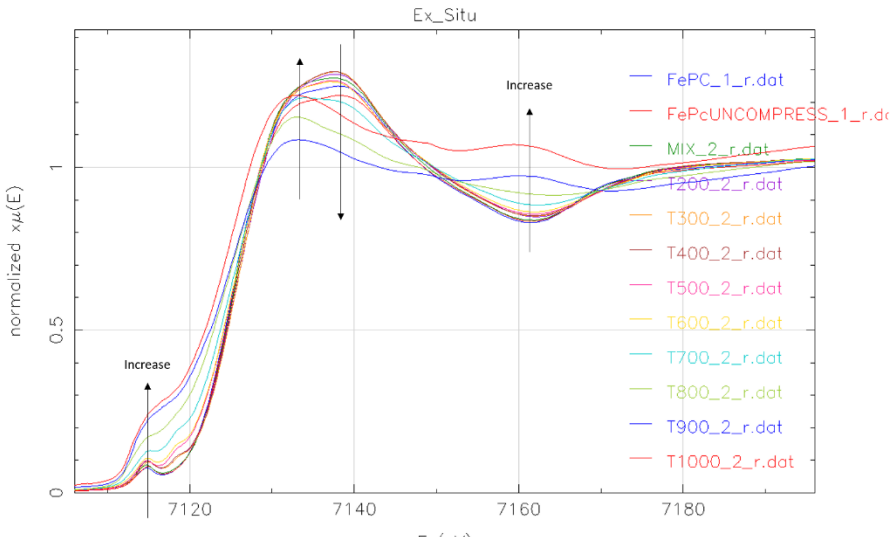

Figure 1 – XANES of the ex-situ samples, highlighting the trends in change of the spectrum

we saw that an important change in the electrochemical behaviour was visible between 600 and 800°C. In-situ acquisitions were performed for temperature steps, in which the temperature was left constant for about 3 hours for each step. A number of acquisitions was performed on the same formulation in order to be sure of the reproducibility of the results.

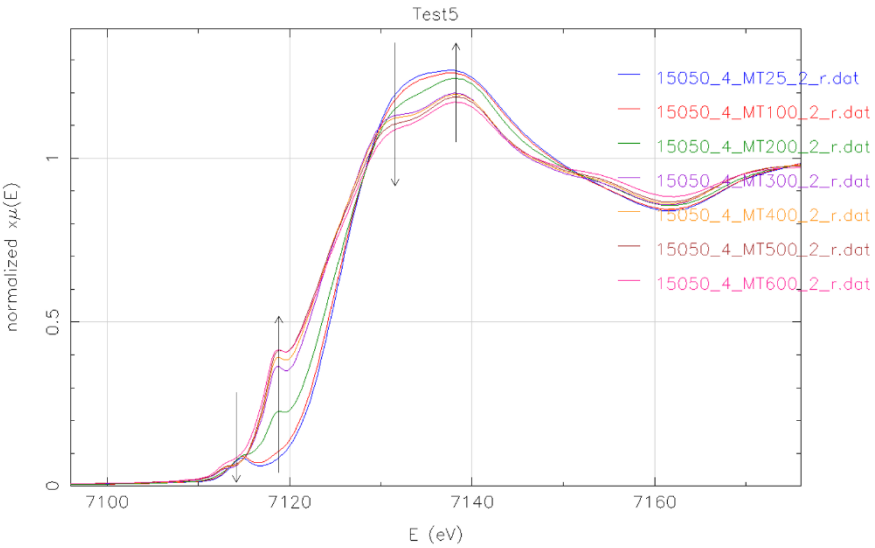

Figure 2 - XANES of the in-situ samples, showing change in peaks with the increase of temp

We were able to track important changes in the XAS spectra:

a) Inside the single ex-situ series (from 25°C to 1000°C, Figure 1);

b) Inside the in-situ series (from 25°C to 650°C, Figure 2);

c) Between the ex-situ and in-situ series

d) We were able to determine also a shifting towards the ex-situ spectra of the samples subjected to the in-situ treatment after a period of time in air.