



	Experiment title: Operando investigation of Fe-N-C oxygen reduction catalyst using X-ray absorption and emission spectroscopies	Experiment number: MA-5765
Beamline: ID26	Date of experiment: from: 12 April 2023 to: 17 April 2023	Date of report: 14/06/2023
Shifts:	Local contact(s): Vinod Paidi	<i>Received at ESRF:</i>
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Report:

1. Brief description of the experiment

The most promising of platinum group metal (PGM)-free for the oxygen reduction reaction (ORR) in the low-temperature proton exchange membrane (PEMFC) type of fuel cell is based on metal-nitrogen-carbon (M-N-C, where M = Fe, Ni, Co, and Mn) composites with metal-nitrogen active sites embedded in stacked carbon graphitic sheets. The catalytic performance of some M-N-C has been reported to be on the order of 10–20% that of platinum (Pt) catalysts, showing exciting potential. However, the durability data reported in the open literature reveals insufficient stability of this class of materials in real fuel cell tests. Recently, LEPMI and ICGM also evidenced that the addition of tiny amount of platinum (Pt) to a Fe-N-C catalyst significantly improves its durability. The MA5765 experiment was thus intended to provide a comprehensive understanding of changes in chemistry and structure of Fe-N-C catalysts in an operating PEMFC device, and to monitor whether the same holds for a combined Pt/Fe-N-C catalyst. For that purpose, different Fe-N-C materials were synthesized by Institut Charles Gerhardt in Montpellier (Frédéric Jaouen's group) and by Ecoles des Mines Paristech (Sandrine Berthon Fabry's lab), and some were modified by 1 wt. % of Pt, which we refer to as Pt/Fe-N-C.

2. Results and discussion

To operate the Fe-N-C catalysts in the custom made single PEMFC cell, membrane-electrode assemblies (MEAs), 1 cm² in surface area, were prepared by Nicolas Bibent at ICGM. These were assembled in the PEMFC cell, and successfully operated (**Figure 1**):

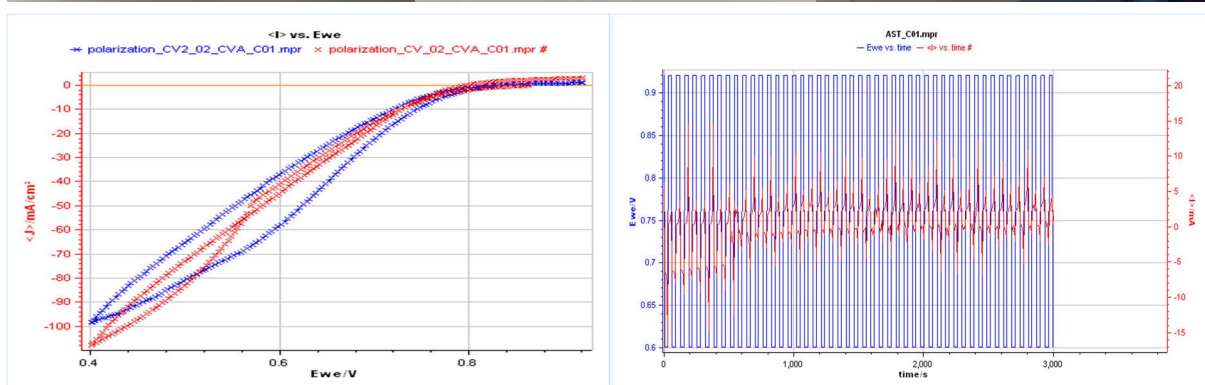
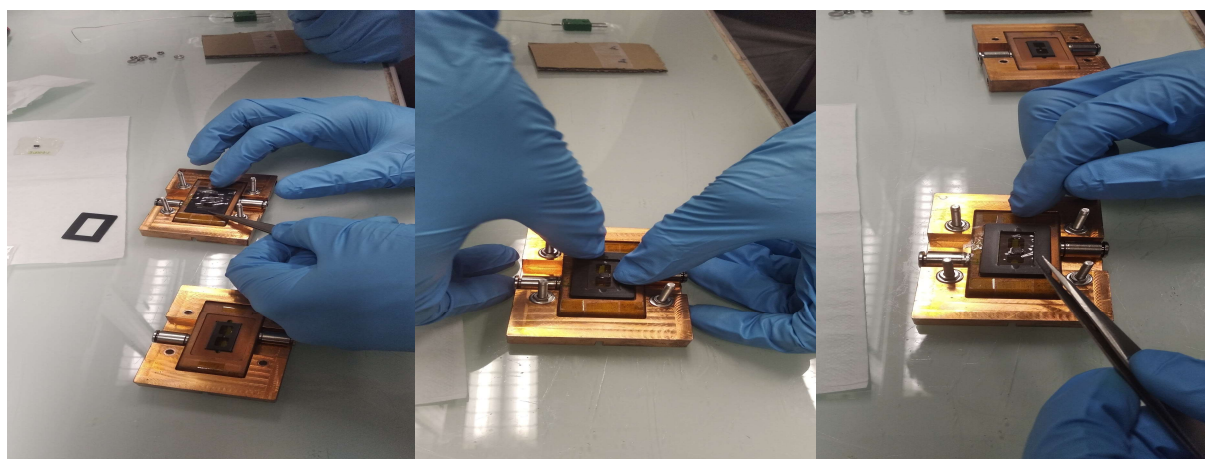


Figure 1. Upper part: Photographs showing the assembly of a 1 cm² size Fe-N-C MEA. Bottom part: beginning of life polarization curve and variation of the current density during the accelerated stress test aimed at ageing the Fe-N-C catalysts.

To highlight structural and chemical changes occurring under PEMFC operating conditions, a bunch of reference materials was prepared and analysed *ex situ*. The list included iron (II) oxide (FeO) and iron (III) oxides, the native Fe-N-C catalysts, those modified by 1 wt. % of Pt and the gas-diffusion layer used to feed the Fe-N-C catalysts with oxygen and to exhaust the produced water in the PEMFC device.

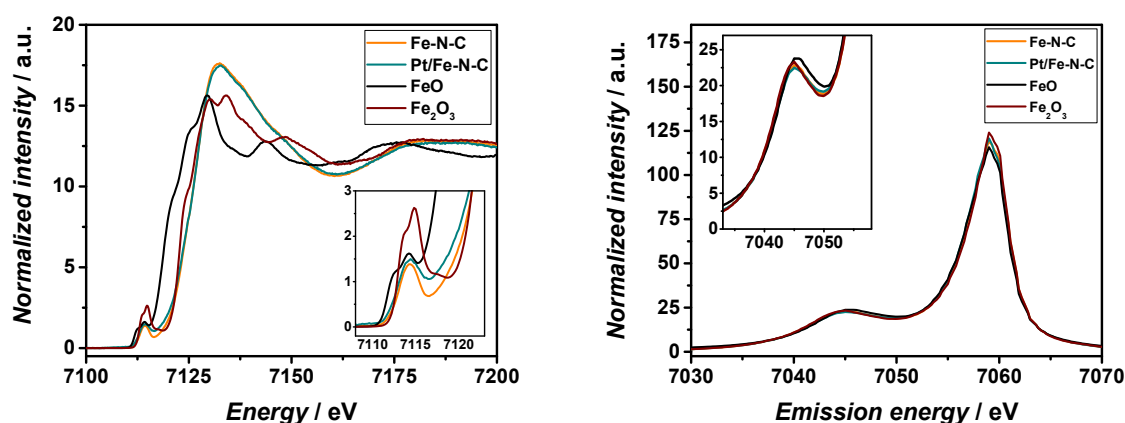


Figure 2. Left: Fe K β HERFD XANES and right: K β mainline obtained on the pristine Fe-N-C and Pt/Fe-N-C catalysts.

The XANES and the K β ' XES spectra showed that Fe is mainly present under the form of single Fe atoms, and mostly present as Fe(III), in the Fe-N-C and Pt/Fe-N-C catalysts (**Figure 2**). A slight change of the pre-edge was noticed when the Fe-N-C was modified by 1 wt. % Pt (see pre-edge on left panel), which we ascribed to the fact that the Fe-N-C catalyst was contacted with an acidic solution for more than 12h to deposit the colloidal solution of Pt.

Interestingly, we observed that Fe atoms change oxidation state upon accelerated stress tests conducted *ex situ*

using rotating disk electrode or gas diffusion electrode set-ups (**Figure 3**). As the *ex situ* data are of high quality, as this has never been observed, this result and should lead to at least one manuscript in a high impact factor peer-reviewed journal.

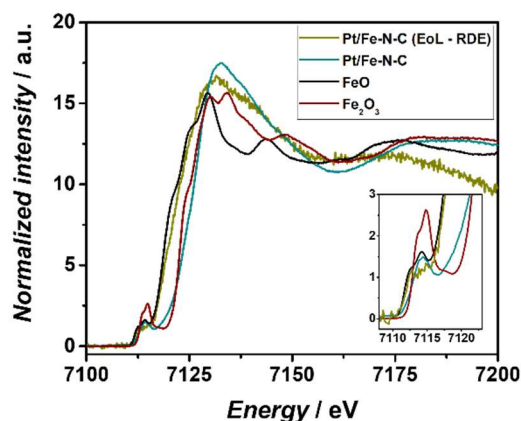


Figure 3. *Fe K β HERFD XANES spectra on the aged Pt/Fe-N-C catalysts.*

Analysis of the *operando* data is currently being performed. We will pay special attention to their interpretation as the *operando* measurements suffered from massive beam effect. Indeed, the XANES and XES measurements were performed at 7 keV and lasted a few minutes/ten of minutes, respectively. In the meantime, the highly-brilliant X-ray beam produced many different radical species ($\bullet\text{H}$, $\bullet\text{OH}$, H_2 , and H_2O_2) by radiolysis with water produced by the ORR. Electrochemically speaking, this was detected from the decrease of the cell voltage as soon as X-rays were shined onto the MEAs. Unfortunately, the degradation was autocatalytic as the produced H_2O_2 molecules readily reacted with Fe cations, producing further radicals ($\bullet\text{OH}$, $\bullet\text{OOH}$) which oxidize the neighbouring catalyst, ionomer and proton-exchange membrane. This was noticed from the aged MEAs, which appeared drilled after the *operando* experiments.

The *operando* data will thus be analysed at the light of these limitations (did we measure changes in Fe-N-C structure and chemistry related to electrochemical ageing or to beam effect?), and the conclusions we'll draw from these should be comparable to those of the *ex situ* spectra measured on the same samples. Should it be the case, another manuscript will be written.

3. Outlook

We managed to measure XAS and XES spectra for Fe-N-C catalysts of different structure under *operando* conditions, *i.e.* in a custom made single PEMFC cell. The *operando* data are currently being analysed, and will be discussed at the light results obtained *ex situ* on the same samples. We are grateful to the local contact, Dr. Vinod Paidi, for his kind help and to Dr. Viktoriia Saveleva, who helps us analyzing the XANES and XES data.