



	Experiment title: Structure and stability of $\text{Fe}_x\text{Zr}_{1-x}\text{O}_{2-\delta}/\text{C}$ as novel ORR catalyst for PEMFC - An operando EXAFS study	Experiment number: MA-4294
Beamline: BM30B	Date of experiment: from: 07/09/2019 to: 17/09/2019	Date of report:
Shifts: 27	Local contact(s): Olivier PROUX	<i>Received at ESRF:</i>
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Report:

Background:

Proton Exchange Membrane Fuel Cells (PEMFCs) have been, in recent years, successfully deployed in several small-scale production of vehicles. Unfortunately, mass commercialization of this technology is hindered by the relatively high cost, mostly due to the amount of Pt required at the cathode electrode, because of the sluggish Oxygen Reduction Reaction (ORR) kinetics. Alternatively, PGM-free catalysts can be employed to decrease catalyst cost due to their high abundance, despite their specific activity and stability being inferior to that of Pt. The most promising candidates so far contain N-coordinated Fe as active species, embedded in a carbon matrix [1]. Aiming at a higher stability in acidic medium, we prepared a ZrO_2 -based catalyst [2], whose ORR activity could be astonishingly boosted [3] by partially substituting Zr^{4+} in the structure with Fe^{3+} , very ORR-active by itself. The nanometric carbon-supported catalyst here considered, denoted $\text{Fe}_x\text{Zr}_{1-x}\text{O}_{2-\delta}/\text{C}$, was already characterized using XRD, Mössbauer spectroscopy and XPS, to get first information about phase and Fe coordination, and tested in a PEMFC (loading of $0.38 \text{ mg}_{\text{cat}}/\text{cm}^2_{\text{MEA}}$) [4]. Previous spectroscopic works investigated Fe-N-C materials by various ex-situ [1] and operando XAS in a liquid cell [1, 5, 6].

Results and conclusions of the study:

In this document we report the XAS operando analysis conducted at the FAME ESRF beamline BM30b in a H_2/O_2 PEMFC on a commercial Fe-N-C (Pajarito Powder, USA) and on a synthesized $\text{Fe}_x\text{Zr}_{1-x}\text{O}_{2-\delta}/\text{C}$ (both at $4 \text{ mg}_{\text{cat}}/\text{cm}^2_{\text{MEA}}$). Such operando analysis was made possible by the use of the setup previously employed at the same beamline and published in [7].

The XANES data collected on the commercial Fe-N-C evidenced the relevant presence of metallic Fe (see Figure 1a), confirmed in the Fourier-transformed data (not shown). Furthermore, the Fe^0 oxidation upon testing is evident from the near edge data and a rough estimate of the atomic fraction upon testing of Fe^0 vs. Fe-N-C and/or Fe at higher oxidation state was performed using a linear combination fit of the Fe^0 standard and the Fe

spectrum of the aged gas diffusion electrode (GDE, see Figure 1a). Due to the relevant presence of Fe^0 , further direct XANES/EXAFS analysis of the Fe-N-C sites and their change upon testing was unfortunately impossible.

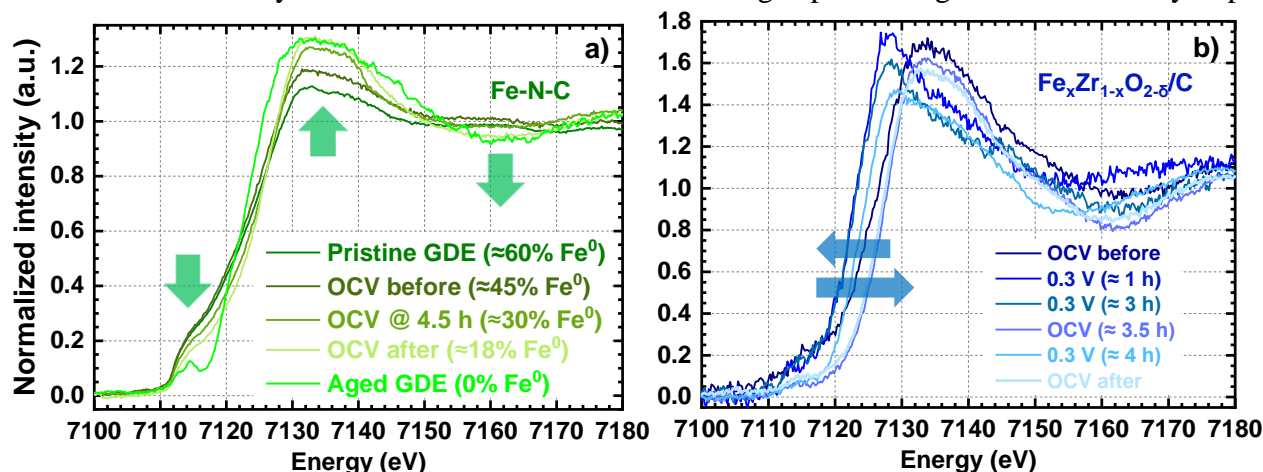


Figure 1: Ex situ/in situ/operando XANES data collections (≈ 25 min., fluorescence yield) in H_2/O_2 PEMFC on a) Fe-N-C and b) $\text{Fe}_x\text{Zr}_{1-x}\text{O}_{2-\delta}/\text{C}$ before, during and after tests at $0.3 \text{ V}_{\text{cell}}$. (GDE = Gas Diffusion Electrode)

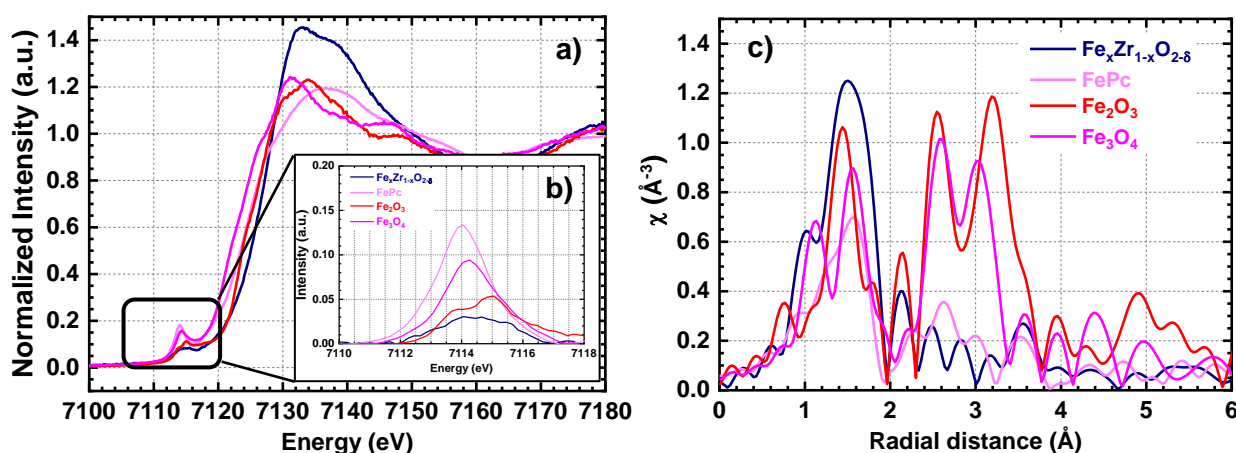


Figure 2: a) Ex situ XANES data (≈ 25 min., fluorescence yield) on a pristine GDE of $\text{Fe}_x\text{Zr}_{1-x}\text{O}_{2-\delta}/\text{C}$ vs. various references, b) pre-edge analysis and c) Fourier transform of the data.

On the other hand, the XAFS analysis of the $\text{Fe}_x\text{Zr}_{1-x}\text{O}_{2-\delta}/\text{C}$ catalyst showed very interesting results. From ex-situ XANES data at the Fe edge (both near-edge, Figure 2a, and pre-edge, Figure 2b) it is evident that iron is mostly in high oxidation state (3+); furthermore, the Fourier-transform of the XAFS data (Figure 2c) show the absence of a second shell of neighbours. These two observations confirm the conclusions drawn in the previous publication [4] about the presence of isolated Fe in the ZrO_2 structure. The operando XANES data at the Fe edge (Figure 1b) show an edge-shift to lower energies (Fe-ion reduction) at $0.3 \text{ V}_{\text{RHE}}$, reversibly coming back to the OCV and a gradual irreversible edge-shift to higher energies at the OCV, likely correlated to the catalyst degradation. Furthermore, Zr K edge XAFS data on $\text{Fe}_x\text{Zr}_{1-x}\text{O}_{2-\delta}/\text{C}$ show changes upon operation (related to Zr valence/coordination, under further investigation).

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