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|  | Experiment title: In situ and operando coherent diffraction imaging of nanostructures during chemical reactions: towards atomic resolution and time-resolved experiment | Experiment number: CH-5346 |
| Beamline: ID31 | Date of experiment: from: 29 mars 2018 to: 03 avril 2018 | Date of report: 24/02/2022 |
| Shifts: 15 | Local contact(s): Dr. Jakub Drnec | <i>Received at ESRF:</i> |
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Report:

First, we would like to apologize for the delay regarding the submission of this experimental report.

The aim of the CH-5346 experiments was to unravel the degradation mechanisms of Fe-based electrocatalysts *in situ* (*i.e.* under potential control) using WAXS and SAXS. A pair distribution function (PDF) analysis of the WAXS data was planned as we knew that this class of materials is structurally amorphous/disordered.

Three different Fe-N-C electrocatalysts were synthesized specifically for the experiment using ZIF-8, Fe acetate, and phenanthroline. The Fe, N and C precursors were mixed via dry planetary ball milling and pyrolysed at 1050 °C under Ar. We labelled the materials as Fe_x, where *x* is the weight fraction of Fe before the pyrolysis step (0, 0.5 or 5.0 weight. %). The catalysts were extensively characterized by X-ray absorption (XAS), transmission electron microscopy, Raman and energy-dispersive X-ray spectroscopy, and Brunauer-Emmett-Teller techniques. We observed that the Fe_{5.0} catalyst comprises Fe carbide nanoparticles surrounded by a shell of N-doped graphitic carbon, while the Fe_{0.5} catalyst comprises Fe cations atomically dispersed in the N-doped carbon matrix. Moreover, the carbon matrix was found more graphitic for Fe_{5.0}, and more amorphous for Fe_{0.5} (the most promising material for oxygen reduction reaction, the cathodic reaction in polymer electrolyte membrane fuel cells).

Figure 1 displays the PDF analyses of the WAXS patterns for Fe_{0.0}, Fe_{0.5} and Fe_{5.0}. As brutto *G*(*r*) graphs were poorly informative, we subtracted the signal of the carbon matrix (Fe_{0.0}) and normalized the intensity of the *G*(*r*) traces by the intensity of the C-C peak at *ca.* 1.41 angströms. Intense bands at 2.60, 3.77, 4.23, 4.57 and 5.19 angströms in the ‘Normalized Fe_{5.0}-Fe_{0.0}’ difference signal confirmed that Fe_{5.0} is essentially composed of Fe₃C nanoparticles, not Fe_{0.5} (at least within the detection limit of the technique).

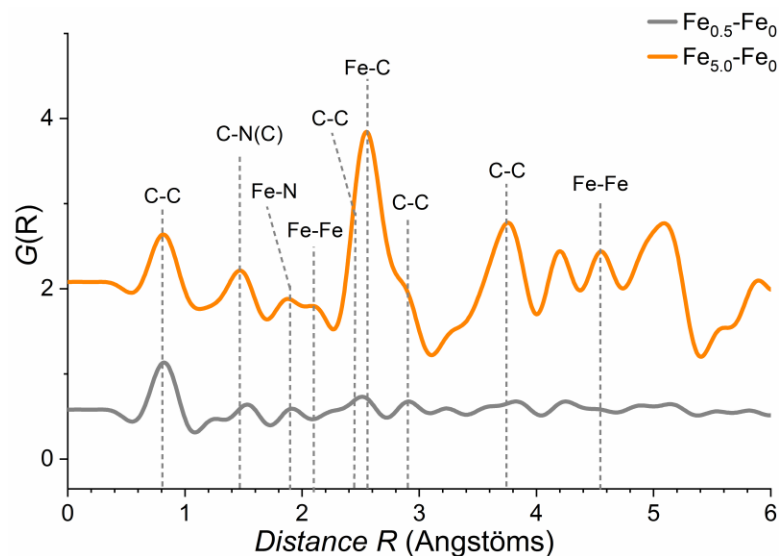


Figure 1. Normalized and the $Fe_{0.0}$ -subtracted-pair distribution function analyses of the WAXS patterns measured *ex situ* (in capillaries).

The weak intensity of the $Fe_{5.0}$ - $Fe_{0.0}$ PDF analyses for the $Fe_{0.5}$ catalyst cast a doubt on the use of WAXS data. This fear has been confirmed as the intensity was noisier and lower after the $Fe_{0.5}$ catalyst was coated with a thin layer of Nafion and immersed in liquid electrolyte for electrochemical measurements. Despite all our efforts, we were unable to extract any relevant information from the *in situ*-measurements on $Fe_{0.5}$.

Nevertheless, a manuscript combining the PDF analyses of WAXS spectra with other data has been written, and submitted to *Applied Catalysis B: Environmental* in January 2022. It is currently under revision, and ESRF will be acknowledged for excellent support and beamtime allocation.