ESRF	Study of fuel cells catalysts atomic structure using x-ray absorption spectroscopy	**Experiment number:** MA 121
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Report:
MA 121 project was dedicated to *in situ* proton exchange membrane fuel cell (PEM FC) investigations leading to accurate information about the mechanisms which govern its operation. Our XAFS measurements were focused on 20%Pt/Vulcan catalyst ($L_{Pt} = 1 mg/cm^2$, reference sample), on different kinds of Pt-based electrodes with Pt loading lower than $1 mg/cm^2$, e.g. 43%PtCo and 43%PtCo modified by Na_2WO_4 supported on Vulcan, and on novel Ru-Se unmodified and modified by Na_2WO_4 catalysts supported on Vulcan.

All *in situ* XAFS experiments were carried out under ambient conditions, using a modified fuel cell optimized for X-ray measurements, designed and realized in our home laboratories (see Figure 1).

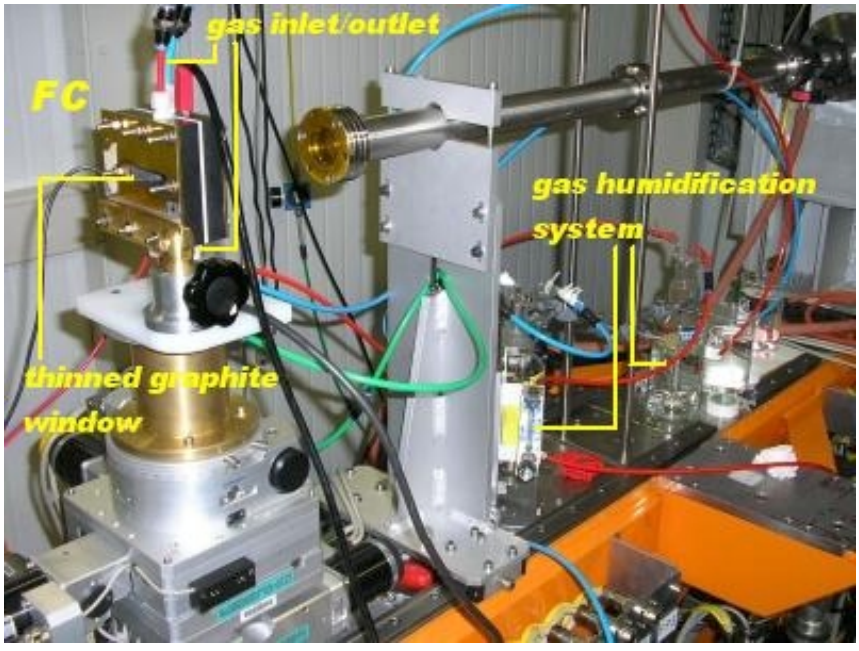

Figure 1. Optimized XAS fuel cell (FC) setup

To reduce the absorption, the overall thickness of the graphite was thinned to create the window for XAS measurement in both modes: transmission and fluorescence. Rectangular holes are parallel oriented with internal gas flow channels. Graphite plates were held together by eight screws, inducing high enough compression of the membrane electrode assembly (MEA) and ensuring good electrical contact.
The cell was operated connecting its inlets to an oxygen and an hydrogen supply and flowing them into the cell at the atmospheric pressure (gases flow was optimized to about 100ml/min). Special gas humidification system (also shown in Figure 1) was mounted together with FC. The cell voltage output (below 1V, changed and controlled by potentiostat driven by a LabView-based computer program) was measured continuously during XAS data acquisition and stored with the structural data.
MEAs, composed of a cathode loaded by studied catalyst supported on Vulcan, Nafion as a proton conductive membrane and an anode loaded by 30%Pd/Vulcan (1mg/cm^2), were prepared by hot pressing in our home laboratory and stored into distilled water. All *in situ* XAFS measurements were performed using transmission geometry in the 11.4–13.1 keV and 22.0–23.7 keV energy range for Pt L_3-edge and Ru K-edge, respectively. XAFS data were collected according the following procedure:
– EXAFS measurements at just mounted MEA (blank);
– EXAFS measurements at open circuit (OCV);
– quick XANES measurements realised during E/i curve collection;
– EXAFS measurements at chosen potentials.

Each measurement was repeated two times. The sampling procedure was chosen to yield high quality data for both pre- and post-edge background analyses used to normalize the spectra.

A preliminary data analysis has been performed for Pt-based electrodes using the GNXAS package. The extracted of high quality EXAFS signals for MEA with e.g. 20%Pt/Vulcan cathode are shown in Figure 2. The fitting procedure has been realized taking into account whole features affecting the absorption spectra near the Pt L_3-edge (multiple-scattering and two-electron excitation effects, particle size distribution and electrode homogeneity).

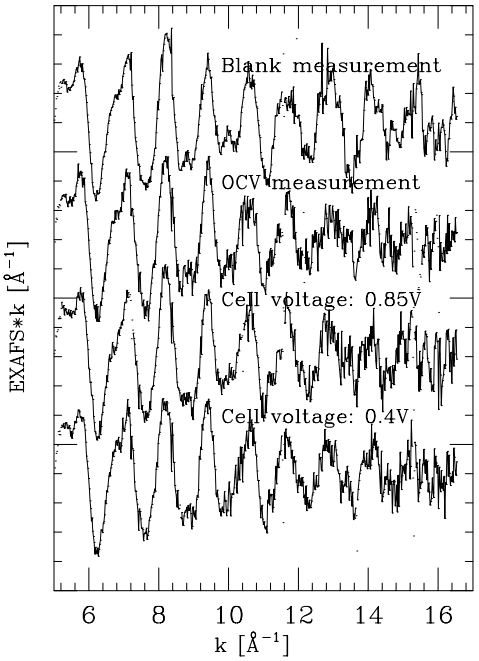

Figure 2. MEA Pt L_3-edge EXAFS signals

The first data analysis results suggest that on the base of measurements performed using optimized XAS-FC setup and sophisticated data analysis, we are able to distinguish electronic and structural changes related to fuel exposure and electrode polarisation. Now efforts have to be devoted to analyze accurately whole data and to obtain precise structural information.