

**Experiment title:**

Novel Pt-Cs-W electrocatalysts for PEM fuel cell investigated by in situ X-ray absorption spectroscopy

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**Report:**

Proton exchange membrane fuel cells (PEMFC) are a promising class of compact devices which has the potential to resolve many problems associated with the production and consumption of energy. However, there are two main obstacles which limit seriously PEMFC ordinary usage: cost and lifetime. During the last two decades a significant reduction of the Pt loading in PEMFCs has been obtained without affecting their efficiency. Now advanced PEMFCs can operate using a load of Pt lower than  $0.1 \text{ mg/cm}^2$ , about two order of magnitude smaller than initial prototypes. Higher durability can be obtained e.g. by supporting nano-catalyst on an inorganic matrix which ensures a mutual metal-support interactions, high dispersion of the catalytic centres and it is resistant on the corrosion process.

The samples studied in this experiment were a nano-powder of Pt dispersed in an innovative electrocatalyst support consisting of a heteropolyacid salt diluted in Nafion and Vulcan XC-72 [1]. To perform in situ XAFS measurements the electrodes have been prepared using a standard procedure (see e.g. [2,3]). During the experiment, we tested the following catalysts:

- $\text{X}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  ( $\text{X} = \text{Cs}, \text{Rb}$ ) chemically doped with  $10\% \text{Pt}^{4+}$ , then reduced electrochemically inside a fuel cell (Pt loading in both catalysts below  $0.1 \text{ mg/cm}^2$ );
- $10\% \text{Pt/Vulcan}$  coprecipitated with  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  (Pt loading about  $95 \mu\text{g/cm}^2$ );
- $10\% \text{Pt/Vulcan}$  mixed with  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  in a proportion (1:2) (Pt loading about  $90 \mu\text{g/cm}^2$ ).

The considered catalysts worked on the oxygen side, as a cathode of PEMFC. The anode (the hydrogen side) has been loaded with 1 mg/cm<sup>2</sup> of Pd (30%Pd supported on Vulcan XC-72, E-TEK). This permits to focus the XAFS investigation at the cathode where the oxygen reduction reaction (ORR) takes place, without a significant influence of the anode absorption.

The core of the XAFS FC set-up (installed at BM29 station) has been a commercial single PEM fuel cell EFC-05-02 (Electrochem. Inc.) modified in order to optimize X-ray absorption spectroscopy measurements on the catalyst still retaining its original electrochemical performance (for details see [4]). The cell has been rotated of 45° to the X-ray beam direction and simultaneously the measurements at the Pt L<sub>3</sub> and W L<sub>3</sub> edges have been realized in fluorescence mode using a 13 channels Ge X-ray detector and transmission mode, respectively. Additionally, a Zn foil (thickness 15 μm) has been positioned between the multi-channel Ge detector and the cell in order to attenuate the strong emission line Lβ<sub>1</sub> of W (9672.4 eV) which affect the intensity of the Pt Lα<sub>1</sub> (9442.3 eV) during XAFS measurements due to detector energy resolution (about 150 eV at 10 keV).

The spectra have been collected in a whole XAFS range as a function of time and then, for a stable catalyst, as a function of working conditions. FC has worked at room temperature and under various potential values, from OCV to 0.3V. Obtained high quality data gave us the possibility to perform analysis in both ranges: XANES and EXAFS (using the GNXAS package and methodology presented in [5]). For the catalysts chemically doped with Pt<sup>4+</sup>, a progressive electrochemical reduction of Pt realized inside the fuel cell has been recorded and platinum nano-particles formation has been clearly observed. Stable platinum nano-structures have been obtained after about 15-20h of reduction. Mean diameter of the nano-particles estimated by EXAFS analysis is in the range of 1.5–2nm (large surface-to-bulk ratio). Then XAFS spectra for working MEA collected in various fuel cell operation conditions have been used to control changes in tungsten and platinum local atomic and electronic structure. Results show that variations in the potential up to 0.6V are associated with significant changes in the platinum local structure (mainly effect of oxidation/deoxidation), while in a W L<sub>3</sub> spectra only slight changes in a white line intensity have been observed. On the base of XAFS information (combined with HRTEM and XRD results) the structural model of these low-Pt innovative catalysts is outlined and some mechanisms which govern their operation are described (papers in preparation).

## References

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