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Local atomic order in low Pt-content nanocatalysts investigated *in situ* by XAS

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Abstract. The unique features of X-ray absorption spectroscopy allow investigations of nanosized catalysts for fuel cells under working conditions. We present the results of an experiment carried out on a low Pt content electrocatalyst supported by a mesoporous heteropolyacid salt and used at the cathode of a proton exchange membrane fuel cell (PEMFC). The analysis of the EXAFS signal at the Pt L₃-edge indicates that upon operating the fuel cell a substantial oxygen desorption from the Pt catalytic surface occurs followed by a tangible structural change on the Pt local order.

1. Introduction

Development of efficient electrocatalysts for the oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFCs) is today regarded as a crucial aspect in research on alternative energy sources. [1, 2] X-ray absorption spectroscopy (XAS) provides the unique opportunity of studying the structural and electronic response of nanocatalysts under variable operating conditions inside PEMFCs. However the loading of advanced catalysts for PEMFCs is limited (less than 0.1 mg/cm²) and the absorption background of the fuel cell components is high. These drawbacks limit severely the insight of the XAS technique for *in situ* studies. Therefore, special setups and suitable experimental strategies have to be devised to guarantee realistic *in situ* conditions and a good quality for the XAS measurements. In this spirit we have modified a commercial PEM fuel cell in order to operate it retaining its electrochemical performance during the XAS measurements on the catalyst. Here, we present the results of an *in situ* XAS experiment (see Ref. [3] for more details) performed using our modified fuel cell and focused on a low Pt content nanocatalyst supported by a mesoporous heteropolyacid salt (Cs_{2.5}H_{0.5}PW₁₂O₄₀).

2. Experimental

A catalyst layer obtained by mixing 10%Pt-Cs_{2.5}H_{0.5}PW₁₂O₄₀, Vulcan XC-72 and Nafion (final Pt loading 0.1 mg/cm²)[4, 5], has been used at the cathode of a special PEM fuel cell optimized for *in situ* X-ray measurements. [6, 3] At the anode side the catalyst was composed by Pd nanoparticles, Vulcan XC-72 and Nafion. Pd is found to be suitable as the anode catalyst and

its X-ray absorption around the Pt L_3 -edge is smooth thus allowing to focus the investigation on the cathode where the ORR takes place.

The XAS experiment has been carried out at the beamline BM29 of the European Synchrotron Radiation Facility (ESRF). The special fuel cell has been installed between two ionization chambers, rotated by 45° to the X-ray beam direction and connected to oxygen and hydrogen gas lines. A 13-channel Ge X-ray detector has been positioned close to the cell at 90° to the incident beam in the synchrotron horizontal plane.

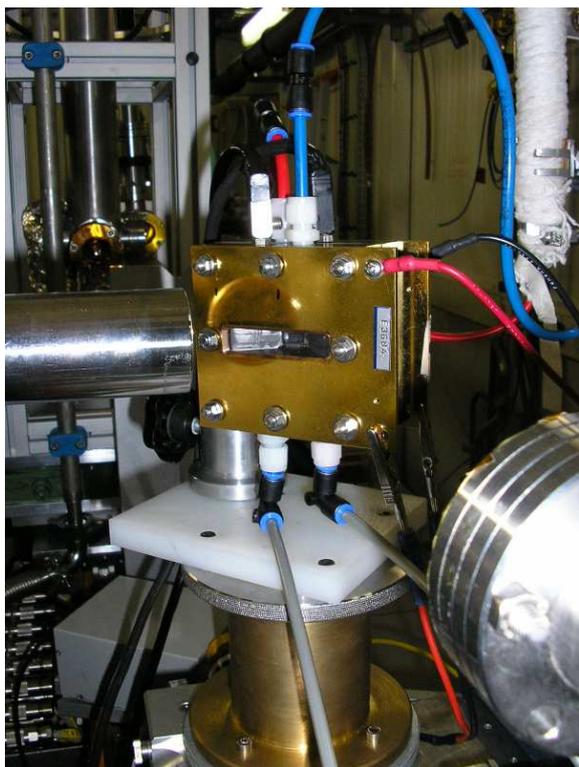


Figure 1. Picture taken at the beamline BM29 (ESRF) showing the special PEM fuel cell connected to the gas lines and positioned close to the X-ray fluorescence detector (on the left).

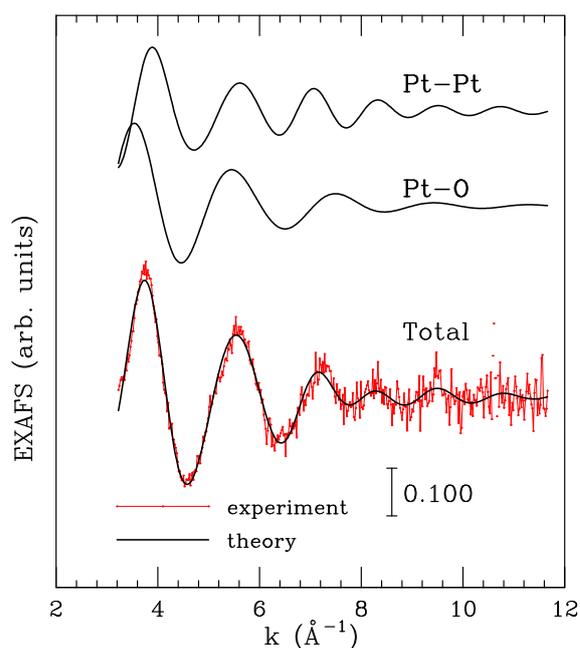


Figure 2. GNXAS analysis of the experimental EXAFS signal (Pt L_3 -edge) related to the Pt nanocatalyst positioned at the cathode of the PEM fuel cell (dry cell conditions, i.e. no gases flux).

A set of energy dispersive X-ray fluorescence measurements has been performed under working conditions (room temperature) at selected fuel cell potentials (0.85 V, 0.6 V, 0.4 V) and on the dry cell (no gases flux). The measurements have been carried out at the Pt L_3 -edge (11564 eV) integrating (10 s per point) the fluorescence photon counts ($I_f(E)$) within an energy region of interest including the Pt L_{α_1} line (9442.3 eV). Due to the high content of tungsten in the catalyst support, the W fluorescence affects the intensity of the Pt L_{α_1} line during XAS measurements as an effect of the detector energy resolution (about 150 eV at 10 keV). Therefore, a Zn foil (thickness $15\mu\text{m}$, K-edge: 9659 eV) has been positioned between the multi-channel detector and the cell in order to attenuate the strong emission line L_{β_1} of W (9672.4 eV).

The high dilution of the Pt catalyst allows us to apply a ‘small sample thickness’ approximation. Within this approximation the X-ray absorption coefficient is simply given by $\mu_{Pt}(E) \propto I_f(E)/I_0(E)$. [3] The Pt L_3 -edge spectra have been truncated prior to the L_1 -edge (12100 eV) thus obtaining EXAFS oscillations up to $k \sim 12 \text{ \AA}^{-1}$.

The XAS data have been analyzed using the GNXAS software package. [7, 8] Phase shifts and theoretical EXAFS signals have been calculated *ab initio* using tangent “muffin tin” spherical potentials. Non-linear atomic absorption background including double electron excitations has been taken into account upon the XAS data fitting procedure. Linear background subtraction and normalization of the X-ray absorption spectra have been carried out to facilitate a qualitative comparison between subsequent measurements.

3. Results and discussion

Fig. 2 shows the quality of a typical EXAFS signal analysis of the Pt nanocatalyst positioned at the cathode of the PEMFC (dry cell case, i.e. without gases flux). The quality of the EXAFS data is good despite the high dilution of the sample and the background absorption of the PEMFC. The experimental EXAFS signal has been fitted using only a first shell analysis including both the Pt-Pt and the Pt-O two-body signals (see Fig. 2). A similar approach has been used for the analysis of the other EXAFS signals associated with the selected cell working potentials (0.85 V, 0.6 V, 0.4 V).

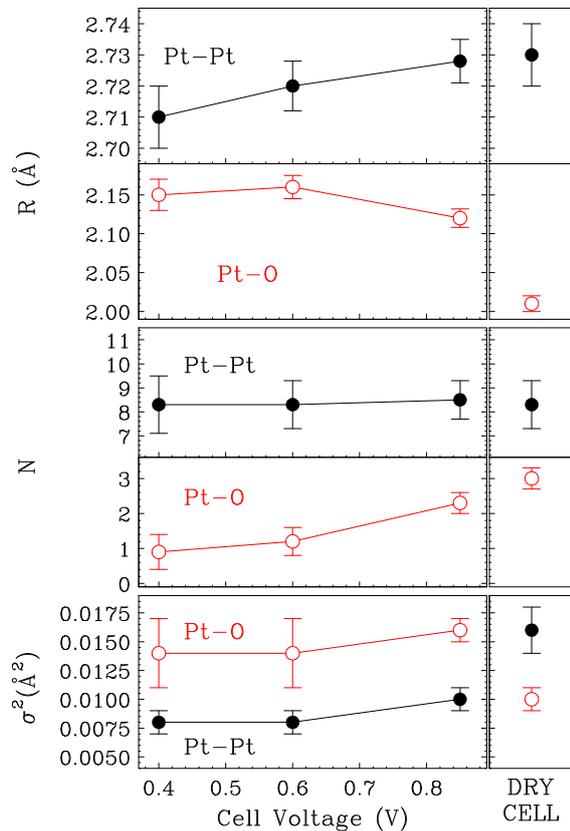


Figure 3. Structural data associated with the first shell of Pt in nanoparticles, used as a catalyst, obtained under various fuel cell working conditions.

Fig. 3 shows the values of the structural parameters describing nearest neighborhood of Pt as a function of the electrochemical conditions of the fuel cell. The coordination number of the Pt-Pt bond (N_{Pt-Pt}) is around 8.3 and remains constant at all the operating conditions. The curve presented in Fig. 4 calculated for fcc quasi-spherical Pt nanoparticles[9], allows to estimate

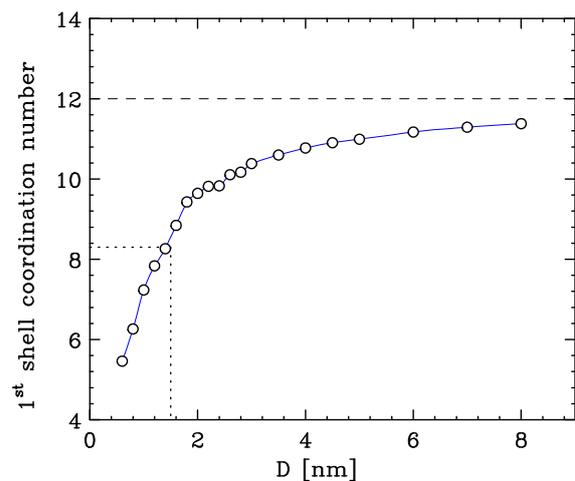


Figure 4. Calculation of the coordination number N in quasi-spherical Pt nanoparticles as a function of their diameter. [9] In bulk Pt (fcc structure) $N = 12$ (dashed line). The dotted lines refer to the Pt catalyst used in this experiment $N \simeq 8.3 \Rightarrow D \simeq 1.5$ nm.

the average nanoparticles diameter using the N_{Pt-Pt} value. The expected average diameter in the catalyst under consideration is around 1.5 nm. This means that about 80% of the Pt atoms are positioned on the surface of the nanoparticles. This further increases the sensitivity of the XAS technique to the structural effects occurring during the catalysis as this process involves only the surface of the Pt nanoparticles.

The Pt-Pt average bond length (R_{Pt-Pt}), which is exceptionally short ($R_{Pt-Pt} \simeq 2.730$ Å under dry cell conditions), due to the presence of Pt-Pt dangling bonds on the nanoparticles surface, exhibits a further gradual contraction down to $R_{Pt-Pt} \simeq 2.710$ Å upon cell voltage decrease. Moreover, the σ_{Pt-Pt}^2 undergoes an abrupt drop when the gases flux is open indicating a substantial increase of the atomic structural order. On the contrary, the Pt-O bond length (R_{Pt-O}) relaxes suddenly after opening the gases flux (open circuit voltage conditions). This effect is accompanied by a steep increase of the σ_{Pt-O}^2 parameter and a gradual decrease of the coordination number N_{Pt-O} . This experimental result is in agreement with recent theoretical simulations [10] indicating that the Pt-O bond becomes weaker under operating conditions thus facilitating the oxygen desorption from the Pt nanocatalyst surface. It is worth to note that the oxygen desorption mechanism is probably responsible for the changes observed in the Pt local structure.

Conclusions

We have presented the results of a XAS fluorescence experiment carried out on a Pt nanocatalyst working on a PEM fuel cell. The unique insight of the XAS technique has shed light on a subtle structural transformation occurring at the nanometric scale during the catalysis process. The structural parameters obtained by XAS analysis indicate a substantial oxygen desorption from the Pt nanoparticles surface just after the activation of the PEMFC, in agreement with recent theoretical calculations. The Pt nanoparticles surface structure, strongly affected by the desorption mechanism, undergoes a structural change. We believe that the plasticity of the Pt local atomic structure revealed by XAS could be regarded as an important peculiarity and could play a significant role in explaining the exceptionally high catalytic activity of Pt supported on mesoporous heteropolyacid salts.

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