Study of the atomic structure and morphology of the Pt$_3$Co nanocatalyst

G. Greco$^1$, A. Witkowska$^2$, Y. Soldo$^3$, E. Larquet$^4$, N. Menguy$^4$, A. Cognigni$^5$, M. Minicucci$^1$, E. Principi$^1$ and A. Di Cicco$^{1,4,5}$

$^1$CNISM, Dipartimento di Fisica, Università di Camerino, I-62032 Camerino (MC), Italy; $^2$Department of Solid State Physics, Gdańsk University of Technology, 80-233 Gdańsk, Poland; $^3$LEPMI, CNRS-Grenoble INP-UJF 1130 rue de la Piscine, 38402 St. Martin d’Hères, France; $^4$Institut de Minéralogie et de Physique des Milieux Condensés, UMR 7590, CNRS, Universités Paris 6 et Paris 7, Paris, France; $^5$Sincrotrone Trieste, ELETTRA, 34012 Basovizza (TS), Italy.

E-mail: giorgia.greco@unicam.it

Abstract. It has been shown that Pt$_3$Co nanoparticles used as a catalyst for cathode of Proton Exchange Membrane Fuel Cells (PEMFC) enhance oxygen reduction reaction (ORR) activity even by a factor of two compared to pure Pt nanoparticles. The local structure and chemical disorder of a commercially available Pt$_3$Co nanocatalyst supported on high surface area carbon were investigated. High-quality XAFS spectra were collected at the ELETTRA synchrotron XAFS 11.1 beamline. XAFS spectra analysis have been performed accounting for the reduction of the coordination number and degeneracy of three-body configurations, resulting from transmission electron microscopy (TEM) and x-ray diffraction (XRD) extracted mean particles diameter, size distribution and expected surface atom contributions. The presence of a Co-Co first neighbour EXAFS signal is shown to be related to the degree of the alloy’s chemical disorder. This is a good starting point for analyzing the atomic structure of Pt$_3$Co nanocrystalline system and their changes as a function of alloy preparation or working conditions when they operate as a catalyst in PEMFC.

1. Introduction

Nanocrystalline metals and alloys are a class of materials which in recent times attract interest due to their particular physical and chemical properties. Understanding structure and dynamics of nanomaterials as well as their physico-chemical properties is currently regarded as a challenging research activity having crucial consequences in material design for various novel applications. For example, platinum alloys are an interesting class of binary compounds due to their significantly higher electocatalytic activities towards the oxygen reduction reaction (ORR) than the platinum alone in low temperature fuel cells [1].

In this work, we focus our attention on the structural characterization of a simple bimetallic commercial nanomaterial (Pt$_3$Co E-TEK$^{TM}$, nominally PtCo) using advanced x-ray absorption spectroscopy (XAS) data analysis. The XAS technique is sensitive to the local structure (two- and even three-body configurations) up to 5 – 10 Å around photoabsorbing sites, selected by their atomic number, for this reason it is a very useful tool for nanostructural materials study. We have performed a first-shell two-edge (Co K and Pt L$_3$) analysis of EXAFS (extended x-ray absorption fine structure) signals by using the GNXAS method [6, 7] in combination with
x-ray diffraction (XRD) and transmission electron microscopy (TEM) accounting for the actual size distribution and morphology. Results presented in this work are a solid starting point for analyzing subtle structural and dynamical local changes occurring during in situ experiments involving nanomaterials for specific applications like an electrocatalyst in the Proton Exchange Membrane Fuel Cells (PEMFC).

2. Experimental technique

XAFS, XRD and TEM measurements were performed on samples of nanocrystalline Pt$_3$Co supported on Vulcan (E-TEK$^TM$), normally used as catalyst material in fuel cell applications. A thin film of Pt$_3$Co alloy prepared by molecular beam epitaxy [4] has been taken as a reference.

The activity of nanocatalysts strongly depends on the particles size, shape and structural details at the atomic level, related to bond distance, ordering and surface composition. Besides, it is known that PtCo alloy can crystallize in both face-centered cubic (fcc) and tetragonal phases (depending on the alloy composition), in ordered and substitutionally disordered form [8]. Moreover, in the case of nano-alloys single phase crystals are rather difficult to obtain. For these reasons, accurate morphological investigation and structural characterization should be performed prior to EXAFS refinement.

TEM images have been taken using a JOEL JEM-2100F. Particles size distribution, on the base of the profile of 500 randomly selected quasi-spherically shaped particles, has been obtained using the ImageJ program.

Reflective x-ray diffraction patterns were obtained by a Philips diffractometer (PW1830 x-ray generator) with Bragg-Brentano geometry and Cu Kα radiation ($\lambda = 1.5406\,\AA$). A step-scan pattern was collected in the 30° to 100° 2Θ range, with 0.02° step and 3s per point counting time. The mean Pt$_3$Co crystallites size has been estimated by the Scherrer equation [9] from width of the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) peaks modeled with a Voigt function.

The XAFS spectra at the Co K and Pt L$_3$-edges of a considered material and Co and Pt foils were recorded at the Synchrotron Light Laboratory ELETTRA (11.1 XAFS station, Trieste, Italy). Data were collected over an extended energy range: 11.4–12.8 keV for Pt, and 7.5–8.3 keV for Co. A pellet was obtained by carefully mixing the 30% Pt$_3$Co supported on Vulcan XC-72 powder (E-TEK$^TM$) and graphite powder (Alfa Aesar). The catalyst mass (metal thickness) was chosen to give optimal jump at the selected absorption edges, i.e. $\approx 0.2$ for Co K-edge and $\approx 0.6$ for Pt L$_3$-edge. The experimental EXAFS data have been subjected to analysis with an advanced technique using theoretical calculations of the x-ray absorption cross-section in the framework of the GNXAS method [6, 7]. In this two-edge analysis only first shell two-body contributions have been considered. To avoid misinterpretation many constraints related to alloyed structure (e.g. $R_{Pt-Co} = R_{Co-Pt}$ and $\sigma^2_{Pt-Co} = \sigma^2_{Co-Pt}$) and nano-size of studied object ($N_{tot} = \text{const.}$ as it results from mean particles size) have been applied. Co-O contribution has also been taken into account to well reconstruct the Co neighbourhood.

3. Results

Fig. 1a shows a typical TEM image of Pt$_3$Co nanoparticles with nearly spherical shape and Fig. 1b presents their size distribution. It should be noted that the distribution is asymmetric and shows a tail extended to large-sized nanoparticles. So, the size distribution can be reproduced rather accurately through a log-normal model: the size distribution maximum and the mean value are $d_{\text{max}} = 3.5 \pm 0.5$ nm, $d_{\text{ave}} = 5.5 \pm 0.5$ nm respectively, whereas the distribution broadening is $\sigma = 2.68 \pm 0.08$ nm.

The average size of Pt$_3$Co nanoparticles, as obtained from XRD analysis by averaging the results of the 5 Bragg peaks is $d_{XRD} = 4.3 \pm 0.9$ nm, in fair agreement with TEM result. No additional peaks or shoulders are observed in the x-ray diffraction patterns. This indicates that the nanoparticles consist of a single phase PtCo alloy. The crystalline structure is consistent
with a fcc phase with lattice parameter $a = 3.835$ Å. Thus, the Pt:Co atomic relation in the considered alloy is 3:1 [10]. A similar stoichiometry (2.6:1) results from the analysis of the XAS jumps.

![Image](image.png)

**Figure 1.** (a) TEM image of 30% Pt$_3$Co/Vulcan catalyst; (b) metallic nanoparticles size distribution obtained from TEM images analysis

Comparison of the Pt$_3$Co nano-alloy and fcc Pt$_3$Co thin film spectra in the EXAFS range (see Fig. 2) shows changes only in the signal amplitude, in particular for Co K-edge (Fig. 2a). Therefore the Pt$_3$Co nano-alloy is interpreted to be an alloy with basal fcc phase and the amplitude signal decreasing is mainly related to decrease of the mean coordination numbers (huge contribution of ill-coordinated atoms from the surface of nano-particles) and to the increase of structural disorder [3].

To gain further structural information on the atomic level two-edge first-shell EXAFS analysis (with $N_\text{tot} = 11$ corresponding to $4.5 \pm 1$ nm mean particles size [3]) have been performed and some preliminary results are presented.

The local structure around Co is found to be characterized by a high level of disorder. This is monitored by the high values of disorder parameters describing the Co neighbourhood and by the presence of the Co-Co contribution in the total signal. For an ordered Pt$_3$Co alloy with $L1_2$ structure (Cu$_3$Au like) this contribution in the first-shell is absent [10]. However, for the considered Pt$_3$Co nano-alloy, the comparison of the fits performed with and without the Co-Co signal (see Fig. 3), demonstrates that the model must contain a well-defined Co-Co first-shell contribution. The best-fit parameters values of Co-Co configuration are: mean bond distance $R_{\text{Co-Co}} = 2.68 \pm 0.05$ Å and Debye–Waller-like parameter $\sigma^2 = 0.013 \pm 0.005$ Å$^2$. Moreover, some contribution associated with Co-O bonds has been detected with a bond length $R_{\text{Co-O}} = 1.90 \pm 0.05$ Å and a coordination number $N_{\text{Co-O}} = 0.5 \pm 0.5$. This indicates that a little oxidation of cobalt atoms takes place on the nano-particle’s surface. On the other hand, no Pt-O signals have been detected.

The Pt local structure is found to be more ordered, as it results from the values of the parameters describing Pt–Pt distribution: $\sigma^2 = 0.006 \pm 0.001$ Å$^2$ and $\beta \approx 0.0$ (Debye–Waller-like and distribution asymmetry parameters, respectively). The average Pt-Pt and Pt-Co bond lengths obtained from EXAFS analysis are $R_{\text{Pt-Pt}} = 2.707 \pm 0.002$ Å and $R_{\text{Pt-Co}} = 2.69 \pm 0.02$ Å, which are consistent with XRD extracted unit cell parameter.

The results described here are only preliminary and indicate high substitutional disorder in the studied nano-alloy and the necessity to perform a more advanced analysis of the EXAFS signals (including of multiple-scattering, higher shells and even triangular configurations).
Figure 2. Experimental $\chi(k)$ signals of Pt$_3$Co/Vulcan (E-TEK$^{TM}$) and Pt$_3$Co thin film: (a) Co K-edge, (b) Pt L$_3$-edge.

Figure 3. Co K-edge Fourier transform (FT) of $k^2\chi(k)$ signal of Pt$_3$Co/Vulcan (E-TEK$^{TM}$) nano-alloy in comparison with FT of the best two-edge fit: (a) with Co-Co signal, (b) without Co-Co signal.

References

[1] E. Antolini, J.R.C. Salgado, E.R. Gonzalez, J. Power Sources 160 957–968 (2006).
[2] Q. Huang, H. Yang, Y. Tang, T. Lu, D.L. Akins. Electrochem. Commun. 8 1220–1224 (2006).
[3] A. Witkowska, A. Di Cicco, E. Principi, Phys. Rev. B 76, 104110 (2007).
[4] C. Meneghini, M. Maret, V. Parasote, M.C. Cadeville, J.L. Hazemann, R. Cortes, and S. Colonna Eur. Phys. J. B 7, 347-357 (1999).
[5] X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES edited by D. C. Koningsberger and R. Prims (Wiley, New York, 1988).
[6] A. Filipponi and A. Di Cicco, Phys. Rev. B 52, 15122 (1995).
[7] A. Filipponi, A. Di Cicco, and C. R. Natoli, Phys. Rev. B 52, 15135 (1995).
[8] C. Leroux, M.C. Cadeville, V. Pierron-Bohnes, G. Inden, F. Hinz, J. Phys. Met. Phys. 18 2033–2051 (1988).
[9] J. Langford, A. Wilson, J. Appl. Cryst. 11 102–113 (1978).
[10] M. Hansen, Constitution of Binary Alloys (McGraw-Hill, New York, 1958), p. 492.