

## Probing structural changes of Pt<sub>3</sub>Co nanocatalysts by EELS and *ex/in situ* XAS measurements

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Pt-M/C (with M = Co, Ni, Fe or Cu) electrocatalysts are now commonly used in low temperature proton-exchange fuel cells (PEMFCs) to accelerate the rate of the oxygen reduction reaction (ORR). The catalytic efficiency of these materials for the ORR largely depends on the fine structural arrangement of Pt and M atoms in the topmost and near-surface layers, and can be further improved by using segregated single Pt surface layer (called Pt "skin" surface)<sup>1</sup>.

Chemical/electrochemical dealloying or thermal annealing are classically used to increase the density of Pt surface atoms (the active elements for the ORR), and improve the stability of the bimetallic alloy. However, the impact of these procedures on the final nanostructure of the bimetallic alloy is hardly accessible especially at the nanometer scale. This study will first provide a survey of the different Pt<sub>3</sub>Co/C nanostructures obtained from chemically dealloying and/or heat treatment procedures. For that purpose, we will use the capabilities of advanced characterization techniques such as electron energy loss spectroscopy in spectrum-imaging mode (EELS-SI), and X-ray absorption spectroscopy (XAS). Although numerous XAS studies have been conducted on the Pt<sub>3</sub>Co/C system since the pioneering study of Mukerjee et al. and Chen et al.<sup>2,3</sup>, rarely the focus has been made on the link between the fine structure of nanoparticles (as induced by their synthesis method) and their X-ray absorption signature.

Besides their high electrocatalytic activity, these "nanostructured" electrocatalysts should be able to sustain the harsh environment of a PEMFC cathode *i.e.* to maintain their ORR activity over time. However, many studies reported that the Pt-shell/PtCo-core structure, *i.e.* the structure that seems to be the equilibrium shape under PEMFC conditions, does not prevent from the leaching of the inner core Co content<sup>4,5</sup>, which further leads to a loss of the catalytic activity of the catalyst<sup>5</sup>. The origin of these structural changes will be addressed by *in situ* XAS measurements at the Pt L<sub>III</sub> and the Co K edges under conditions where surface oxidation occurs on these nanomaterials.

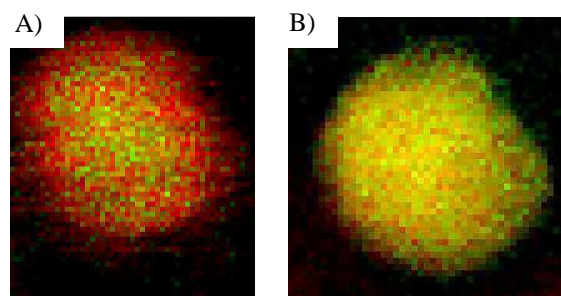


Figure 1. EELS spectra of individual Acid Treated-Pt<sub>3</sub>Co/C (A) and Heat-Treated Pt<sub>3</sub>Co/C (B) nanoparticles. The Pt N<sub>3</sub> signal is shown in red and the Co-L<sub>2,3</sub> signal is shown in green on the colour map.

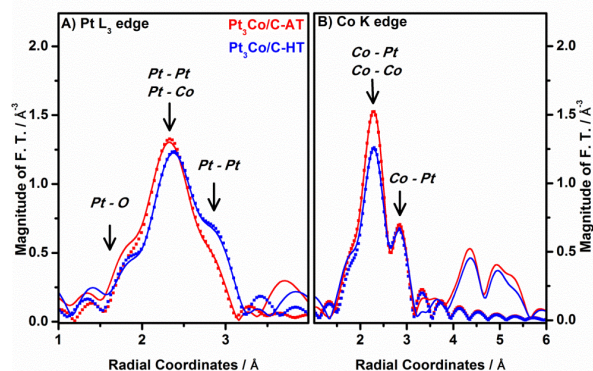


Figure 2. Fourier Transform magnitudes of  $k^2\chi(k)$  EXAFS spectra at the (A) Pt L<sub>3</sub> and (B) Co K edges for the Acid Treated-Pt<sub>3</sub>Co/C (in red) and the Heat-Treated Pt<sub>3</sub>Co/C (in blue) catalysts. The full lines are the experimental data and the dotted lines are the fitted data.

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