Characterization of PtPd core-shell nanoparticles by *in-situ* EXAFS

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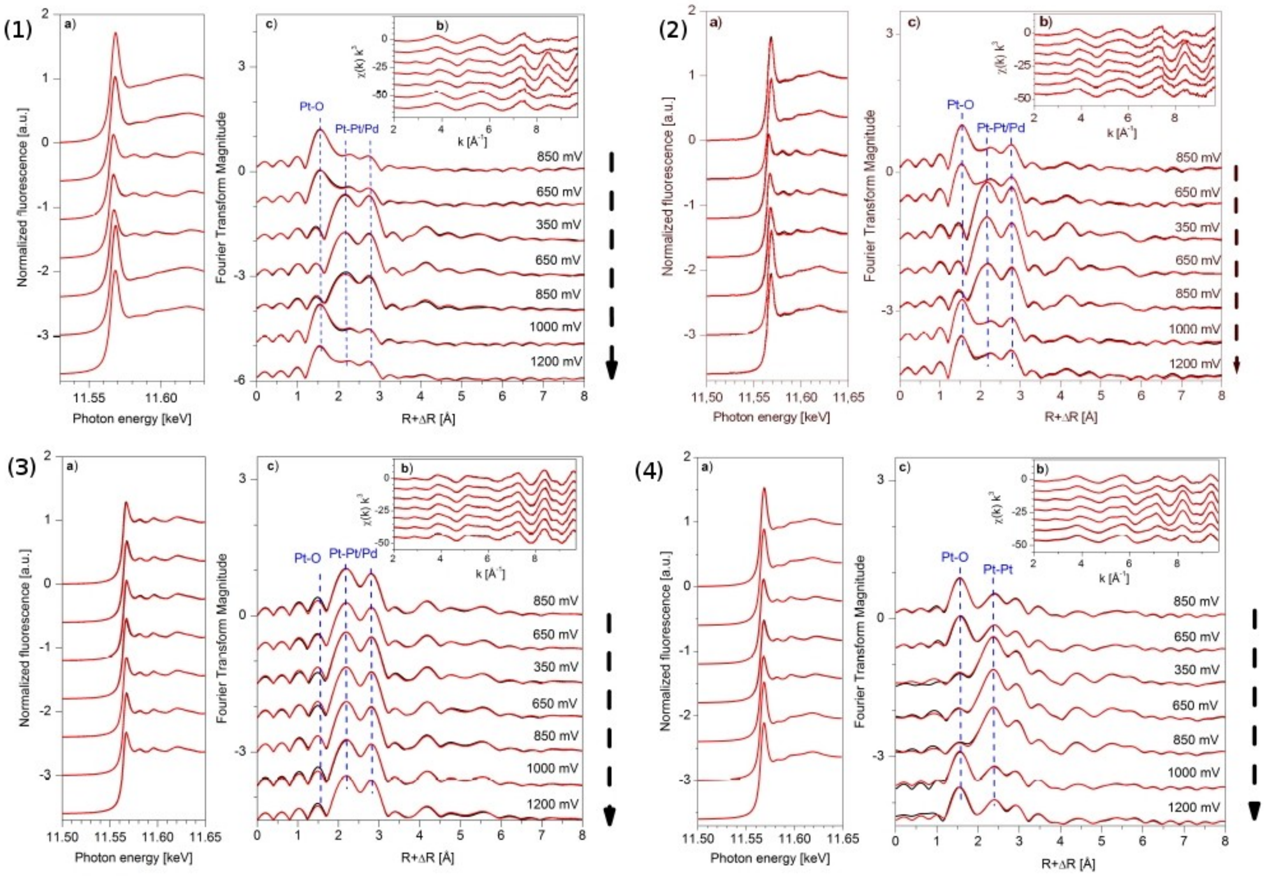
Platinum-palladium nanoparticles are highly investigated regarding their catalytic activity for the oxygen reduction reaction (ORR) and their possible usage in fuel cells. Core-shell nanoparticles synthesized by galvanic replacement with different preparation times conduct to different structures, from Pd cubic to core-shell PtPd concave nanoparticles and chemical compositions. The particles were studied by Transmission Electron Microscopy (TEM) and *in-situ* X-ray absorption fine structure (XAFS) measurements at Pt-L_{III} edge. *In-situ* measurements allow the investigation of the ORR at different potentials using the Iterative Transformation Factor Analysis (ITFA). The creation of a two-components system constituted by the metallic Pt-Pd and the related oxide and the evolution of the concentrations of the oxide with the potential permitted to compare the particles at different potentials.

The measurements were performed using a three electrodes system with a home-made cell filled with a $HClO_4$ (0.1 M) aqueous solution. The counter electrode was a plain carbon covered by conductive graphite, and an Ag/AgCl wire was used as reference electrode. The working electrode was a plain carbon cloth covered by conductive graphite and the deposition of an ink containing the particles. After the monitoring the open circuit potential (5mn) and 80 CV cycles from 0.05 to 1.10 V at 0.1 V·s-1, the measurements at Pt-L_{III} edge were done at different potentials: 0.65, 0.85 V (oxidation), 1.20 V (vertex point), 1.00, 0.85, 0.65 and 0.35 V (re-reduction). The fitting of the spectra was performed using WinXAS software.

The evolution of the spectra XAFS spectra at different potentials was studied using the Iterative Transformation Factor Analysis (ITFA) with a calculus of Varimax and Iterative Target Test (ITT) with a program developed by A. Rossberg, A. C. Scheinost et al. The Principal Component Analysis (PCA), first step of the IFTA allowed us to determine the maximum number of independents components required to reproduce the experimental spectrum. After the determination of the number of independents components, and the reconstruction of the experimental spectrum of one sample, the evolution of the relative concentrations components was investigated using the Varimax method and the Iterative Target Test (ITT).

For each sample, XAFS spectra were measured at the characteristic potentials of the ORR cycle resulting in seven spectra per sample and after the PCA, the spectra were reproduced using a FEFF model based on two component based on oxide and metal (with an higher weight for the metal). For the particles synthesized in 8 h, the experimental spectra can be reproduced with only one component, suggesting the presence of only one component. The determination of coordination numbers (CN), interatomic distances R, Debye-Waller factors (σ^2), and energy shifts (ΔE_0) are similar to the values determined by *ex-situ* EXAFS measurements. It could be remarked that for the *ex-situ* and, the *in-situ* EXAFS spectra at 0.35 V, the peak that corresponds to the Pt-O bond (R~ 1.8 Å) is not visible and the spectra can be fitted assuming only Pt, Pt-Pd and Pd metal clusters with face-centered cubic (*fcc*) structure. Thus, the absence of oxide at an applied potential of 0.35 V is confirmed.

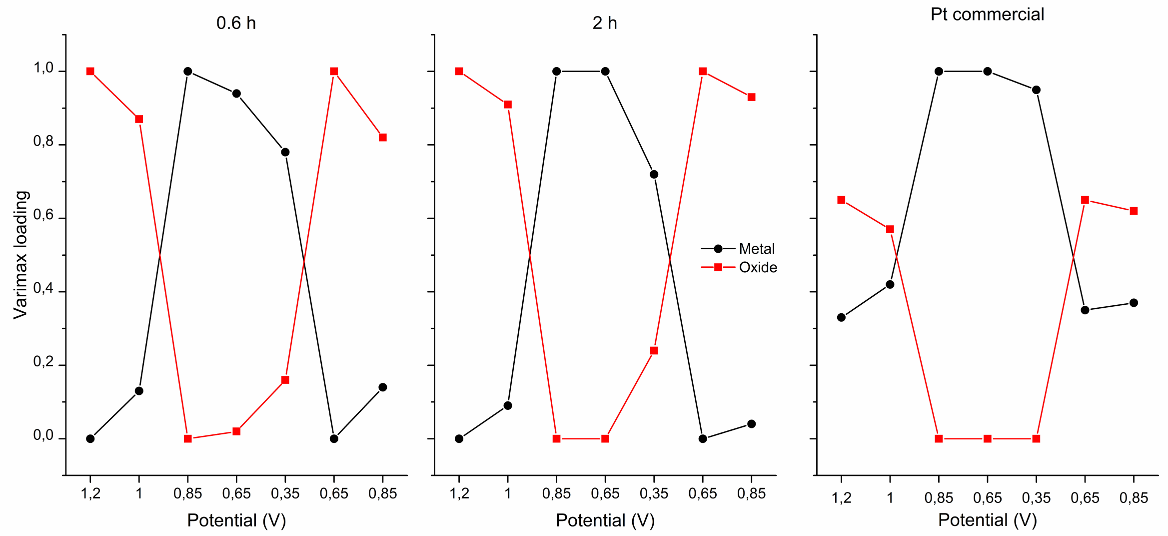
After the PCA, the reconstruction of the spectra (XANES and EXAFS) with two principal components (Pt metal and Pt oxide) enables to follow the evolution of the samples with changing potential. The FEFF-based model of a Pt oxide cluster yields a peak at ~2 Å, corresponding to a theoretical length of the Pt-O bond of 2 Å.



Evolution of the experimental (black) and reconstruction (red) of XANES (left), EXAFS (insert) and FT EXAFS spectra (right) with the potential: (1) 0.6 h, (2) 2 h, (3) 8 h, (4) Pt commercial.

For all samples , the Fourier-transformed EXAFS spectra feature a For all samples (excluding the Pt-Pd 8-h NPs), an apparition/disparition of a peak at R ~1.8 Å, and the inverse behavior for the double peak between 2 and 3 Å attributed to the Pt-Pd and Pt-Pt bond (only Pt-Pt for the commercial platinum) is visible on the FT EXAFS spectra at different potentials. From 0.85 to 0.35 V, the single peak disappears, and is again visible when the potential return to 0.85 V. After comparison with the EXAFS database, this peak was assigned to the Pt-O bond. This could be traduced the formation of a thin layer of Pt oxide with oxygen atoms adsorbed on the surface of the particles when the potential is higher than 0.85 V. At 1.0 V and at 1.2 V, the highly visible peak corresponding to the Pt-O bond is really distinct in the spectra, except for the 8 h NP.

The results of the curve fitting (Table 5), including the Pt oxide in the model, are validated by small residual factors. Like for the EXAFS spectra measured at 0.35 V, the small Debye-Waller factors confirmed well structured particles. The lengths of the Pt-O bond, approximatly 1.99Å, are close to the theoretical value (2.07Å) but the CN are smaller (CN=6 in theory for pure Pt oxide). This is principally coming from the presence of Pt oxide present at 1.00 V and less structured compared to the well organized Pt and Pd atoms in a *fcc* crystalline system. Considering the experimental errors, the lengths of the Pt-Pt and Pt-Pd bonds are not really far to the theoretical values (2.807 Å for the Pt-Pt bond and for the Pt-Pd bond) and to the bonds lengths at 0.35 V. For the particles synthesized in 0.6 and 2 h, a slight asymmetry is present for the double peak, with a higher peak height at 2.2 Å for the small potentials, progressively corrected with the increase of the potential. No significant change with the potential are present on spectra for the PtPd nanoparticles prepared in 8 h and the spectra can also be reproduced with only one component. And so, the formation of an oxide layer is improbable for these particles.



Evolution of the relative concentrations of oxide (red) and metal (black) with the potential for the different samples.

After the ITT and the reproduction of the spectra with only two components, these were assigned to the oxide and the metal and the changes of their relative concentrations with the potential were studied. The concentrations were normalized using the achieved data of the commercial Pt sample, considering only one metallic component and a surface is constituted of pure platinum metal when the applied potential is 0.35 V and of platinum oxide when the potential is 1.00 V. Following this hypothesis, the evolution of the relative concentration was examinated: when the potential is decreasing, the concentration of metal is increasing, while the concentration of the oxide is increasing with increasing potential. For the PtPd NPs prepared in 8 hours, whose spectra are based only on one component, the concentrations could not be studied using this model.