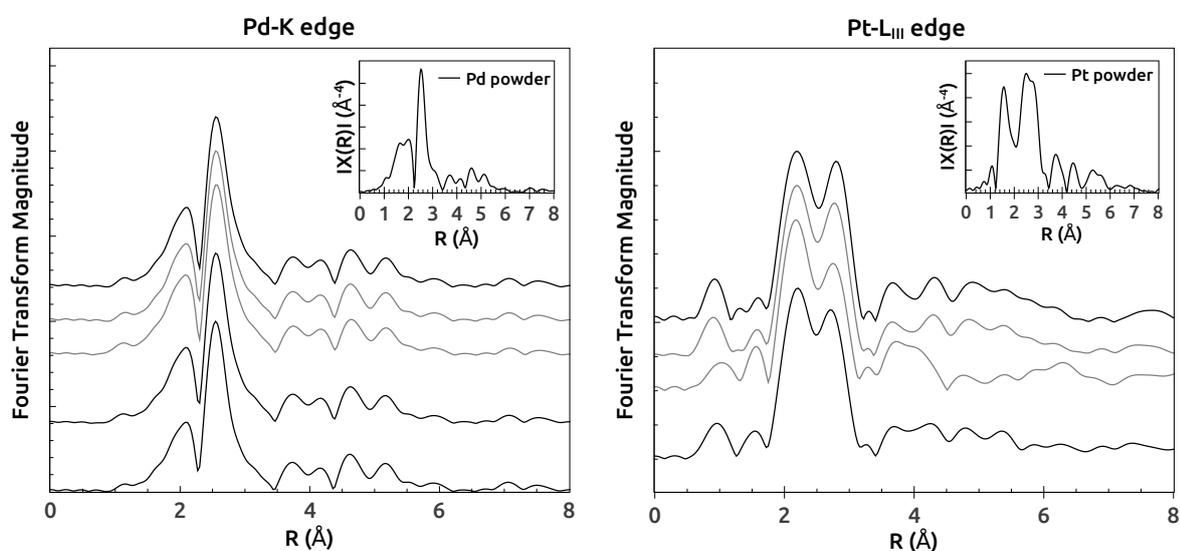


## EXAFS measurements at Pd-K and Pt-L<sub>III</sub> edges for the particles synthesized by galvanic replacement after different times of synthesis

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The PtPd nanoparticles, from pure Pd nanocubes to PdPt core-shell nanoparticles synthesized using different methods are studied as catalysts for the oxygen reduction reaction (ORR). The galvanic replacement is an attractive method to prepare PtPd bimetallic nanoparticles with high catalytic activity. The influence of the time with the transformation from pure Pd nanocubes to concave core-shell PtPd nanoparticles synthesized by galvanic replacement was investigated after different times of preparation. The structure of the particles was monitored by transmission electron microscopy (TEM) coupled with energy Dispersive X-ray spectroscopy (EDS) for the chemical composition. The crystallographic structure and its parameters (size, lattice parameters, d-spacing, and composition) were determined via XRD. The chemical bonds between Pt and Pd atoms were investigated by EXAFS measurements at Pd-K and Pt-L<sub>III</sub> edges. The measurements were realized with particles coated on carbon (40 % weight) and comprimed to form pellets. After measurements, the fittings of Fourier transformed spectra ( $k^3$  weighted,  $k$  range 2-15) were realized using WinXAS software.

At Pt-L<sub>III</sub> edge, the Pt-Pd and Pd-Pd data revealed Pt atoms surrounded by both Pt and Pd neighbors at distances of 2.72 to 2.74 Å, in line with the crystallographic value of 2.74 Å. With the sum of both Pt-Pt and Pt-Pd CNs close to 12, a Pd:Pt ratio slightly above 1 and the relatively small Debye-Waller factors, the fittings confirmed XRD measurements, validating a *fcc* structure where Pt atoms reside in local structure surrounded by Pt and Pd atoms.



Fourier-transformed EXAFS spectra of the particles at Pd-K (link) and Pt-L III (right) edges. Pd nanocubes (marine) and PtPd NPs: 0.6 h (red), 2 h (green), 4 h (orange), 6 h (violet), 8 h (brown), 17 h (blue). Insets: pure Pd and Pt powder Fourier-transformed EXAFS spectra.

At the Pd-K edge, the Pd-Pd distance of the nanoparticles is also 2.74 Å, as expected for the *fcc* structure. The Pd-Pt bond length of 2.71 Å was slightly but significantly smaller than the bond length of the Pd-Pd pairs. The Pd-K edge based CNs suggested that the Pd is prevalently surrounded by other Pd atoms (CNs between 9.5 and 11.2) and only by a smaller number of Pt atoms (CNs between 0.6 and 1.8). The variation of the CNs among the time of synthesis was not statistically significant.

The results of the analysis of the EXAFS spectra from both the Pd-K and Pt-L<sub>III</sub> edges can validate PdPt core-shell nanoparticles composed by a well-structured Pd metal core where most of the Pd atoms possess Pd neighbors and surrounded by a thin Pt shell with most of the Pt atoms having Pd neighbors. The higher coordination numbers for the Pt-Pt bond at the Pt-L<sub>III</sub> edge support an aggregation of Pt in the surface, with a little increase for the long time of synthesis (8 and 17 h). The results of the EXAFS analysis (at Pd-K and Pt-L<sub>III</sub> edges) are in accord to the TEM-EDS observations , validating PdPt core shell nanoparticles.