

Experiment Report Form



Experiment title: At the bases of Pt activity in fuel cells by operando X-ray absorption spectroscopy on model Pt clusters	Experiment number: CH-5545	
Beamline: BM-08	Date of experiment: from: 20/11/2018 to: 27/11/2018	Date of report: 24/02/2020 <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Francesco D'Acapito Giovanni Orazio Lepore	
Names and affiliations of applicants (* indicates experimentalists): Roberto Della Pergola Martina Fracchia* Paolo Ghigna* Cristina Locatelli Alessandro Minguzzi Alberto Vertova* Sandra Rondinini		

Report:

This proposal was related to allow a rational design of Pt-based materials as cathodes for the oxygen reduction reaction in acid/basic media (here reported for the first case) in low-temperature fuel cells. Here we focused on $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ and $[\text{Pt}_{24}(\text{CO})_{30}]^{2-}$ clusters, whose structures were previously determined by X-ray absorption and diffraction and infrared spectroscopies and that show electrocatalytic activity higher or comparable to the one of conventional Pt nanoparticles. Another great advantage in considering Pt clusters is their extremely controlled structure: once deposited onto active carbon and thermally treated to remove CO ligands (at 150°C in N_2 atmosphere), they became equivalent to atomically defined nanoparticles.

Moreover, being all Pt atoms equivalent and behaving as surface atoms, these clusters represent the ideal candidate for the definitive operando XAS study on fuel cell and metal air batteries catalysts as both promising alternative to Pt particles and as an ideal model system for surface local structure investigations.

Pt clusters were synthesized and deposited on Vulcan XC72R carbon. A dispersion of the composite was deposited onto a glassy carbon support where they are glued using a Nafion[®] suspension. The final electrode was held in the spectro-electrochemical cell already successfully adopted by us at the ESRF (CH-3511).

X-Ray absorption measurements were performed at the Pt L_{III}-edge at room temperature in the fluorescence mode. First of all, XAS spectra were acquired on the dried electrodes in order to get information on their structural properties. Figure 1 shows the XANES spectra of $[\text{Pt}_{24}(\text{CO})_{30}]^{2-}$, which will be referred to as "Pt24" for brevity, and of $[\text{Pt}_{24}(\text{CO})_{30}]^{2-}$, thermally treated at 150 °C (TrPt24). It can be noted that the spectra of the samples show a larger intensity of the main edge peak (white line, WL) with respect to the spectrum of the platinum foil. For the Pt L_{III} edge, the WL is due to the transition from filled 2p_{3/2} orbitals to empty 5d orbitals; since XANES is a probe for the density of empty states, a larger intensity of the WL can be correlated to a lower electronic density on Pt. In case of Pt/C and Pt/Graphene, the interaction between Pt and C leads to a lower density of the empty states on Pt and therefore to a larger intensity of the WL with respect to Pt. The larger intensity of the White Line is therefore a confirmation of the presence of Pt-C bonds.

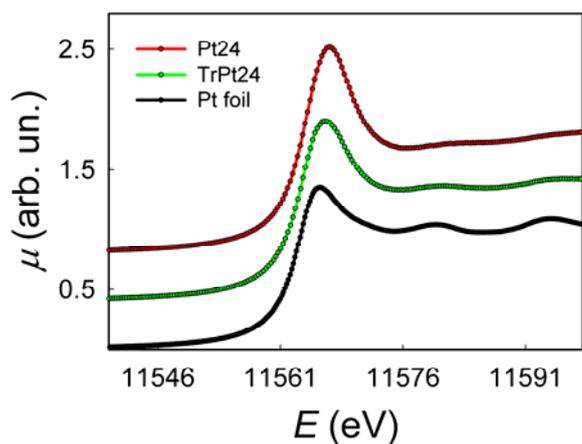


Figure 1. XANES spectra at the Pt L_{III} -edge of Pt24 (red dotted line) and TrPt24 (green dotted line).

Moreover, the spectrum of Pt24 shows a larger intensity with respect to TrPt24, indicating that the number of these bonds is lower when Pt24 undergoes a thermal treatment. For energies above the absorption edge, the spectra are indeed similar to that of the platinum foil, with the exception of a notable damping of the absorption coefficient oscillations, as expected for small nanometer-sized clusters. The EXAFS fitting confirmed this finding; in fact, for both Pt24 and TrPt24 the number of platinum atoms surrounding the photoabsorber has a figure of 9 and is therefore lower than that expected for bulk metallic platinum (12). Moreover, the EXAFS showed the strong presence of Pt-C bonds, that are however partially detached after the thermal treatment. This preliminary analysis, coupled with other measurements in the laboratory, shows that probably the preparation of the slurry leads to the disappearance of the initial Pt-CO clusters, leading instead

to atomically defined Pt nanoparticles anchored to the support through Pt-C bonds. It should be noted that the number of neighboring Pt atoms remains equal to 9 even after the thermal treatment, thus indicating that the treatment does not lead to any aggregation of the nanoparticles.

After this first structural analysis, full XAS spectra were recorded on Pt24 in aqueous 0.1M $HClO_4$ under different applied cathodic potentials (see Fig. 2, left panel), with the aim of observing in operando the

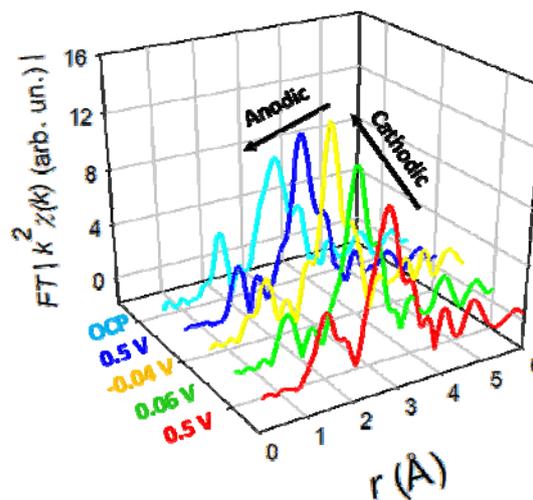
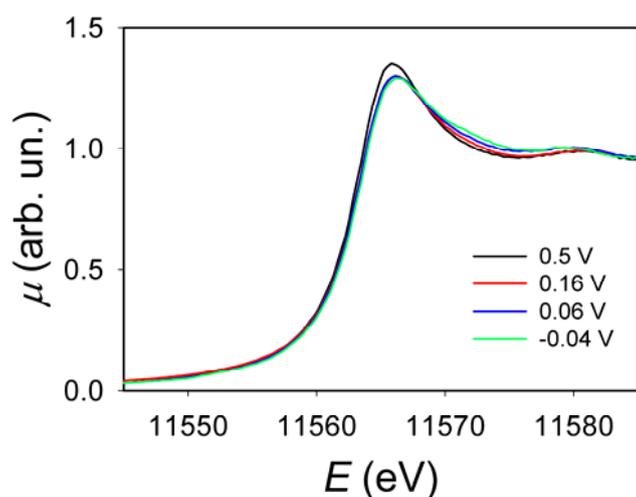


Figure 2. (Left panel) XANES spectra of Pt24 at different applied cathodic potentials (Right Panel) Fourier Transform (FT) signal at different applied potentials.

behavior of the electrode under hydrogen evolution.

It can be observed that at cathodic potentials the intensity of the white line decreases, while the feature at *ca.* 11575 eV progressively increases and reaches its maximum below 0 V vs RHE, when H_2 starts to evolve. This can be attributed to the adsorption of H^+ at the surface of the Pt metallic clusters. If we look at the Fourier Transform signals (Figure 2, right panel), it can be seen that while decreasing the potential from 0.5 V to -0.04 V, the signal shows a progressive increase in intensity, which can either be attributed to a decrease of the Debye-Waller factor at more cathodic potentials or to an increase of the number of the first-neighbouring platinum atoms, possibly due to a reconstruction of the surface as a consequence of the hydrogen absorption. Very interestingly, upon reversing of the potential, the initial signal is re-obtained, with the same intensity as at the beginning of the polarization. This means that no aggregation process is occurring during the electrocatalytic activity: these Pt clusters are therefore particularly stable, and can be considered as promising novel candidates as catalysts for the fuel cell technology.