

**Experiment title:**

Surface structure evolution of polycrystalline Pd catalysts during electrochemical oxidation

Experiment number:
MA-2153

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Names and affiliations of applicants (* indicates experimentalists):

- Francesco Di Benedetto*- Università degli Studi di Firenze (Firenze, Italy)-Main proposer
dibenefr@geo.unifi.it
- Giordano Montegrossi*- CNR-IGG, (Firenze, Italy)
montegrossi@igg.cnr.it
- Claudio Zafferoni*-Università degli Studi di Firenze (Firenze, Italy)
claudio.zafferoni@unifi.it

Report:*Introduction*

The experiment was aimed to study the effect of the oxidation and use of Pd catalysts with specific relationship to the valence state and of the structural changes at both the short- and mid-range orders. The information regarding the surface modification of the palladium may clarify and identify the chemical species which can potentially affect the catalytic activity of the material against the oxidation of ethanol. We planned to operate in both the XANES and EXAFS regions at the Pd K edge (24350 eV), to underline the main structural change of Pd after different electrochemical treatment. We also planned to perform and test the possibility to investigate the electrooxidation of palladium samples in an alkaline solution with an in-situ experiment by FEXRAV.

Experimental part

During the experiment we analyzed two kind of samples by XAS measurements

- Thin films of palladium grown on carbon substrate with the presence or the absence of CeO₂ as cothallist that undergone different oxidative potential in order to evaluate the presence of oxidized species.
- Thin films of palladium grown on carbon substrate with the presence or the absence of CeO₂ used as real catalyst inside a electrochemical cell

The reference samples used during the experiment referred to the different oxidative state of palladium (+2, +1, 0) and consisted of a PdO, PdCl₂ and a Pd-foil sample.

We used an in-situ set up consist of a home made three electrode cell for the FEXRAV experiment. An Ag/AgCl/KCl saturated reference electrode and a graphite rod as counter electrode were used to evaluate the oxidation of a Pd/C sample during cyclic voltammetric cycles in an alkaline solution (0.1M KOH). This solution is the common electrolyte used during the standard catalytic measurement for the oxidation of ethanol in solution.

Preliminary Results

The XAS spectra collected for the *ex-situ* palladium samples showed a complicate dependence of the valence state of Pd in response to the conditions operating on the electrode during its use (Fig. 1a). Namely, the oxidated PdO phase was prevalent in the samples after oxidative treatment and in the samples used as real catalyst inside a cell (Fig. 1b). The collected spectra confirm the effectiveness of the XAS measurements for these kind of thin films samples. The relationship between the presence of CeO₂ and the higher or lower level of oxidative palladium is not yet investigated.

On the other hand, the attempt of using FEXRAV for the *in operando* study of oxidation/reduction reaction that involve the morphological and structural change of the catalyst resulted promising. The FEXRAV technique was used monitoring the structural change of a palladium sample supported on carbon during an electrochemical oxidative/reduction cycle. The intensity of the signal related to the Pd phase was monitored during the oxidation and recorded during reductive scan as reported in Figure 1c.

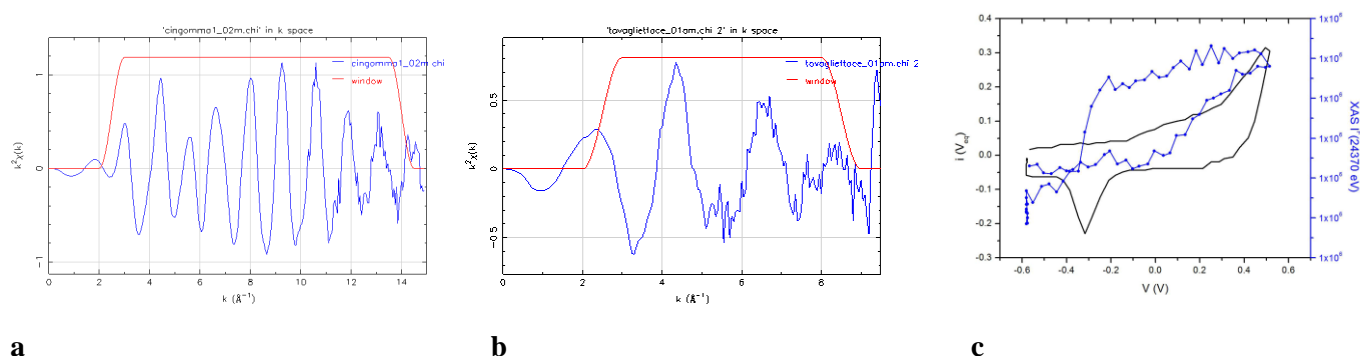


Figure 1: a) Exemplar spectra of a) Pd electrode and b) exhausted PdO electrode. c) voltammogram recorded in the 0.1M KOH solution for a Pd/C electrode, overlaid with the FEXRAV signal related to the XAS signal at 24370 eV

In operando XANES and quick EXAFS measurements were also performed at selected relevant fixed applied voltage after the FEXRAV measurement in order to accurately reveal the starting potential of palladium oxidation. In this contest both the FEXRAV signal and the current signal of the cell that simultaneously change during the scan potential represent an unique and powerful point of view regarding the electrochemical and structural evaluation of a surface at the same time.

The same technique will be used in future for a deeper investigation regarding the relationship between the applied potential and the real active chemical species during an important catalytic reaction as the ethanol oxidation reaction (EOR).