



	<b>Experiment title:</b> <b>In situ XAS investigation of Pd mono- and multi-layer architectures during the electrooxidation of small organic molecules</b>	<b>Experiment number:</b> <b>CH-6101</b>
<b>Beamline:</b> BM08	<b>Date of experiment:</b> from: 06/10/21 to: 12/10/21	<b>Date of report:</b>  <i>Received at ESRF:</i>
<b>Shifts:</b> 18	<b>Local contact(s):</b> Baroni Tommaso	
<b>Names and affiliations of applicants</b> (* indicates experimentalists): <b>Enrico Berretti*</b> - CNR ICCOM (Florence, Italy) Alessandro Lavacchi - CNR ICCOM (Florence, Italy) <b>Francesco Di benedetto*</b> - University of Ferrara, Earth Sciences Dept. (Ferrara, Italy) <b>Giordano Montegrossi*</b> - CNR IGG (Florence, Italy) Andrea Giaccherini – University of Florence, Chemistry Department (Florence, Italy)		

**Report:**

We started by acquiring in-situ XAS of three sets of samples in different electrolytes, being actively polarized at different potentials, in order to define the time threshold enabling clear FEXRAV acquisition, and also to assess the influence of the inmost metallic Pd on the surface Pd<sup>2+</sup> XAS signal during voltammetric cycling. For this reason, we tested : a) 5 nm Pd (PVD deposited), b) 2.5 nm Pd (PVD deposited) and 1 monolayer (ML, produced by Electrochemical ALD deposited by UnderPotential Deposition of Cu + Surface limited Redox Replacement with Pd). Palladium was deposited on on flat polycrystalline isooriented Au (1 1 1) surfaces. XAS on the various substrates was performed in the three electrode cell described in the proposal, and already succesflully used on the same line, using bare NaOH, NaOH + EtOH and NaOH + Formate, moving the working electrode potential towards more oxidative values by steps, and acquiring a full XAS spectra after a rest. This testing was needed also in order to experiment the line set-up after the refurbishment toward the use of FEXRAV. During the potential step experiments, we were able to follow the oxidation of the topmost exposed layers of Pd by XAS for the PVD deposited samples. Interestingly this phenomenon was not seen for the electrochemical ML sample, in which almost all the Pd atoms were in contact with the Au substerate, suggesting a stabilization effect from the noble electrodic surface toward the oxidation of Palladium.

Sadly, the long beam-down which occurred on Saturday was detrimental for the experiment, and made us lost almost more than a shift.

Apart from the data obtained from dynamic cycling, which is the subject of an article under completion, during the experiment we were also able to collect static stability information (without potential application on the electrode) on Pd in these systems, which were useful to finalize another article on previous ESRF experiments on the same topic:

**Experimental evidence of palladium dissolution in anodes for alkaline direct ethanol and formate fuel cells, E. Berretti a, M.V. Pagliaro a, A. Giaccherini b, G. Montegrossi c, F. Di Benedetto d, G.O. Lepore e, F. D'Acapito f, F. Vizza a, A. Lavacchi, Electrochimica Acta, Volume 418, 20 June 2022, 140351**