

**Project title:** Novel Pt-Cs-W electrocatalysts for PEM fuel cell investigated by in situ XAFS.

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**Involved researchers:**

dr Agnieszka WITKOWSKA, *Dept. Solid State Physics, Gdansk University of Technology, Poland*

dr Sonia DSOKE, *Chemistry Dept., University of Camerino, Italy*

dr Emiliano PRINCIPI, *Dept. Physics, University of Camerino, Italy*

dr Aneta KOLARY-ZUROWSKA, *Chemistry Dept., Warsaw, Poland*

prof. Roberto MARASSI, *Chemistry Dept., University of Camerino, Italy*

prof. Andrea DI CICCIO, *Dept. Physics, University of Camerino, Italy*

Today the study of alternatives energy sources is one of the main research subject at world level. In particular the objective of achieving more sustainable energy systems (SES) and services is of great strategic importance for European Union's. Fuel cells (FC) are promising SES which may replace in the long term most current combustion systems in all energy end-use sectors, from electric vehicles to power plants. Currently efforts are particularly focused on the research of new FC catalysts that can guarantee higher efficiencies, lifetimes of FC and sustainable production costs for a widespread use. Platinum has been found to exhibit excellent catalytic properties but its high costs and poor availability make this element unsuitable for large scale applications. This drawback could be overcome decreasing the requested Pt loading in the FC electrodes developing Pt alloy catalysts which retain good performances with smaller quantities of Pt.

The aim of the present proposal is to shed light on the processes which govern the catalysis process in novel catalysts with extremely low Pt content (Pt densities even smaller than  $0.1\text{mg}/\text{cm}^2$ ) feasible for proton exchange membrane fuel cell (PEM FC). A novel catalysts containing Pt nanoparticles modified by heteropolyacids such as  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  or acidic cesium salts have been studied *in situ* conditions using XANES (X-ray Absorption Near Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure) techniques characterized by high sensitivity to the atomic and electronic structure. XAS spectra have been collected at the Pt and W L-edges (from 10keV to 15keV), using a transmission mode (for W L-edges measurements) or a 13 channels fluorescence detector (for Pt L-edges measurements) and setup optimized for *in situ* fuel cell measurements installed at BM29 (see also report of MA-121 experiment). All *in situ* XAFS experiments were carried out under ambient conditions, with gases flow about 100ml/min and 150ml/min for hydrogen and oxygen, respectively. The cell voltage and current were measured continuously during XAS data acquisition and stored with the structural data.

Initial materials and just prepared electrodes have been fully characterized by means of microscopic (SEM and TEM) techniques in order to measure the size distribution of catalysts particles and to estimate catalytic layer homogeneity relevant to the XAS measurements. This structural insight is also crucial for carrying out a reliable XAS data analysis.

Now efforts have to be devoted to analyze accurately in the framework of the GNXAS method whole XAFS data and to obtain precise structural information. A preliminary analysis show that the electrochemical cell optimize for XAS experiment permits the acquisition of high quality spectra at both measurement modes (transmission and fluorescence). On the base of these data, differences in both geometric and electronic structure could be observed as a function of kind of acidic salt used to modify electrocatalyst and methods of preparation (impregnation and electrochemical method). Changes appearing as a result of various working conditions are also noted. The work is still in progress.