EUROPEAN SYNCHROTRON RADIATION FACILITY

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Experiment Report Form

	Experiment title: Nanostructured catalystst in Fuel cells: Pt(Sn)-cerium oxide	**Experiment number**: CH 3264
Beamline: ID 32	**Date of experiment**: from: 10. 2.2011 to: 15. 2. 2011	**Date of report**: 15.3.2011 *Received at ESRF:*
Shifts: 15	**Local contact(s)**: Blanka Detlefs	

Names and affiliations of applicants (* indicates experimentalists):

Prof. Vladimir Matolin
Charles University in Prague, Czech Republic

Report:

Radio frequency (rf) magnetron sputtering was used to deposit CeO_2 and Pt-CeO_2 thin films on glassy carbon, carbon foil, sputtered carbon thin film deposited on a Si wafer and the reference Si(100) wafer. The Pt-CeO_2 thin films were deposited by using two magnetrons (Pt and Ce oxide). The samples with various content of Pt were used. Samples were prepared in duplicates; each twin sample has been checked before the experiment by the laboratory XPS and HRTEM in order to determine the sample composition and structure. Performance of Pt doped catalysts was tested in the proton exchange membrane fuel cell fed with hydrogen. The Ce 3d, Pt 4f, O 1s, and C 1s core levels were probed by HAXPES on ID32. Pt and Ce chemical states were investigated as a function of element concentration and preparation conditions.

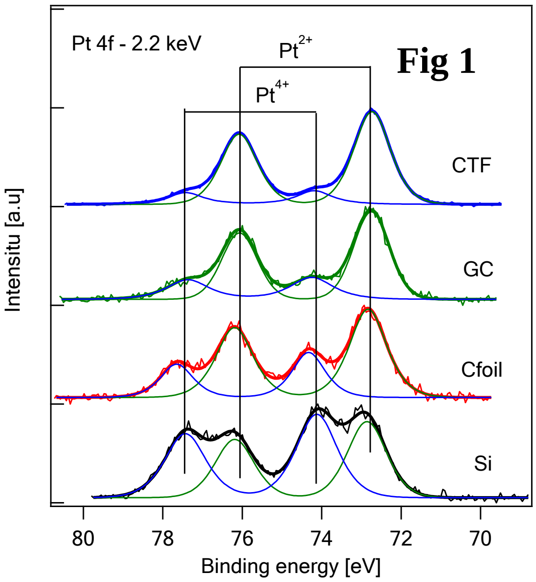

Fig 1

Contrary to the original proposal we did not used the Sn doped samples and we did not investigate CNT supported catalysts. The reason was that the experiment was scheduled nearly one year after its proposition and in the meantime we investigated the Sn doped catalysts and coated CNTs at Spring 8. Also we did not perform the temperature dependent experiment because the heated manipulator was not available. On the other hand we added investigation of new promising catalyst – PtOx thin film prepared by reactive sputtering.

Because of the porous structure of the catalyst film with active sites at the surface and the boundaries of grains inside the pores and the formation of multiple chemical states of dopants and Ce atoms ($Ce^{3+,4+}$), HAXPES is a suitable technique for such studies. This method combine high resolution and high information

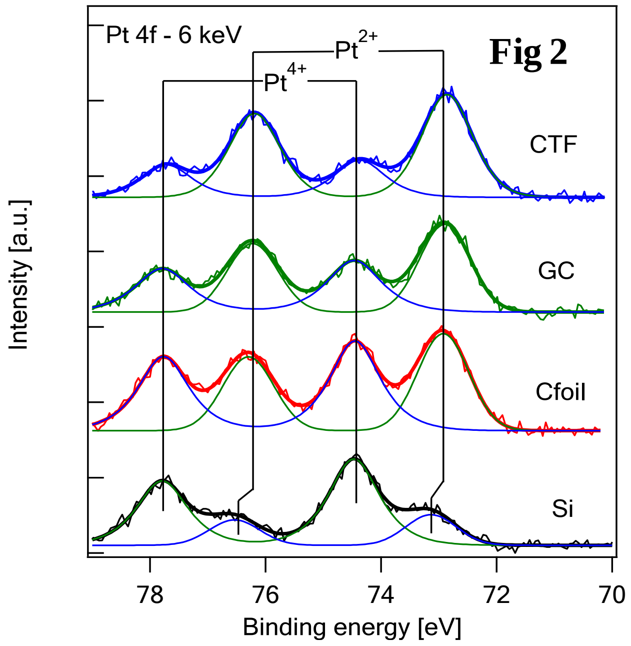

Fig 2

depth. We used a tunable hard x-ray source in order to be able to change the information depth. We used three photon energies: 2.2, 6 and 8 keV.

In Fig. 1 we show an example of influence of the catalyst–substrate interaction on chemical state of platinum for following substrates: silicon wafer covered by native oxide layer (Si), graphite foil composed of sheets of graphene (C foil), glassy carbon (GC), sputtered carbon thim film (CTF). Pt 4f taken at 2.2 keV photon energy spectra are composed of two doublets corresponding to Pt^{2+} and Pt^{4+} states showing that Pt is fully oxidized.

Fig. 2 displays similar results as those of Fig. 1 obtained for photon energy of 6 keV. The difference between results from Figs. 1 and 2 are in different information depth, which is higher for higher photon energy (approx. 10 nm for 6 keV and 2 nm for 2.2 keV)

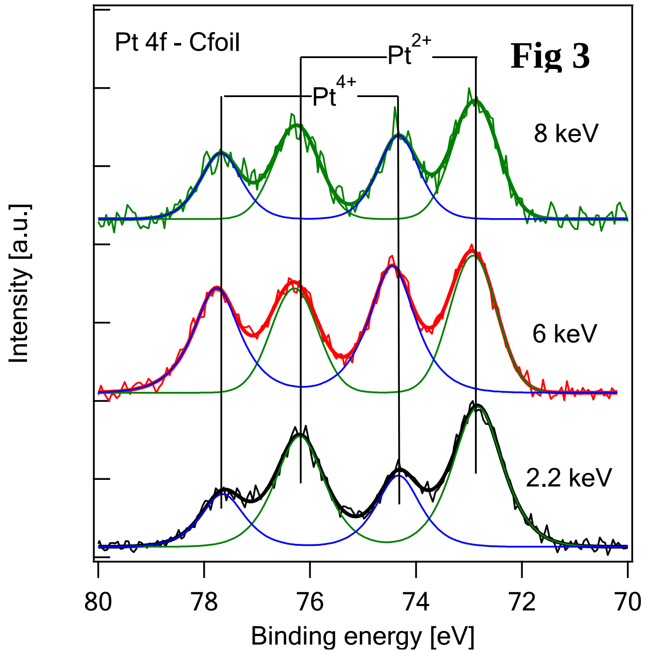

Fig 3

An example of a variation of chemical state of platinum with photon energy, i.e. with information depth is shown in Fig. 3 for the case of the Cfoil substrate. It is clearly shown that Pt^{2+}/Pt^{4+} intensity ratio is higher for lowest and highest photon energy showing that in the case of the Cfoil substrate platinum oxide is more reduced at the surface and at the interface.

The above shown examples confirmed clearly that stoichiometry of the catalyst depends on the film-substrate interaction and it is inhomogeneous across the film thickness. In this experiment we got a matrix of results, by combining composition of layers, substrates and photon energies, which would permit us to elucidate mechanism of the catalyst film growth, which is important for tuning their parameters and catalytic properties. Combination of PES and microscopy studies provided very rich experimental data showing also a link between the film chemical composition and porosity (Fig. 4 shows an example of a SEM normal and tilted view on the Cfoil supported Pt-ceria film).

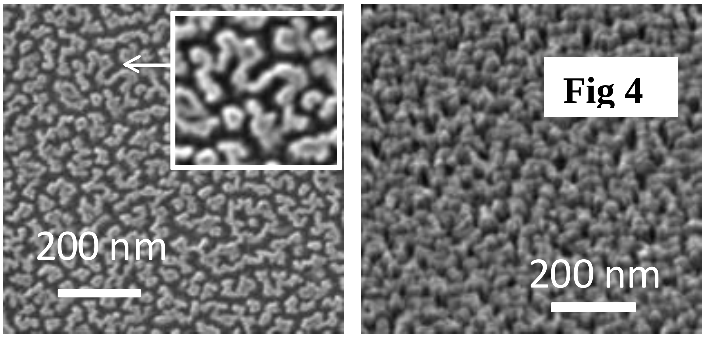

Fig 4

The experiment was scheduled in February 2011, therefore the data treatment is not completely finished yet. However due to rich and complete set of data we believe that we

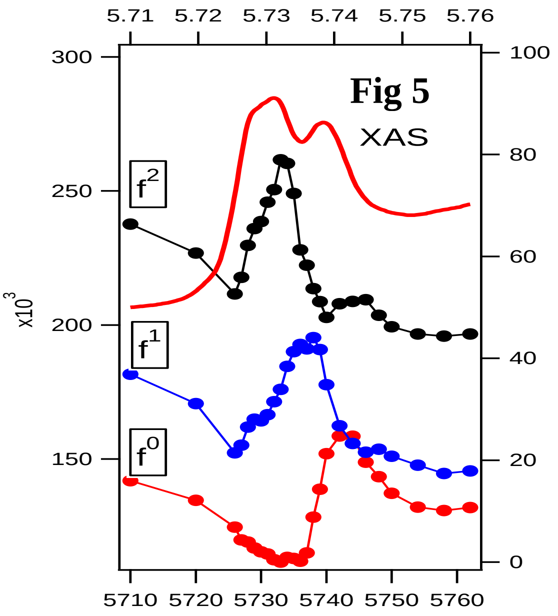

Fig 5

would be able to prepare a draft of a publication before June 2011.

We also tested possibility of investigation of the catalyst film composition and chemical state by XANES performed at photon energy of 5700 eV (Ce L_3). HX RPES has been performed by measuring resonant profiles Ce $3d_{5/2}$ f^2, f^1 and Ce $3d_{3/2}$ f^0 of both Ce^{4+} and Ce^{3+} states. Figure 5 shows as an example preliminary HX RPES and XANES measurement performed on pure cerium oxide film during the ID32 experiment.

We are concluding that the photon energy resolved experiments confirmed previous indirectly supported hypothesis of stoichiometry variation giving Pt^{2+} rich composition at the film surface and interface. This is one of the most important results because Pt^{2+} is the most active specie for protonic hydrogen formation.