EUROPEAN SYNCHROTRON RADIATION FACILITY
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Experiment Report Form

	Experiment title: Electrochemical Promotion of Catalyzed Surface Reactions	**Experiment number**: SI-2124
Beamline: ID03	**Date of experiment**: from: 22.9.2010 to: 28.9.2010	**Date of report**: 24.2.2011
Shifts: 18	**Local contact(s)**: Dr. Olivier Balmes	*Received at ESRF:*

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Report: Electrochemical Promotion of Catalyzed Surface Reactions

This project aimed at the atomic scale elucidation of the so-called NEMCA effect, which allows the activity control and promotion of a particular surface reaction by simply applying a polarisation voltage. In these experiments the model CO oxidation reaction over single crystalline model electrodes Pt(111)/YSZ(111) I studied to ascertain whether the promoting effect is related to the polarisation-induced formation of a surface oxide.

During this beamtime we commissioned successfully the new sample holder for the in-situ electrochemical reaction experiments including the potentiostatic control of the sample. An important feature to be checked was the long-term stability of the sample holder at high sample temperatures over 10-12 hours to aquire reliable SXRD data during the CO oxidation reaction and under various applied external electrical potentials. The working electrode of the model electrochemical cell was prepared prior to the beamtime at the JLU by pulsed laser deposition (PLD) of Pt (typical several 100nm thick) onto a single crystalline YSZ(111) wafer (10mm x 10mm). During the beamtime at ID03 we could demonstrate that that the sputtered Pt films on YSZ(111) are single crystalline and at the same time porous enough to let oxygen permeate through the Pt(111) film without exfoliation of the Pt film and without reducing the YSZ(111) substrate. Altogether, high-resolution SXRD experiments could be performed with this kind of NEMCA model electrode.

We could demonstrate that the sample holder including the multilayer Pt(poly)-YSZ-Pt(111) assembly was mechanically stable at 750K for more than 12 hours. However, in order to achieve this stability the sample has to be hold at 650K in vacuum for several hours (typical: 3-4h) prior to the actual eperiment.
In the first experiments we were able to follow the oxidation process of the Pt(111) film in pure oxygen and without applying an external potential. The resulting Pt oxide was shown to be only one monolayer thick and the oxide disappeared when the chamber was evacuated while keeping the sample temperature above 500K. A self limiting growth of 1ML Pt-oxide on Pt(111) has also been identified by Ellinger et al. in a recent SXRD experiment **[1]**.
The signal to noise ratios in the h- and l-scan were unfortunately quite poor since the used 2D pixel dector had many fluctuating pixels with saturated intensities causing high noise and a high background (cf. **Figure**). Due to this problem with the 2D detector we were not able to correlate unambigiously structural with activity changes in the CO oxidation when polarizing the model electrode.
First experiments indicate tiny changes in the oxidation behaviour of the Pt(111) film when polarizing the electrode (see **Figure**). However, these changes were in comparison to the produced noise from the detector too small to be convincing and publishable in a scientific journal (see **Figure**). We need clear-cut experiments to pinpoint the reason for the NEMCA effect on the atomic scale.

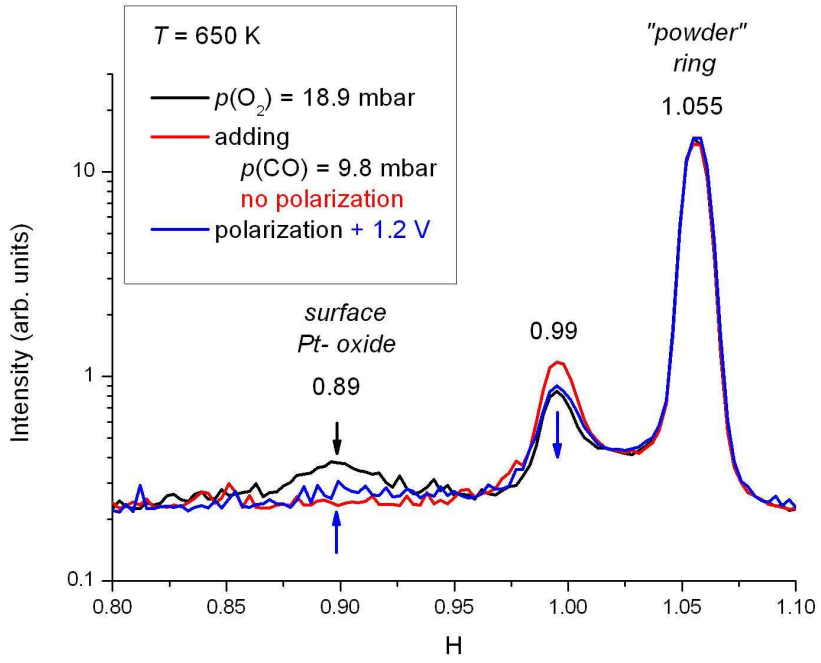

Figure. The Pt(111)/YSZ film exposed to 19 mbar oxygen at 650 K develops a surface Pt-oxide. Adding 10 mbar CO results in the reduction of the oxide. The oxide reemmerges by polarizing the film to 1.2 eV anodically.

Unfortunately, the commissioning and testing of the new NEMCA sample holder consumed more time of our last beamtime than we expected. To understand the NEMCA effect on the molecular level systematic variations of the temperature and partial pressure of O_2 and CO have to be performed, while monitoring the reaction rate and surface strucuture with and without external potential.
Therefore we need an additional beamtime to conclude successfully this challenging project and producing SXRD data which are worth publication in a high ranking scientific journal.
For the next beamtime we shall use a new 2D pixel detector (MAXIPIX) with low noise and background (available at ID03 since the beginning of 2011) in order to systematically study the effect of the external electrical polarisation on the surface structure of the model electrode while monitoring the CO oxidation rate.

[1] C. Ellinger, A. Stierle, I.K. Robinson, A. Nefedov, H. Dosch, J. Phys.: Condens. Matter **20** (2008) 184013.