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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

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Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

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All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

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- 1st March for experiments carried out up until June of the previous year;
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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** **In-situ X-ray absorption experiments in a working fuel cell under dynamic conditions**	**Experiment number:** ME-1132
Beamline: BM29	**Date of experiment:** from: 22/06/05 to: 27/06/05	**Date of report:** 17/08/05
Shifts: 15	**Local contact(s):** O. Mathon	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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In-situ X-ray absorption experiments in a working fuel cell under dynamic conditions

Aim of the experiment:

Compared to pure platinum, Pt-Ru electrocatalysts show an improved CO tolerance in catalyzing the hydrogen oxidation reaction at the fuel cell anode in the presence of CO impurities. However, the mechanisms of the increased performance are not yet completely understood. The aim of the experiment is to follow changes in the catalyst structure and the adsorbate coverage in a real working fuel cell. The results obtained in these in-situ experiments will be used to develop more active, stable and less expensive catalysts.

Experimental set-up:

Three membrane electrode assemblies (MEAs) with different anode catalysts were prepared for the XAS measurements: a) with a carbon-supported Pt-Ru alloy catalyst, b) with a mixture of carbon-supported Pt and carbon-supported Ru, and c) with plain Pt supported on carbon for comparison. All MEAs were operated in different working conditions; with pure hydrogen, with a mixture of 150 ppm CO in hydrogen and with vaporized 1 M methanol solution as the anode feed. Spectra were recorded at different potentials at the Pt L_3- and the Ru K-edge (Fig. 1). In each case, spectra were taken before operation at elevated temperatures but without gas feed, serving as reference spectra. Approximately 120 spectra were recorded during the beamtime, which are to be analyzed in detail over the next months.

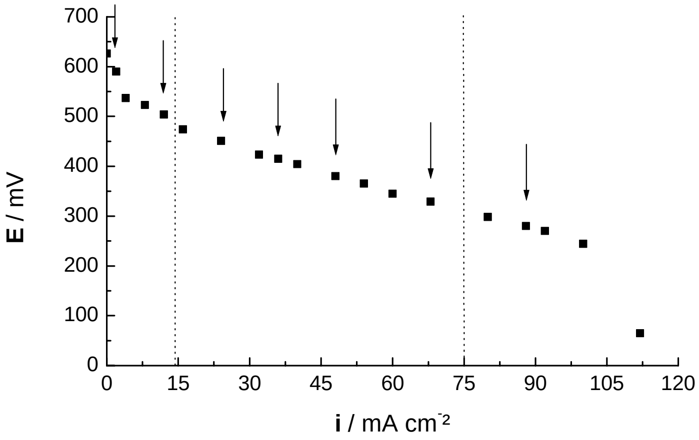

Fig. 1. Spectra were recorded at the Pt L_3- and the Ru *K*-edge in different regions of the current-voltage curve; operation with 1 M methanol as anode feed, arrows mark positions where spectra were recorded

The optimum set-up for our experiments was found to be the commercial fuel cell hardware with a Kapton™ foil beam window in fluorescence geometry (Fig. 2, [1]). This geometry is especially suited for measurements at the Ru edge at 22 keV yielding excellent spectra with good signal-to-noise ratio.

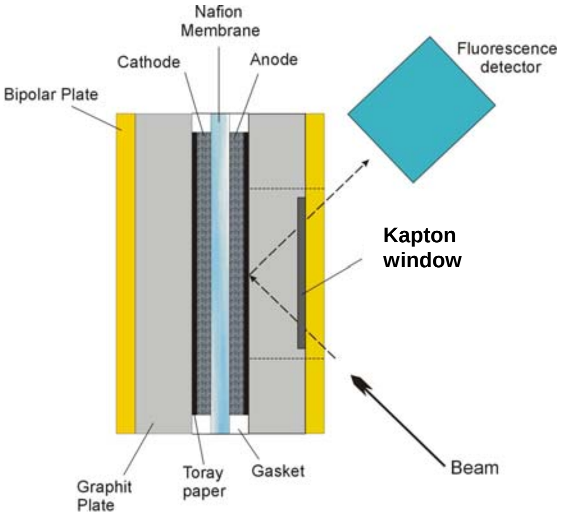

Fig. 2. Set-up of the in-situ fuel cell in fluorescence geometry

New method for analysis:

Only recently, a new difference file technique (Δμ XANES) has been developed by our partner Dave Ramaker at Washington university [2]. This novel method enables us to directly follow the adsorption and desorption of H, O(H), and CO adsorbates on the catalyst surface in a working fuel cell. It is even possible to distinguish between species adsorbed on Pt sites and those adsorbed on Pt with neighboring Ru atoms [3].

Figure 3 shows the steps applied sequentially in data processing; the edge step of all spectra is carefully calibrated and aligned, and a reference spectrum, where no adsorbate is present on the surface, subtracted from each spectrum obtained at different potentials (Fig. 3c). After subtraction a "signature" is obtained which is specific for the adsorbed species and the adsorption site on the surface (Fig. 3d).

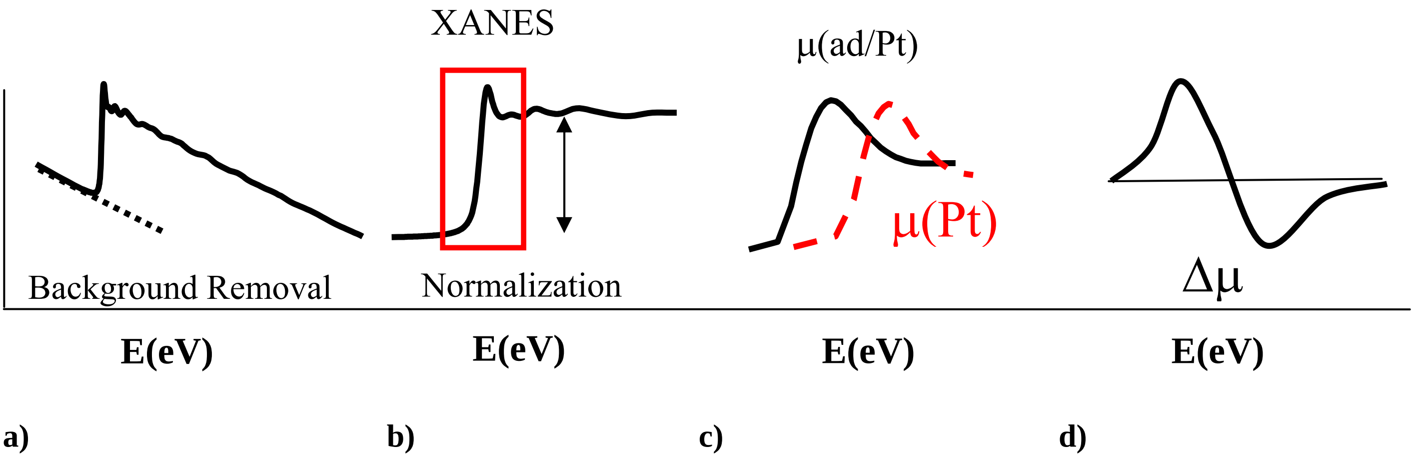

Fig. 3. The new $\Delta\mu$ XANES difference file technique – steps in data processing

Results:

Conventional analysis

The EXAFS results before operation allow considerable insight into the Pt-Ru particle morphology; 1) the sum of the coordination numbers $N_{Pt\text{-}Pt} + N_{Pt\text{-}Ru}$ resulting in around 9 indicates particle sizes of approximately 2.5 nm containing about 400 metal atoms, 2) a Pt-Ru/Pt-Pt coordination ratio of 1/8 or less is observed. The remaining large share of unalloyed Ru is believed to exist on the surface of the Pt particles as hydrous ruthenium oxide. Upon the first contact of the catalyst with the fuel, the O(H) (O or OH) coverage decreases dramatically from the as prepared "blank" catalyst (by a factor of 10 decreased white-line), along with a corresponding decrease in the Pt-O coordination number and rapid increase in the $N_{Pt\text{-}Pt}$. The $N_{Pt\text{-}Ru}$ coordination ratio increases much slower with increasing current, indicating a much slower reduction of the Pt near Ru.

New $\Delta\mu$ XANES technique

In methanol, both O(H) and CO signatures are separately visible with the $\Delta\mu$ XANES technique (Fig. 4, left). When the signature intensities are plotted vs. current density (Fig. 4, right), the data reveal a sharp drop in CO and an increase in OH coverage in the range 65-90 mA/cm^2, i.e. the ignition region, and a pre-ignition region where OH/PtRu begins to form. These results are consistent with the well-known bi-functional mechanism often proposed in literature. Furthermore, an electronic effect is observed due to direct formation of OH on Pt-Ru shifted to more negative potentials by almost 0.1 V. Consequently, the new analysis method enables us to directly observe and verify the mechanisms proposed for a working fuel cell.

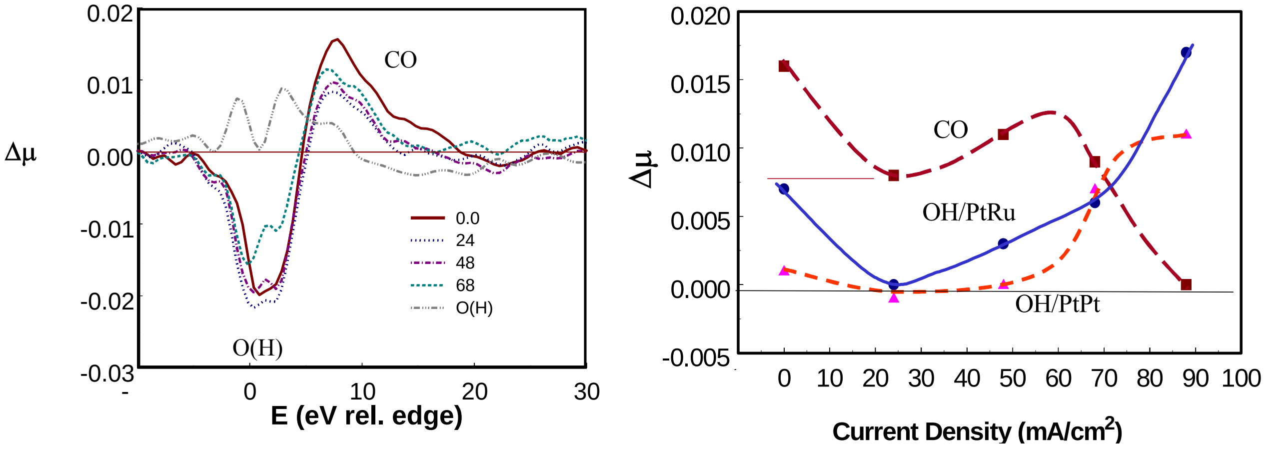

Fig. 4. left: O(H) and CO signatures at different potentials, right: development of adsorbate coverage with potential in methanol operation

Obstacles for measurements in methanol mode:

During recent measurements, problems occurred when measuring in fluorescence geometry using vaporized 1 M aqueous methanol solution as anode feed. These are presumably linked with the increased amount of liquid in the in-situ cell, both lowering the transmitted intensity and corrupting the signal-to-noise ratio. Since these problems occur mainly during long-term operation at one potential (45 minutes are required in order to obtain a reasonable spectrum), we think measurements at beamline ID24 might prove helpful. At this energy-dispersive instrument it is possible to reduce the spectra acquisition time to less than 1 s. Moreover, time-dependent changes in catalyst structure and adsorbate coverage could be assessed more precisely. However, the success of this approach is very much dependent on the data quality.

[1] C. Roth, N. Martz, M. Mazurek, F. Scheiba, H. Fuess, ‘Development of an in-situ cell for X-ray absorption measurements during fuel cell operation’, *Adv. Eng. Mat.,* 2005, in press.

[2] M. Teliska, V. S., Murthi, S. Mukerjee, and D. E. Ramaker, Proc. of the Electrochemical Society, 204th Meeting, Fundamental Understanding of Electrode Processes in memory of Prof. Ernest B. Yeager, in press.

[3] C. Roth, N. Benker, Th. Buhrmester, M. Mazurek, M. Loster, H. Fuess, D. C. Koningsberger, D. E. Ramaker, ’Determination of O(H) and CO Coverage and Adsorption sites on PtRu electrodes in an Operating PEM Fuel Cell’, *JACS,* 2005, accepted.