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ESRF

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.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

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Reports supporting requests for additional beam time

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

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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.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

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:** **Changes in catalyst structure and adsorbate coverage in a working fuel cell**	**Experiment number**: CH-2217
Beamline: ID24	**Date of experiment**: from: 20/09/06 to: 26/09/06	**Date of report**: 02/02/07
Shifts: 18	**Local contact(s)**: M. Newton	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Changes in catalyst structure and adsorbate coverage in a working fuel cell

Aim of the experiment:

The processes in a fuel cell were already observed with conventional EXAFS measurements and seem to be very fast. The aim of this experiment is to observe more precisely the time-dependent changes in catalyst structure and adsorbate coverage in a working fuel cell. The energy-dispersive instrument used makes this possible by reducing the spectra acquisition time to less than 1 s.

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 ((1:1), 60 wt% on Vulcan), b) with a carbon-supported Pt-Ru alloy catalyst ((1:1), 80 wt% on Vulcan), and c) with plain Pt supported on carbon (50 wt% on Vulcan). For all the MEAs, the cathode catalyst is plain Pt supported on carbon at 20 wt%. Two MEAs were prepared each, and one of the two was tested as "new" and the other after working for a week, so that we could compare the performance of a new MEA to a used one.

As we wanted to observe the changes on the anode side, we had to scrape off part of the cathode side (approx. 5 x 5 mm), so that we could record only the signal of the anode catalyst.

All MEAs were operated in pure hydrogen as the anode feed. Spectra were recorded at the Pt L_3-edge as the gases were switched on and then for different potential jumps (see table 1). In each case, spectra were taken before operation without gas feed, serving as reference spectra. Approximately 30 spectra sequences were recorded during the beamtime, which are to be analyzed in detail over the next months.

Table 1. Spectra were recorded at the Pt L_3- edge for different potential jumps; operation with hydrogen as anode feed.

Initial potential	Final potential
800 mV	650 mV
650 mV	800 mV
400 mV	760 mV
200 mV	800 mV
800 mV	0 mV

The optimum set-up for our experiments was found to be a commercial fuel cell hardware with a Kapton™ foil beam window in fluorescence geometry (Fig. 1a, [1]). Unfortunately, this geometry could not be used at the beamline ID24, so that we were required to measure in transmission geometry (Fig. 1b). This made it necessary to remove part of the cathode catalyst, which might affect the current distribution in the fuel cell and have an influence on the final operation parameters.

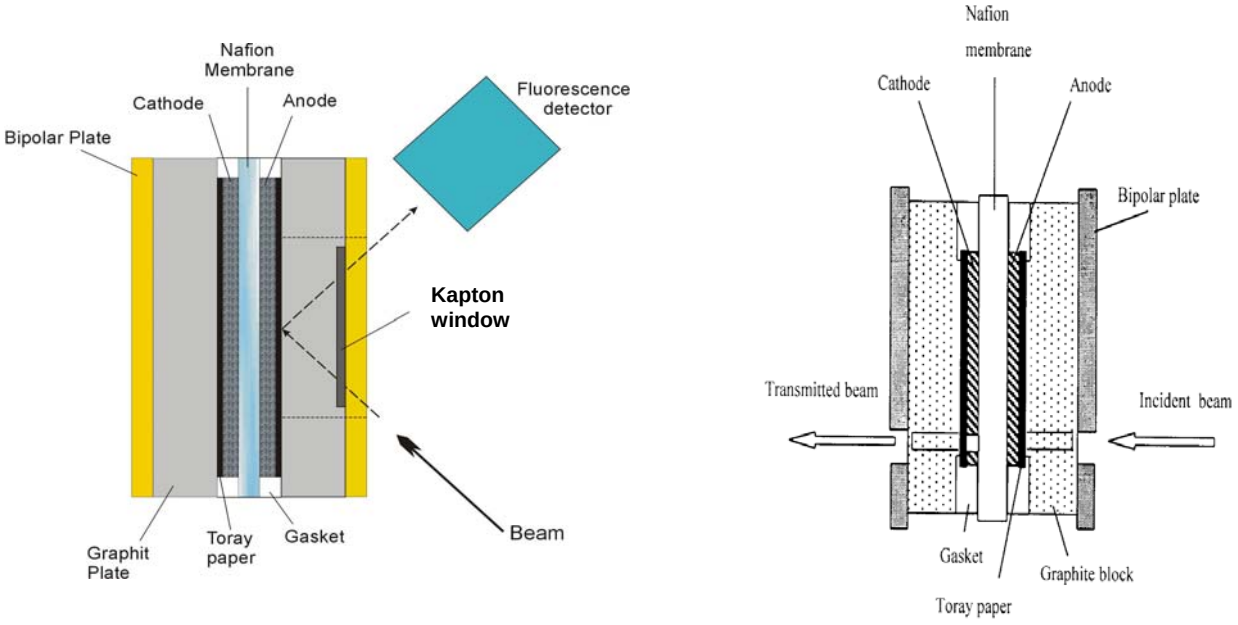

Fig. 1. Set-up of the in-situ fuel cell in (a) fluorescence geometry and (b) transmission geometry

Results:

Due to the quality of the measurements and spectra, a complete EXAFS analysis proved to be impossible. Some first observations concerning the white-line have been obtained, but the results have to be analyzed in more detail the next time, in particular using the Δμ XANES method [2, 3]. Spectra were recorded in dynamic mode, while the feed gases were switched on. Using changes of the white-line intensity as indication, we could follow qualitatively and with high time resolution the reduction of the anode catalyst by hydrogen. In Figure 2, the evolution of the spectra with time is shown. The white-line decreases from spectrum number 150 to number 175 and then remains constant. This means, the complete reduction of the catalyst occurs in very little time (less than a second).

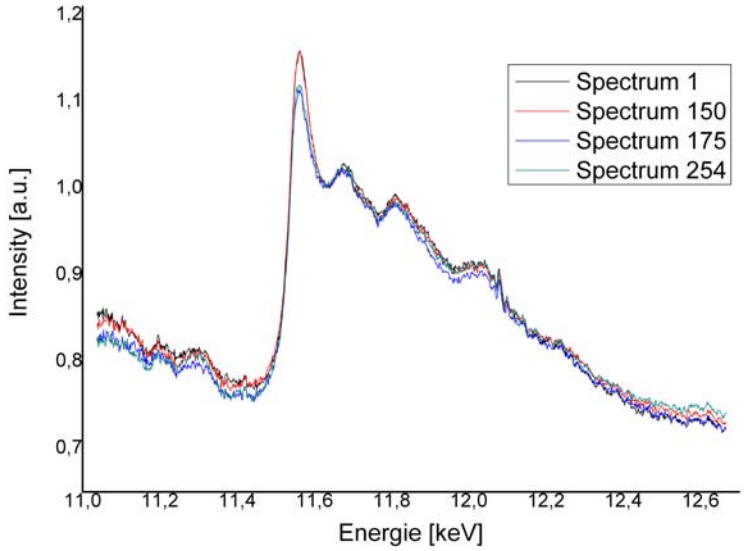

Fig. 2. Raw EDE absorbance spectra while the feed gases were switched on

Obstacles for measurements:

The first experimental obstacle was that measurements in fluorescence geometry were not feasible. The obligation to scrape off part of the catalyst layer might trouble the electrochemical processes in the cell, so that the experiment can not be considered as a test under real conditions. Furthermore, water droplets form specifically in this place and disturb the measurement decreasing the spectra quality significantly. Moreover, the beamline is more adequate for mesurements at high energy, e.g. the Ru K-edge, and the signal for our measurements on the Pt L_3-edge was very low for the MEAs with the lowest amount of platinum. Another problem was the (micro)beam, which has about the same size as the particles of our catalysts and is also detrimental to the measurements. For some tests, we even could not get any signal from the catalyst.

As described in a publication by Newton [4], the absolute dimension of the beam relative to the intrisic particle size of the material plays an important role in determining the quality of the EXAFS data obtainable. It could thus be interesting to try the experiment again with an enlarged beam size (if possible). We also have to further optimize our set-up for the in-situ measurements. However, we are currently in discussion with the

scientists of beamlines ID24 and ID26, in order to see if it is possible to combine time resolution on ID24 and high resolution on ID26 using the same sample environment for a new series of catalysts.

A great many thanks are due to all the staff from ID24 for receiving Virginie Croze for one month and for the time and patience they kindly took to prepare this experiment and make it possible.

[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**, *7 (10)*, 952.

[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**, *127*, 14607.

[4] M. Newton, "Beamsize related phenomena and effective normalisation in energy dispersive EXAFS for the study of heterogeneous catalysts, powder materials, and the processes they mediate: observations, and (some) solutions", *in press*.