

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:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

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

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.

Published papers

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.



	Experiment title: In-situ XAFS measurements at fuel cell catalysts in methanol operation	Experiment number: ME608
Beamline:	Date of experiment: from: 01/08/03 to: 07/08/03	Date of report: 27/08/03
Shifts:	Local contact(s): O. Mathon	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): T. Buhrmester*, N. Martz*, M. Mazurek*, C. Roth* Institute for Materials Science TU Darmstadt Petersenstr. 23 D-64287 Darmstadt, Germany		

Report:

In-situ XAFS measurements at fuel cell catalysts in methanol operation

Situation:

A special in-situ fuel cell has been developed to enable X-ray absorption measurements during operation using either pure hydrogen or 1 M aqueous methanol solution as anode feed. The main aim of these investigations is to monitor changes in the structure of the carbon-supported 20 wt.% Pt-Ru (1:1) anode catalyst with potential.

Preliminary investigations have been carried out at beamline X1 at HASYLAB, Hamburg, in transmission geometry [1]. However, it was not possible to obtain spectra at the Ru *K*-edge because of the strong absorption of the platinum present in the electrode. This has been a severe drawback for the measurements, since data at both edges were to be recorded simultaneously.

Consequently, another approach has been adopted for the in-situ fuel cell experiments at beamline BM29 at the ESRF. The fuel cell was modified with a Be window at the front plate to allow for measurements in fluorescence geometry. It was planned to measure the Pt *L*₃-edge and the Ru *K*-edge in turn with increasing potential in both hydrogen and methanol operation. Beamline BM29 is especially suited for these experiments due to the excellent fluorescence detector available.

Measurements and drawbacks:

Five different membrane electrode assemblies (MEAs) were prepared for the XAS measurements: two commercially-available ones, two in-house prepared MEAs with a commercial Pt-Ru alloy catalyst and one MEA with separate Pt and Ru phases in the anode catalyst. The first four were operated in-situ with hydrogen (and partly methanol) and spectra taken at different potentials at the respective Pt and Ru edge, while the last one could only be measured ex-situ due to problems in operation. In figures 1 and 2, spectra recorded ex-situ at the Pt (fig. 1) and Ru edge (fig. 2), respectively, and in operation at maximum load are compared. They already differ significantly in E space, and a draft analysis using WinXAS reveals differences in R space as well. However, a more detailed evaluation of the data (fitting of the EXAFS and analysis of the AXAFS features) will be carried out in due course.

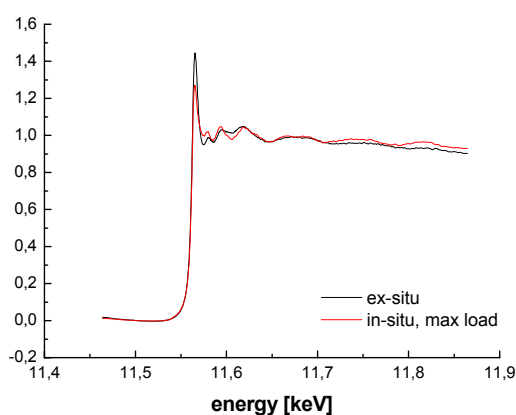


Fig. 1. Comparison of the spectra in E space; black = ex-situ, red = at full load in hydrogen operation, Pt L_3 -edge

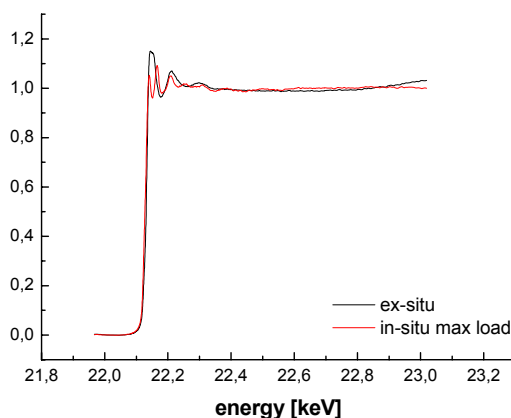


Fig. 2. Comparison of the spectra in E space; black = ex-situ, red = at full load in hydrogen operation, Ru K -edge

Comparing the Ru edge at different potentials in hydrogen operation, no significant differences were observed (fig. 3), while the spectra at the Pt edge exhibit different features at first glance (see e.g. white-line intensities, fig. 4). In this case, fitting of the spectra will provide further information.

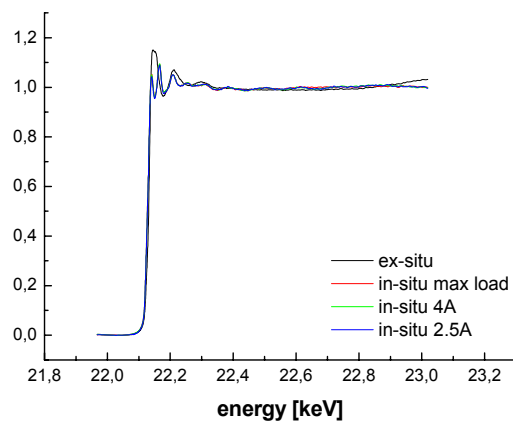


Fig. 3. Comparison of the Ru spectra in E space at different potentials; black = ex-situ, red = at full load, green = 4A, blue = 2.5A in hydrogen operation, Pt L_3 -edge

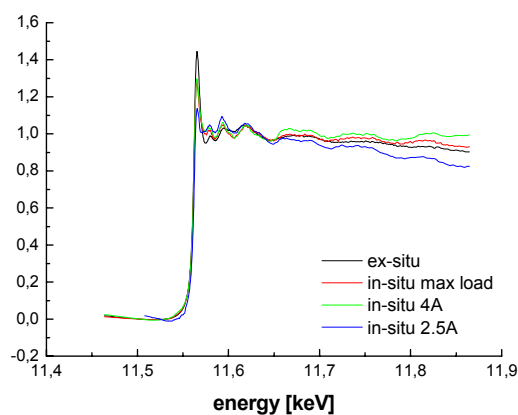


Fig. 4. Comparison of the Pt spectra in E space at different potentials; black = ex-situ, red = at full load, green = 4A, blue = 2.5A in hydrogen operation, Ru K -edge

Despite these interesting findings, several drawbacks occurred during the experiments: a) difficulties to record the Pt L_3 -edge in fluorescence due to a strongly-absorbing water film on the Be window (fig. 5), b) Ru dissolution at potentials >700 mV, which crystallizes on top of the Pt 'masking' it for further measurements. Due to these limitations, only very noisy spectra were taken in methanol operation, since the amount of liquid in the cell hampered the measurements.

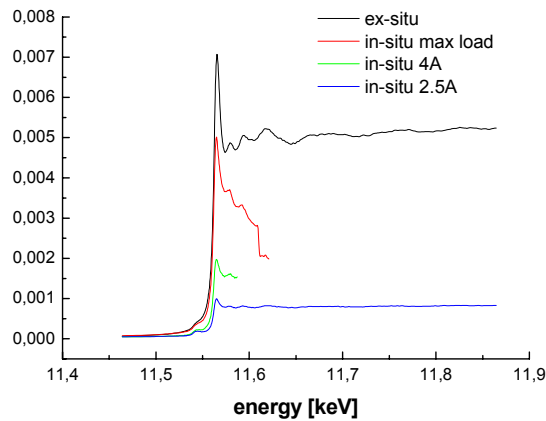


Fig. 5. Spectra at the Pt L_3 -edge with increasing potential and increasing amount of water in the fuel cell

Ideas for improvement:

- 1) Pt should be measured in transmission and Ru in fluorescence, both should be measured in turns at increasing potentials (up to Ru dissolution).
- 2) The cell should be modified to reduce the water in the gas flow field and in front of the Be window. This can be done by using a graphite flow field with serpentine flow (creating a pressure drop in the cell to get rid of excess water). In addition, a small ‘reservoir’ could be cut into the graphite plate below the window to trap the water in there.

We will apply for additional beamtime at BM29 for the next period. With the improvements listed above it should be possible to enhance the quality of the data and thus enable the online-monitoring of the structure of different catalysts in operation.