



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 XAS Investigations of the Structure and Stability of Pt shell – Pd Core Electrocatalysts	Experiment number: CH-3117
Beamline: BM26A	Date of experiment: from: 12 th March 2010 to: 17 th March 2010	Date of report: 2 nd February 2011
Shifts: 15	Local contact(s): Dr Sergey Nikitenko	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): * Prof. Andrea E. Russell * Miss Anna Wise * Mr Peter Richardson All of the School of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ , UK Main contact: a.e.russell@soton.ac.uk		

Report:

The aim of the experiment was to conduct simultaneous in situ EXAFS, SAXS and WAXS measurements of Pd@Pt_{xML}/C PEM fuel cell catalysts under potential control. To accomplish this aim we:

1. Employed a newly developed electrochemical cell (shown in Figure 1) which enabled the simultaneous collection of EXAFS, SAXS and WAXS data while the catalyst electrode was under potential control in 0.5 M H₂SO₄. This meant that the catalyst electrodes could be studied in the oxidised and reduced states synonymous with those experienced in a working fuel cell environment. The electrocatalysts studied in this experiment were Pd@Pt_{0.5ML}/C and Pd@Pt_{1ML}/C, investigating the effect of Pt-shell thickness on the structural response of the catalyst to the applied electrode potential using both fresh and electrochemically aged samples.
2. BM26A was set up for the first time to record simultaneous EXAFS, SAXS and WAXS. EXAFS was recorded initially at the Pd K edge after which the energy was changed to the Pt L₃ edge. SAXS and WAXS measurements were then recorded after stabilisation of the in situ cell current, followed immediately by three EXAFS scans. Each measurement was carried out at four potentials, obtaining data in the double layer region, the oxide region and at two potentials in the hydride region to study hydride adsorption as well as hydride absorption into the Pd core.

The SAXS data obtained could not be fully analysed due to the low concentration of metal nanoparticles in the samples – for future experiments higher catalyst loadings will be used. The WAXS data was analysed qualitatively, with differences seen between the catalysts at different potentials, however, an angular reference was not obtained which meant that the data could not be analysed quantitatively.

The EXAFS data collected was of good quality. At the Pd K edge, a phase shift could be seen in the data for Pd@Pt_{0.5ML}/C at 0.0 V corresponding to lattice expansion due to hydride absorption, thus indicating that the Pd core was exposed in places as would be expected from 0.5ML Pt coverage. Oxide growth, however, was not seen at 1.0 V which would have been expected if the core was exposed. One possible explanation for this is that the Pd oxide was dissolving. Evidence of Pt oxide growth was seen in the Pt L₃ edge data. For the Pd@Pt_{1ML}/C, the phase shift due to hydride absorption in the Pd K edge data was not observed, whereas Pd oxide growth was seen. This suggests that whilst the Pt coverage was high enough to prevent lattice expansion, it was not complete enough to prevent Pd oxide growth. The Pt L₃ edge data showed oxide growth at 1.0 V. Further differences were seen between the fresh and cycled electrodes and the results are currently being compiled for publication.

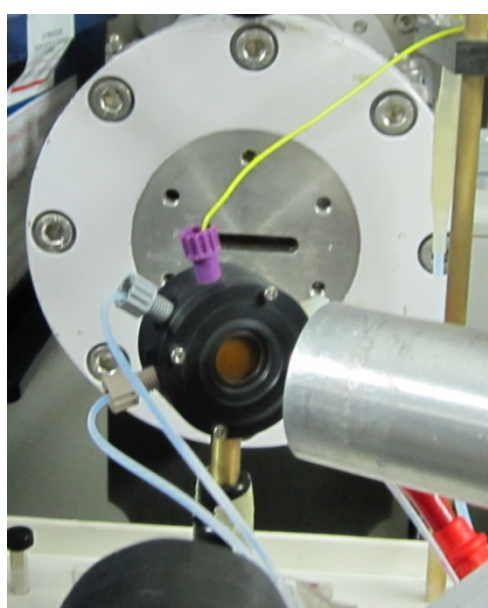


Figure 1. In situ electrochemical cell shown on BM26A in position for EXAFS, SAXS and WAXS measurements.

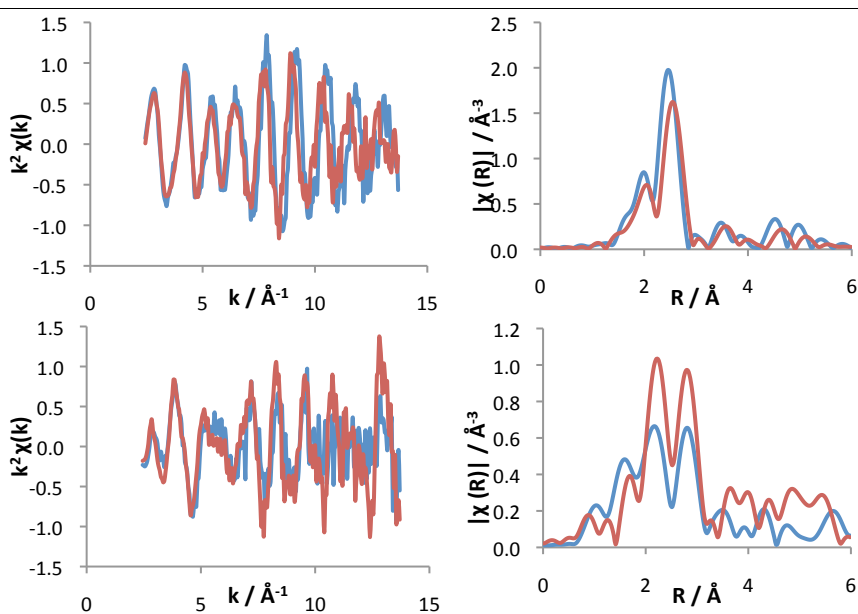


Figure 2. Pd K (top) and Pt L₃ (bottom) edge data collected at 0.0 V (red) and 1.0 V (blue) vs. RHE of Pd@Pt_{0.5ML}/C in 0.5 M H₂SO₄

Results of this work were presented as an invited oral contribution at the International Symposium on Electrocatalysis in August 2010 at Kloster Irsee, Germany, and as a poster at the annual meeting of the International Society of Electrochemistry in September 2010 in Nice, France.

We would like to thank Sergey Nikitenko, Miguel Silveira and Wim Bras for all of their assistance during the experiments.