

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

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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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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: Operando XAFS with proton exchange membrane fuel cell	Experiment number: CH-3012
Beamline: BM-29	Date of experiment: from: 28/10/2009 to: 03/11/2009	Date of report: 25/01/10 resubmitted 27/05/12
Shifts: 15	Local contact(s): Dr. Carmelo Prestipino	<i>Received at ESRF:</i>
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Report:

Introduction

In recent years, the study of electrocatalysts for proton-exchange membrane fuel cells (PEMFC) has been strongly promoted by the use of XAS[1]. The wealth of information on the metal particles accessible by XAS has in particular triggered considerable effort to measure XAS data under conditions as close as possible to realistic reaction regimes. While this goal was first approached with electrochemical cells, in which the working electrode was combined with a conventional counter electrode via a separator e.g. a nafion membrane, XAS studies with real proton-exchange membrane (PEM) fuel cells had to cope with the problem that state-of-the-art membrane-electrode assemblies (MEAs) contain significant amounts of platinum both in cathode and anode. Therefore, in earlier cells for transmission XAS the catalyst in the beam path was removed from the counter electrode [2] or non-Pt counter electrodes were used (e.g. [3]), which causes serious interference with the reaction regime. Meanwhile, fluorescence detection, which is mandatory for minority components, has been also extended to the measurement of Pt spectra [4]. However, due to the very small thickness of catalyst layers and membrane, one has to expect significant contributions from the counter electrode platinum at the typical angles of primary beam incidence (around 45 °). Therefore, the cells proposed so far, work with Pd counter electrodes as well [5, 6].

We have therefore developed and built a new cell construction in which the incoming X-ray hits the electrode at a very small angle, which permits to exclude contributions from the counter electrode effectively. The cell has been derived by introducing relatively small modifications to a standard test cell used in the industry for the characterization of newly developed MEAs in research labs, which makes sure that the electrochemical performance of the catalyst is measured under state-of-the-art conditions. The modifications concern in particular the thinning of the flowfield wall in a narrow section to allow entrance of the beam into one of the gas channels, where it is lead to the point of interest. Above this point, the upper wall of the flowfield is thinned as well, and the collector and end plates are perforated to allow collecting the fluorescence signal. The first operando testing of this cell with two MEAs, monitoring the state of the Pt/C (A) and Pt-Co/C (B) cathodes (anodes – Pt/C) was the goal of the beam time.

Experimental

The measurements were carried out at BM29. The complex gas feeding system, consisting of a mass-flow controller unit, a moistening unit, the cell, which is included in an electrical measurement circuit with an electronic load and a supporting voltage, and a dryer unit for the exhaust gases, was installed without problems. The beam adjustment with this system is a challenge, but the provisions included in our construction as leads for finding the measurement channel in the (entirely closed) cell construction turned out to be practical, and with the help of Dr. Prestipino, the intensity could be successfully optimized for the Pt/C cathode (MEA A).

For each state of this MEA, the PtL_{III} and L_{II} XANES were measured in order to allow assessments of the d-band filling. For most states (initial state in inert gas, initial state under feed, after stabilization and every second point of the polarization curve (cf. Fig. 2)), the PtL_{III} EXAFS was measured as well, with acceptable signal/noise level. After submitting the feed, the MEA was stabilized at a current density of 0.5 A/cm² for 8 h, then its state was investigated at open-circuit voltage and along the polarization curve in steps of 0.2 A/cm².

With this setup, it was possible to measure meaningful PtL_{III} spectra, although not with very high quality. At 0.8 A/cm², however, strong fluctuations of the signal started so that measurements were completely impossible. We interpreted the fluctuations as being due to formation and movement of water droplets in the gas diffusion layer, which is passed by the beam at a small angle. Increasing the oxygen flux dosed on the cathode (the H₂ anode flux as well) indeed solved the problem so that the series could be successfully finished.

With the Pt-Co/C MEA (B), only L_{III} XANES and EXAFS were measured with Pt, and studies at the Co edge were attempted. It was, however, found that the brilliance of the station was not sufficient to get satisfactory CoK spectra (the Co concentration being just 0.02 mg/cm²; Pt – 0.18 mg/cm²). With long accumulation times, XANES could be registered in rather mediocre quality, but there was no way for EXAFS. As elemental concentrations in this range are typical for leached alloy MEAs, it was concluded that a horizontally focused beamline would be necessary for measurements of this type.

Results

Figure 1 shows the polarization curve measured with MEA A at a gas pressure of 1.5 bar. It is compared with curves measured for the same type of MEA with the same gas flows, but pressures of 1 and 2 bar in the laboratories of Umicore & Co KG. These curves bracket our experimental curve well, except for the high current densities where our curve deviates to higher voltages – apparently a consequence of the enhanced gas flows applied to avoid the condensation of water (see above). Obviously, our cell (and the whole equipment) behaves like state-of-the-art test equipment.

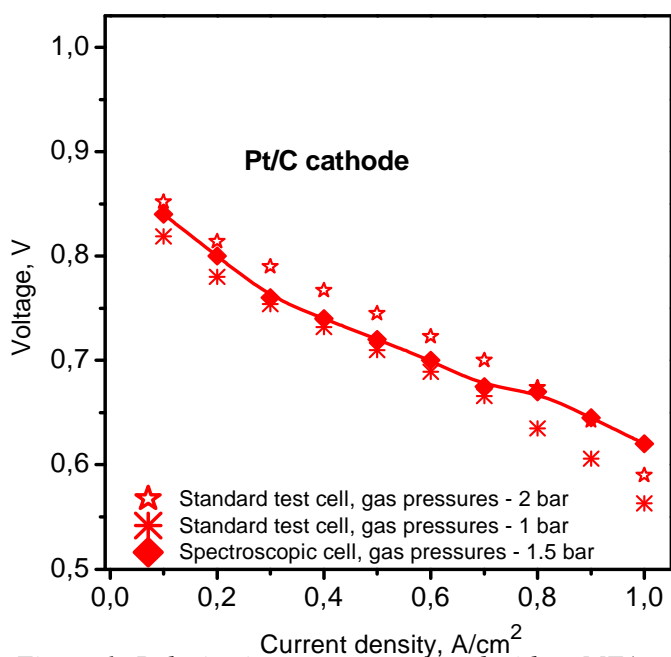


Figure 1: Polarization curves measured with a MEA containing a Pt/C cathode (0.4 mg Pt/cm²). Comparison with data from a standard setup, obtained at different gas pressures).

Figure 2 gives an impression on the quality of the data from MEA A. The initial spectrum (in inert gas) and a spectrum at 0.5 mA/cm² is compared to the transmission spectrum and that of a Pt foil. There is a reliable tendency up to ca. 14 Å⁻¹, which allows a clear evaluation of the first shell (not shown) while information on higher shells is doubtful. Due to the high Pt concentration in this cathode, the data had to be treated with a self-absorption correction, for which the initial cathode had to be measured in transmission as well (taking a half-MEA provided by Umicore). The comparison of the spectra shows that the structural properties of the catalyst were not changed significantly during the experiment.

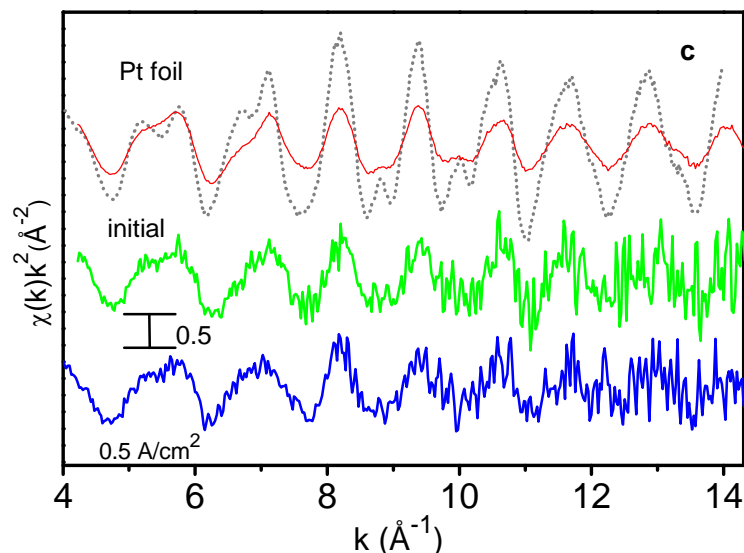


Figure 2: PtL_{III} EXAFS of a Pt/C cathode (0.4 mg Pt/cm^2) measured in the spectroscopic cell under inert gas and operando at 0.5 mA/cm^2 . Comparison with initial spectrum in transmission (half-MEA) and with Pt foil

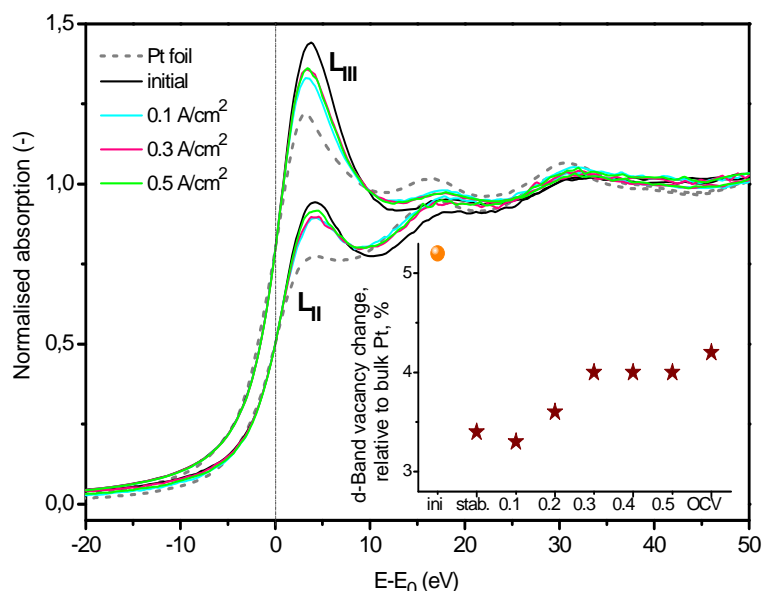


Figure 3: $Pt L_{III}$ and L_{II} XANES of Pt foil and of a Pt/C cathode (0.4 mg Pt/cm^2) at different current densities (fluorescence measurements, corrected for self absorption). Inset: Assessment of d-band occupancy – percentage decrease relative to bulk Pt.

The XANES data measured with this MEA show, however, that changes occur in the electronic structure (d-band filling) depending on the conditions (Figure 3). The Pt d-band occupancy was derived from the difference between L_3 and L_2 edge XANES using the formalism proposed in refs. [7] and [8]. In the inset of Fig. 3, the percentage change relative to bulk Pt is shown. A significant drop can be seen between the initial state (in air) and the state after stabilization, probably because of the removal of some oxidized (maybe even chemisorbed) species. With increasing current density, the difference to bulk Pt increases again. The effect is rather small, between 3.3 and 4.2 %, causing the number of unfilled d states ($Pt - 1.60$) to increase just from 1.65 to 1.67. However, the absence of significant scatter in the series shows that the method can differentiate these minute changes. In a subsequent measurement at open circuit, the d-band vacancies remained at the previous level (Fig. 3, inset) which suggests that the changes are not related to the changes in electrode potential. Rather, we track here irreversible changes in the structure of the metal particles which are probably too small to be reflected in the geometrical quantities accessible via EXAFS at least at the level achieved in this beamtime.

The measurements with the Pt-Co/C cathode (MEA B), though not providing publishable data, gave a strong hint on significant changes of the cathode during the measurements. There were changes in the Pt spectra, although not to trace reliably with the present data, and there was a strong increase of the CoK white line indicating an oxidation, probably a leaching of Co. We intend to study this phenomenon in a subsequent beamtime, for which we will have to find, however, a horizontally focused beamline. Despite these problems, we would like to state that the data obtained in this beamtime are the

first proof of principle of our cell and an important step in its further development and utilization.

References

- [1] A.E. Russell, A. Rose, Chem. Rev. 104 (2004) 4613-4635.
- [2] C. Roth, N. Martz, T. Buhrmester, J. Scherer, H. Fuess, PCCP 4 (2002) 3555-3557.
- [3] R.J.K. Wiltshire, C.R. King, A. Rose, P.B. Wells, M.P. Hogarth, D. Thompson, and A. E. Russell, Electrochimica Acta 50 (2005) 5208-5217.
- [4] C. Roth, N. Benker, M. Mazurek, F. Scheiba, H. Fuess, Adv. Eng. Mat. 7 (2005) 952-956.
- [5] E. Principi, A. Di Cicco, A. Witkowska, R. Marassi, J. Synchrotron Rad. 14 (2007) 276-281.
- [6] E. Principi, A. Witkowska, S. Dsoke, R. Marassi, A. Di Cicco, Phys. Chem. Chem. Phys. 11 (2009) 9987-9995.
- [7] A.N. Mansour, J.W. Cook Jr., D.E. Sayers, J. Phys. Chem. 89 (1984) 462-469.
- [8] F.Y. Lai, L.S. Sarma, H.L. Chou, D.G. Liu, C.A. Hsieh, J.F. Lee, B.J. Hwang, J. Phys. Chem. C 113 (2009) 12674-12681.