

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 via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can 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: Sustainable oxygen production by water oxidation: XAS study on the catalytically active species	Experiment number: CH-3941
Beamline: ID26	Date of experiment: from: 5/12/2013 to: 9/12/20123	Date of report: 30/08/2014
Shifts: 12	Local contact(s): Eduardo Salas	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Matthias Bauer, Department Chemie, Universität Paderborn, Warburger Str. 100, 33098 Paderborn *Roland Schoch, Department Chemie, Universität Paderborn, Warburger Str. 100, 33098 Paderborn *Rahel Schepper, Department Chemie, Universität Paderborn, Warburger Str. 100, 33098 Paderborn		

Report:

The need for clean and abundant fuels will be one of the greatest challenges to mankind in the near future, as the peak oil discussion has settled, stating that the peak of oil production will be reached within the next 10-20 years. Fuel cells are one of the most promising alternatives, since their working principle is mostly understood and recent activities are focused on increasing their efficiency. However, the production of “fuels” for fuel cells, i.e. hydrogen H_2 and oxygen O_2 in the simplest case, remains one bottleneck that prevents fuel cells to be already considered a serious alternative to fossil fuels. Water splitting reactions are a very promising approach to overcome this limitation, since “*The ultimate solution to satisfy the world’s energy demand is the cleavage of water into its atomic building blocks, hydrogen and oxygen*“.¹

Empiric studies identified molecular Ir(III) complexes (left in figure 1) in presence of cerium ammonium nitrate CAN as catalysts of high activity for water oxidation (i.e. O_2 production), as revealed by increasing numbers of high-impact publications.² However, the fate of these complexes in course of the reaction is unclear. We thus studied a set of molecular complexes under water oxidation conditions to gain a detailed insight into the formed species. These complexes were of complex nature based on oxazoline ligands, but also more simple complexes like iridium chloride and iridium acetylacetonate, in comparison to IrO_2 . These compounds were investigated by thorough XAS experiment, both the precatalysts and under water oxidation conditions. The XANES spectra were analyzed by LC-XANES fit in order to determine the oxidation state ratio of Ir(III)/Ir(IV), which is unequivocally formed under reaction conditions, but with unknown concentrations. The EXAFS data was then analyzed first also with respect to this oxidation state ration in an indirect way by determination of the Ir-backscattering pair characteristic for the precursor. The reduction in the respective coordination number under water oxidation conditions can be correlated with a decrease in the precursor oxidation state +III, which fits to the results determined by LC-XANES fit.

Since the iridium in the state +IV could be proved to be of some IrO_2 character by other methods, in a second step of the EXAFS analysis a relative size determination of the IrO_2 species was performed. The results were difficult to interpret, since no clear trend between oxidation state ratio and IrO_2 size was obvious. The spectra and obtained results are shown in figure 1, the final interpretation achieved by help of other methods in figure 2. Although further studies need to follow, the current interpretation is that depending on the point of the

reaction, both Ir(III) and Ir(IV) are catalytically active. At the beginning of the reaction, molecular Ir(III) makes the reaction, while towards the end, Ir-oxo species do.

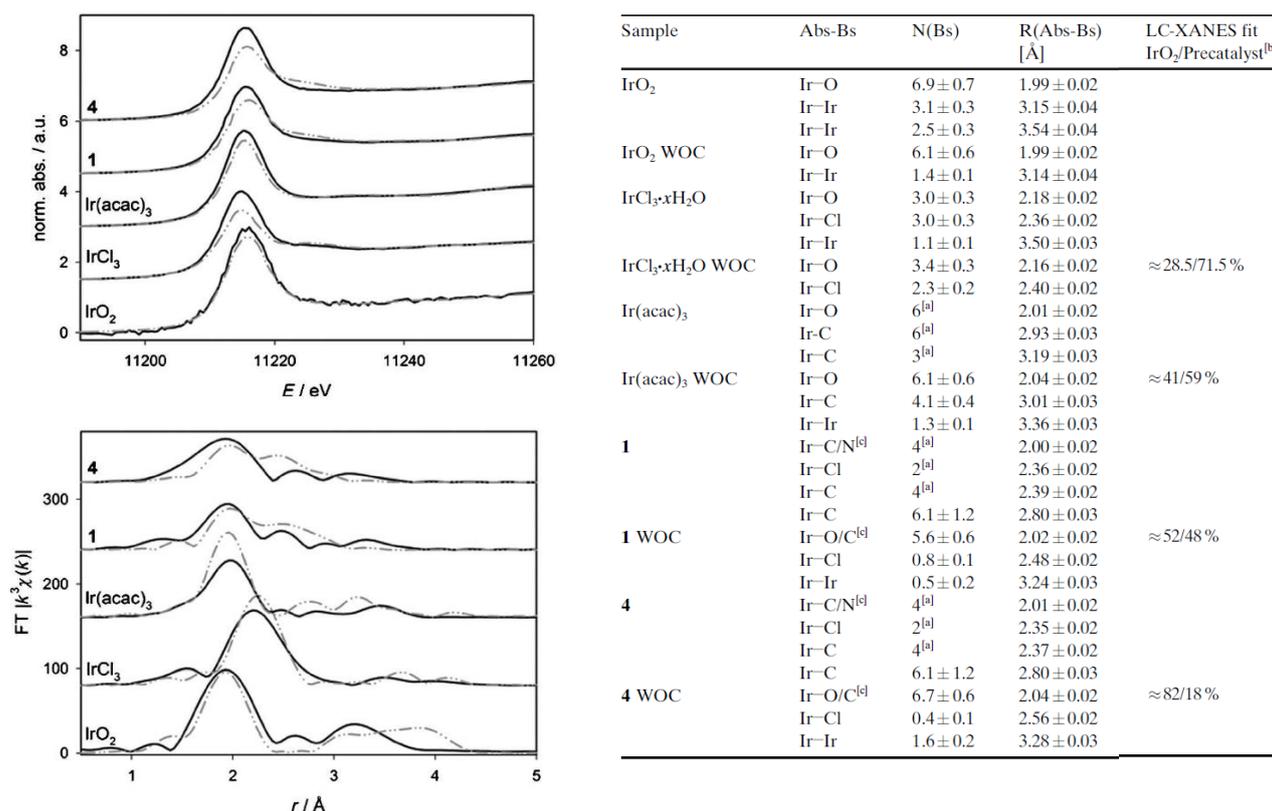


Figure 1: XANES (top left) and EXAFS (bottom left) spectra of the precatalyst (grey dashed line) and under water oxidation conditions (black solid line). The results from the EXAFS analysis and LC-XANES fit are summarized in the table.

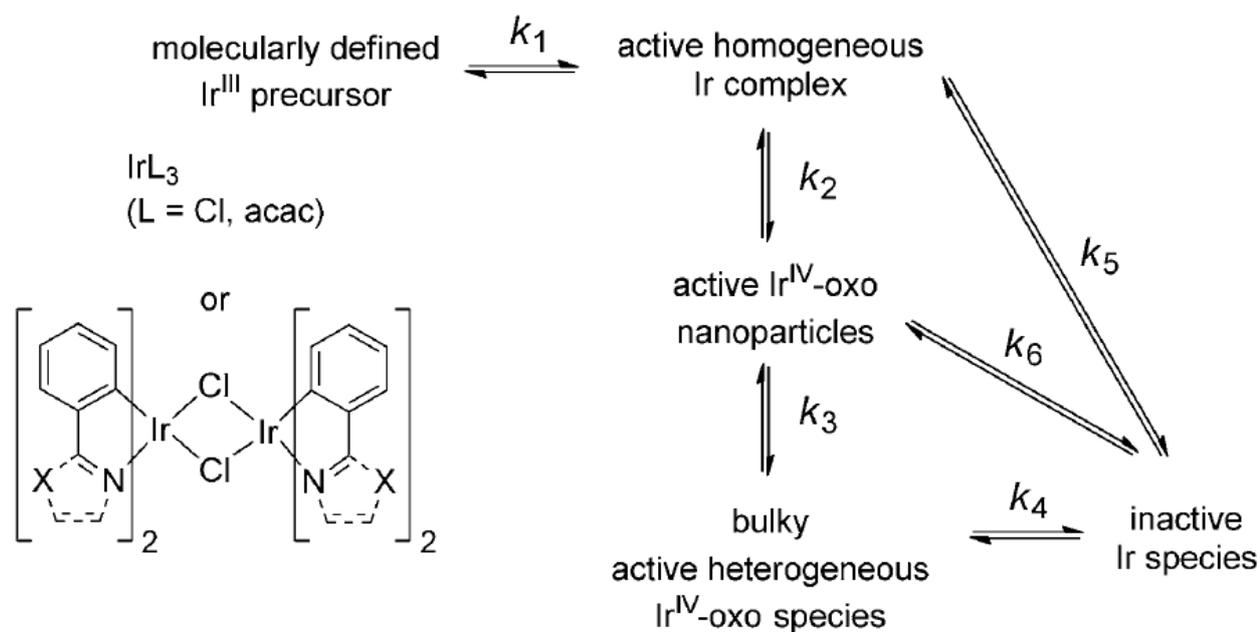


Figure 2: Summary of the spectroscopic results on water oxidation with Ir complexes.

[1] M. Beller, *ChemSusChem* 2008, **1**, 463. [2] M. Beller et al., *ChemSusChem* 2011, **4**, 1598; M. Beller et al., *Chem. Eur. J.* 2012, **18**, 3220.