EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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 via the User Portal:

https://wwws.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.

ESRF	X-ray diffraction to in-operando monitor the non-stoichiometric state of a material to overcome chemical reaction equilibrium	**Experiment number**: MA-3410
Beamline: ID22	**Date of experiment**: from: 19 Jun 2017 to: 26 Jun 2017	**Date of report**:
Shifts: 15	**Local contact(s)**: Catherine DeJoie	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

This report is on the in-situ study of a fixed bed chemical looping reactor performed on ID22. The reactor overcomes chemical reaction equilibria constraints of conventional mixed reactors. Problems faced with the use of traditional oxygen-carrier materials are also overcome. The chemical reaction studied was the water-gas shift reaction, which involves the periodic feeding of water and carbon monoxide to opposite ends of a packed bed of $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF641).

The work makes use of an upgraded version of the furnace and flow system used in experiment MA 2914 with an increased isothermal zone and a more modular and robust design. This new design allowed for a 17 cm bed to be positioned inside an isothermal section (+/- 10 ˚C). This furnace was designed for vertical orientation as before, with narrow slots running down the furnace for x-ray ingress and exit. The flow system remained unchanged. Further details of the flow system and furnace's operation and design can be found in forthcoming publications.

Instillation of the equipment into the experimental hutch was carried out on a machine day to maximise beam time utilisation. The beamline was calibrated for 35 keV operations with spot size of approximately 1 mm x 1 mm. The first shift was slated for safety inspection and bed alignment checks which were completed on time. The next shift was used to heat up the reactor and calibrate gas measurement systems. Subsequently, preliminary scans were taken to determine the optimal acquisition times and scan ranges. The fastest scans used for kinetic experiments were performed over a range of 2.2 degrees at a scan speed of 30 degrees/minute in two theta (approx. 5 seconds).

Initial scans were carried out on a reactor bed made of α-Al_2O_3, to determine the temperature gradient inside the reactor. The Al_2O_3 bed allowed for the temperature gradient in the bed during flowing and non-flowing conditions for unreactive gasses to be defined. The furnace was then cooled so that a pure LSF641 bed could be added before reheating the bed.

The bed (along with the Al_2O_3) were brought up to temperature. A variety of experiments were carried out using the bed without technical difficulties. An individual point, one third of the way along the bed, was measured continuously *in operando* as the bed went from its initial state to stable cycling, to discover how gas phase steady cycling and solid state steady cycling was linked. After the

bed had been operating steadily for over an hour, 16 locations in the bed was recorded, each over 2 non-consecutive cycles to determine the kinetics of the bed material and define how the bed changed over a cycle. These experiments were then repeated with the direction of the flows reversed.

Further experiments were carried out using this bed to determine bench mark cubic cell parameters for different locations in the bed using CO/CO_2 buffer gasses. As before, the way in which a single point in the bed changed as a function of time was recorded until steady state before the same set of 16 locations in the bed were scanned. During these experiments it was discovered that the positioner table used to change the location in the bed being studied was not capable of sustaining the moment the cantilevered furnace exerted, this led to 1 shift being required to redistribute weight on the table and to add additional counterweight to the back of the set up to help balance the forces.

Upon comparing the lattice parameters obtained during cycling operation with the bench mark values, it became apparent that the temperature profiles of the bed were different with or without the chemical reaction occurring. To quantify the temperature changes *in situ*, a new bed was created in which yttrium oxide was added to LSF461 with a mass ratio of 1:5. The peaks for yttrium oxide do not overlap with those of LSF641 making it ideal for this application.

The next 2 shifts were used to cool down, change the bed to the yttrium loaded one and reheat the reactor. The bed was then studied using the same methods detailed above. After this the bed was cycled between the different buffer gases to give controlled inlet conditions to aid simulation of the system. These combined experiments made it possible to map the temperature of the bed in different buffer gasses and the effect of cycling on the bed as seen in figure 1A. This along with the buffer gas holds allowed for the unit cell parameters from the LSF641 bed to be converted into the delta state, (3 minus the oxygen content). The values for a point a third of the way along the bed can be seen in Figure 1B where they are compared to a thermodynamic simulation of the reactor. This simulation was carried out based on literature values for the equilibrium constants. It can be seen that the model closely follows the thermodynamic simulation. It is only the high resolution of ID22 that allows us to determine composition changes in O of +/- 0.01 from cell parameter changes of just 0.005 Å..

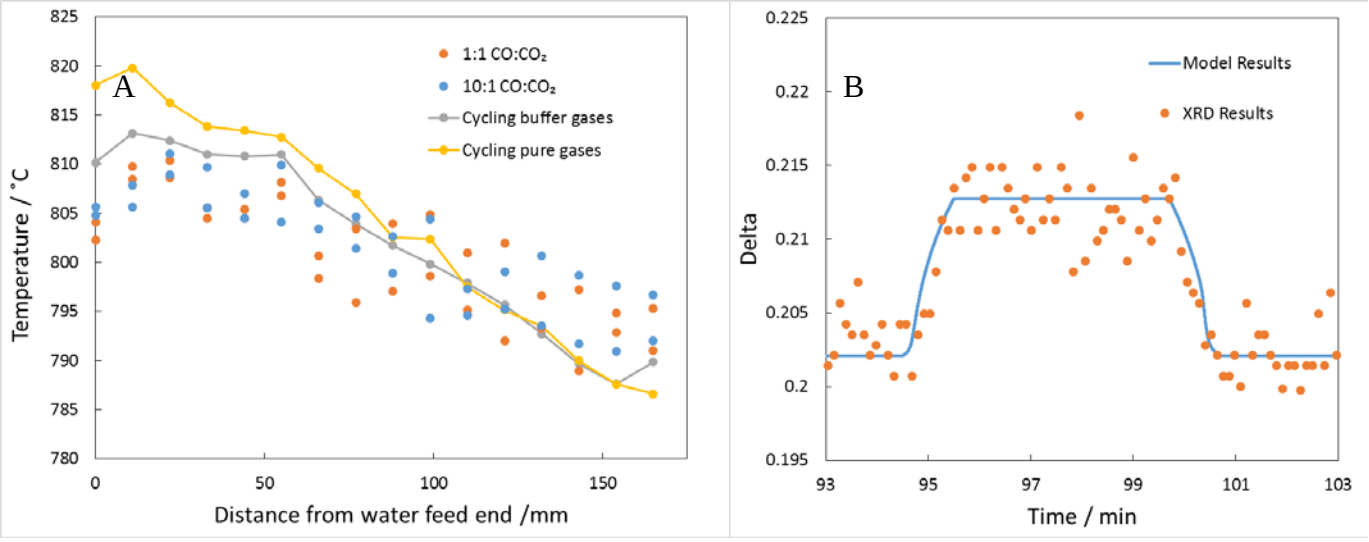

Figure 1A: Time average temperature once steady state or cycling has been achieved of the bed at given points for buffer gasses and over steady cycling of 5% H_2O/5% CO and of 1:1 CO_2:CO/10:1 CO_2:CO. B Delta state at a third of the way along the bed from the water feed side as a function of time during steady cycling compared to the value predicted by a thermodynamic model.

Overall the experiment was a success allowing us to determine how the oxygen non-stoichiometry changes over steady cycling as well as an in-operando understanding of the heat of reaction and its effect on the material. This gives significant insight into the functioning of our memory reactor and how its performance could be improved.