



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.



	X-ray diffraction to in-situ monitor the non-stoichiometric state of a material to overcome chemical reaction equilibrium	Experiment number: MA-4239
Beamline: ID22	Date of experiment: from: 3 Oct 2018 to: 8 Oct 2018	Date of report: 15/11/18
Shifts: 15	Local contact(s): Catherine DeJoie	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Ian Metcalfe ^{a*} , John Evans ^{b*} , Wenting Hu ^{a*} ^a Newcastle University, School of Engineering, Newcastle upon Tyne, United Kingdom ^b University of Durham, Department of Chemistry Science Laboratories, Durham, United Kingdom		

Report:

This report will summarise a study carried out on the use of novel perovskite-type materials in an in-situ fixed bed chemical looping reactor carrying out the water-gas shift reaction or methane oxidation for hydrogen production. In comparison with mixed reactor systems, the use of temporally separate counter-current feed streams allows for the production of unmixed product streams thereby eliminating the need for additional separation stages, and allowing for the chemical reaction equilibria constraints associated with mixed reactions to be overcome. Carbon monoxide was used as the reducing agent for $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (LSF641) and Mn-doped LSF (LSFM6473), while methane was used as the reducing agent for a $\text{La}_{0.8}\text{Ce}_x\text{Ni}_y\text{Ti}_z\text{O}_3$ (LaCeNiTi) family member. In order to quantify the temperature changes occurring during the chemical reactions in situ, Y_2O_3 or ZrO_2 was added to the material beds in a ratio of 1:5 by mass.

The same furnace and flow system that was successfully used in experiment MA-3410 was also used in this study. In order to maximise the use of available beam time, the installation of the equipment was carried out during a machine day. The beamline was calibrated for 35 keV operation with a spot size of approximately 1 mm x 1 mm. The first shift was slated for safety inspection and bed alignment checks and these were completed on time. For cycling experiments, data collection protocols were established to allow for diffraction patterns to be collected in as little as 13.2 seconds. Downtime during set-up was used to carry out scans of capillaries containing materials of interest, and the reactor furnace was set to heat up.

During the next shift scans were taken at a central point of a bed of LSF641 being fed various oxygen buffer gases at 1013 K, 1053 K, 1093 K and 1133 K. These allowed for the lattice parameter of the material to be determined at higher oxygen partial pressures than before. Afterwards the furnace temperature set-point was set to 1093 K for the next experiment.

The next shifts were allocated to carrying out a series of experiments with a bed of LSF6473. Some of these involved flowing CO/CO₂ buffer gases to the reactor, where two points at either end of the bed were scanned until reaching steady state, after which two scans at 15 different positions were taken going up and down the bed. This allowed for the lattice cell parameters to be determined as a function of position, and was useful in determining how the material properties of the bed were changing as it went from an oxidised state to a more reduced state and vice versa compared with the outlet gas analysis.

Further experiments involved counter-currently feeding 5% CO and 5% H₂O streams to the bed for 60 cycles to carry out the chemical looping water-gas shift process. For the first 15 cycles, measurements were taken at a point near the bottom of the bed, while in the subsequent 15 cycles measurements were taken at a point towards the top of the bed. For the final 30 cycles, measurements were taken at 15 points on the bed each over 2 non-consecutive cycles. The changes in the lattice cell parameter at each position in the bed over the course of a cycle can be seen in Fig. 1a, which also demonstrates the high resolution that can be achieved

using the ID22 beamline. The same bed was also cycled between the most oxidising and most reducing CO/CO₂ buffer gases (ratios 1:20 and 20:1 in argon) to see how the material changed when using CO₂ as the oxidising agent as well as to give controlled inlet conditions for comparison to bed simulations. It was found that there was an approximately 70 K difference between the temperature determined from the yttrium oxide measurements and the set-point temperature of the furnace (1093 K) as seen in Fig. 1b.

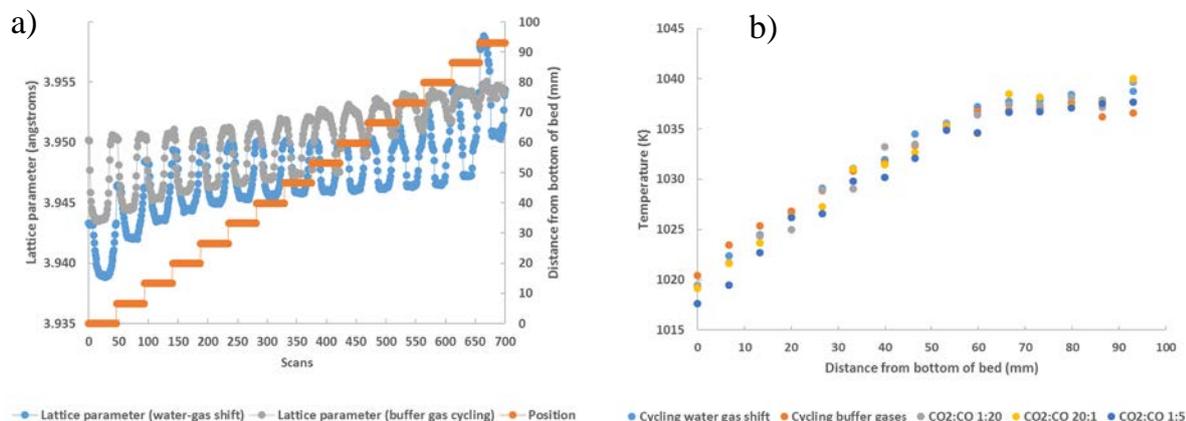


Figure 1: a) Lattice parameter changes for 15 cycles at each point in the LSFM6473 bed during water-gas shift and buffer gas cycling, b) Average temperature at each point in the LSFM6473 bed during steady cycling or steady state.

During the next shifts, the furnace was set to cool down so that two LaCeNiTi beds could be loaded. A temperature programmed oxidation experiment was then carried out to fully oxidise the bed and determine its oxygen capacity. This was followed by a methane temperature programmed reduction (MTPR) experiment up to 1023 K to determine the structural changes in the material that correlate to the methane oxidation (see Fig. 2a). XRD scans revealed that the conversion in methane coincided with a phase transformation of NiO to Ni metal and, at the same time, with a slight shift and broadening of the perovskite peaks (Fig. 2b). Following the MTPR experiments, a number of cycles were then carried out feeding 5% CH₄ and 5% O₂ from the top of the bed.

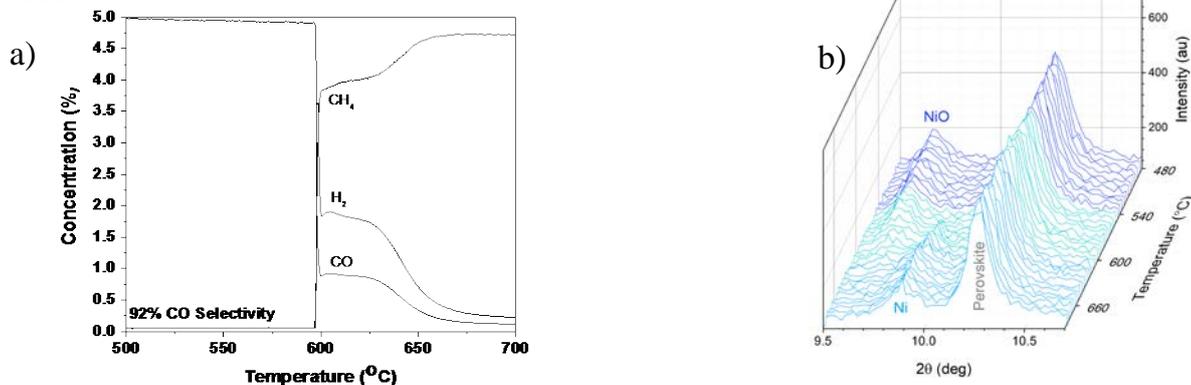


Figure 2: a) Methane temperature programmed reduction of LaCeNiTi, b) In-situ XRD patterns of LaCeNiTi while undergoing methane temperature programmed reduction.

Further cycling experiments on a larger LaCeNiTi bed were carried out aiming to determine the effect of feed length durations on the structure of the material. As before, a temperature programmed oxidation experiment was carried out prior to cycling to fully oxidise the bed. Finally another experiment was carried out cycling between 5% CH₄ and 5% H₂O to determine the structural changes occurring during water to hydrogen conversion within the material. The remainder of the time was spent scanning a total of 50 capillaries containing different LaCeNiTi samples.

Experiments were successful allowing us to extract valuable information about changes in the material's properties in-situ. The data acquired provided valuable insight on the phase, lattice parameter and nanostructure changes of the studied materials under redox cycling. Results obtained are complemented by outlet gas analysis that can be used to directly correlate the material's activity to the changes in its structure. Overall, the experiments carried out will allow for a deeper understanding of the materials and the process that will lead to the optimisation of both.