

# In-situ neutron diffraction study of cathode/electrolyte interactions under electrical load and elevated temperature



F. Tonus\*, S.J. Skinner

Department of Materials, Imperial College London, Prince Consort Road, London SW7 2BP, UK

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## ABSTRACT

Fuel cells are proposed as a future energy conversion technology that will reduce greenhouse gas emissions at the point of operation due to their ability to produce electrical energy from non-hydrocarbon fuel sources. The Solid Oxide Fuel Cell (SOFC) is amongst the most efficient fuel cell types, however, due to the high cell operating temperature cation diffusion occurs between the different components of the cell, resulting in rapid degradation of the power output. In this paper we investigate cation migration between the promising intermediate temperature-SOFC cathode  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  (LSCF) and a fluorite type electrolyte  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$  (CPO). The crystallographic structure evolution and degradation of the materials were studied by neutron diffraction *in-situ* under pseudo-operating conditions, i.e. at 600 °C under air and under electrical polarisation. The lattice parameter and cation occupancy evolution were analysed by Rietveld refinement as a function of time and applied potential. The materials were found to be stable, as no impurity formation, lattice parameter or site occupancy evolution was observed during the experiment. However La migration prior to the experiment from LSCF to CPO was observed as well as B-site vacancies in LSCF.

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## 1. Introduction

In order to mitigate the effects of climate change, reduction in carbon-based emissions is necessary and significant research efforts have been directed towards low emission power generation. As such research on fuel cells and particularly on Solid Oxide Fuel Cells (SOFCs), has been extensively developed as the only waste produced is water, assuming a non-hydrocarbon fuel is utilised. However due to high operating temperatures ( $\approx 800\text{--}1000$  °C), cells are subject to issues such as delamination [1,2], cation segregation [3–5] and interdiffusion of cations [6,7], which can cause rapid ageing of the cells. In order to decrease these effects, lower operating temperatures (500–700 °C) are targeted and so new materials with enhanced performance at these temperatures are required. However the phenomenon of cation diffusion through the interface is still not very well understood, particularly during operation. Yang et al. [8] showed, for example, the effect of temperature on the degradation of the material: after annealing an yttria stabilised zirconia (YSZ)/ $\text{LaSr}_x\text{MnO}_3$  (LSM) symmetrical cell

at 1400 °C for 48 h they highlighted by scanning electron microscopy (SEM) and X-ray diffraction (XRD) the formation at the interface of a passive phase composed of cations originating from both YSZ and LSM. Harvey et al. [9] showed additionally by secondary ion mass spectrometry (SIMS) the influence of temperature on the diffusion of La and Mn from a LSM thin film into  $\text{Ba}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  (BSCF). Backhaus-Ricoult et al. [10] and Huber et al. [11] on the other hand highlighted the influence of the potential between the electrodes on the cation migration. They showed *in-situ* by X-ray photoelectron spectroscopy (XPS) and Scanning X-ray Photoelectron Microscopy (SPEM) or SIMS at high temperature (600–650 °C) under vacuum the migration of cations at the surface between either LSM or  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Mn}_y\text{O}_{3-\delta}$  (LSCrM) and YSZ depending on the polarisation. Backhaus-Ricoult et al. showed first the migration of Sr and Mn from LSM to YSZ under cathodic polarisation which was reversible for Mn when applying an anodic bias whilst Huber et al. showed the same results between LSCrM and YSZ.

Whilst these studies provide valuable information on the ageing mechanism of SOFCs, they were not performed under realistic operating conditions and concern only high temperature SOFC materials when conceivably the future lies in intermediate temperature SOFC (IT-SOFC) materials, particularly for mass market

\* Corresponding author.

E-mail address: [f.tonus@imperial.ac.uk](mailto:f.tonus@imperial.ac.uk) (F. Tonus).

combined heat and power operations. In this study we analyse the interaction between a promising IT-SOFC cathode ( $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ : LSCF) and electrolyte ( $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ : CPO) by *in-situ* neutron diffraction under operating conditions (under air, under polarisation at 600 °C).

## 2. Experimental

Due to the high conductivity of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF6428) leading to resistances beyond the measurement range of the *in-situ* stage, only the  $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2-\delta}$  (CPO) and 50:50% LSCF/CPO mixture were studied. CPO was synthesised using a sol gel route described elsewhere [12] and LSCF was supplied by Praxair Surface Technologies (Lot #03-P6171DM) (99.9%). One of the most promising IT-SOFC electrolytes is currently  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$  (CGO), however it was not possible to carry out the experiment on this material due to the high Gd neutron absorption cross-section (11.5 b for Pr vs. 49700 b for Gd). As some studies previously showed that CGO and CPO had a similar crystallographic structure [13] and close transport properties ( $\sigma_{\text{T}}(\text{CPO}) \times 10 \approx \sigma_{\text{T}}(\text{CGO})$ ) [14–17], the experiment was performed on CPO as an analogue for CGO. Whilst  $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-\delta}$  (CSO) would be a better electrical analogue this phase also suffers from high neutron absorption cross-section (5922 b) and hence the best option structurally was viewed as CPO. Sintering of the samples was performed under the same conditions for each pellet. 13 mm diameter pellets were pressed uniaxially at a pressure of 5 tons then isostatically pressed at 300 MPa to ensure the maximum green density was achieved. The samples were then sintered for 1 h at 1200 °C to minimise the diffusion of cations from one phase to the other during the synthesis stage. Platinum paste was deposited on both faces of the pellet and annealed for 30 min at 900 °C to ensure a good contact with the electrodes. Phase purity of the prepared samples was verified using X-ray diffraction (Bruker D2 Phaser,  $\text{CuK}\alpha$ ,  $\lambda = 1.5406 \text{ \AA}$ ).

CPO and LSCF/CPO stability under polarisation in an air atmosphere was then studied *in-situ* by time-of-flight neutron diffraction (Fig. 1). The experiment was carried out at the spallation neutron source (ISIS) at the Rutherford Appleton Laboratory, Oxfordshire, UK on the POLARIS diffractometer. The collected data were refined using the Rietveld method with the FullProf Suite [18]. Both the CPO and LSCF/CPO samples were heated at 600 °C in a

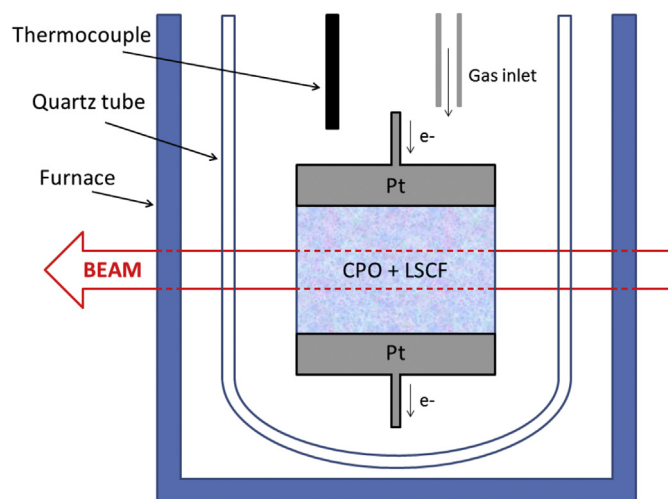


Fig. 1. Schematic diagram of the experimental set-up used for *in-situ* combined structural and electrical measurements.

quartz ampoule under flowing air. The samples were kept at this temperature during the experiment, and neutron diffraction data were collected every hour, applying different potentials to the material sequentially. The potential was applied using a Keithley 2400 source metre limited to a maximum current of 3 A. Voltages of +0.5, +1.0 and +1.5 V followed by −0.5, −1.0 and −1.5 V were applied sequentially to the CPO sample while collecting diffraction data, and the material was held under these conditions for between 4 and 6 h at each voltage. Afterwards the experiment was repeated on the mixture of LSCF/CPO, applying a voltage from +0.5 to +1.5 V and −0.5–1.5 V, and finally increasing the potential to −5 V and +5 V for 1 h at each potential at the end of the experiment to test the material stability in extreme polarisation conditions although being far from normal operating conditions.

## 3. Results and discussions

The fit of the refined structural model obtained from neutron diffraction data of LSCF6428 recorded at room temperature is shown in Fig. 2 (rhombohedral symmetry, *R*-3c space group). The refinement of the occupancies of the elements on the A- and B-sites showed that they correspond to the expected formula within the refinement error (Table 1). The oxygen stoichiometry was found to be 3.00 (compared to the 2.98 found by Kuhn et al. in the same atmosphere and at the same temperature [19]), meaning an average oxidation state of +3.4 on the B-site, close to values obtained in previous studies [20].

As mentioned in the experimental section, no significant voltage could be applied to the LSCF material due to the limitation of the potentiostat and so data collection focussed on the  $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2-\delta}$

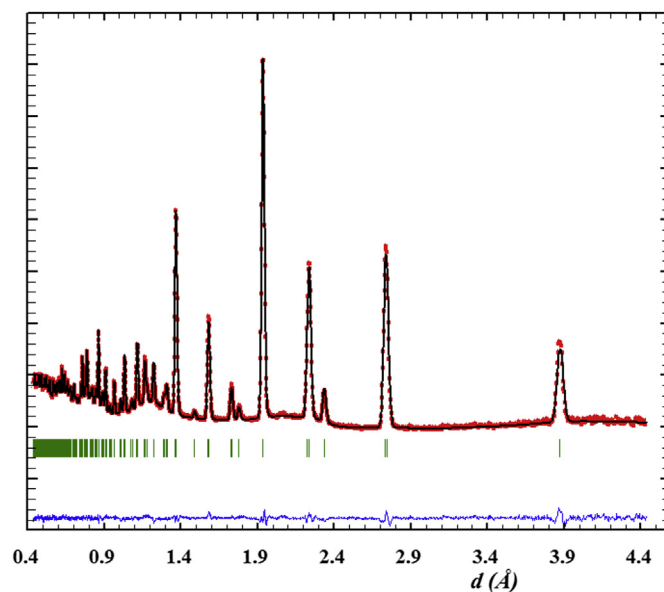


Fig. 2. Rietveld refinement of the structural model of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  from neutron diffraction data collected at room temperature under a flowing air atmosphere. The background originates from the quartz sample holder.  $R_{\text{wp}} = 2.55$ ,  $R_{\text{Bragg}} = 3.21$ ,  $\text{Chi}^2 = 2.25$ .

Table 1  
Calculated cation occupancies in LSCF6428 at room temperature.

	La	Sr	Co	Fe
Theoretical occupancy (fraction)	0.60	0.40	0.20	0.80
Refined occupancy (fraction)	0.59 (2)	0.41 (2)	0.188 (3)	0.812 (3)

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