



	Experiment title: Operating oxygen permeable membranes; in-situ powder diffraction studies.	Experiment number: CH-1345
Beamline: ID11	Date of experiment: from: 20/2 2003 to: 25/2 2003	Date of report: 6/5 2004
Shifts: 15	Local contact(s): Gavin Vaughan	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Poul Norby, *Yohann Breard, *Yael Yatziv Hercz, Department of Chemistry, University of Oslo, N-0315 Oslo, Norway *Stefan Marion, Centre for Materials Research, University of Oslo N-0349 Oslo, Norway		

Report:

Membranes for high temperature oxygen separation is an active research field, both for industrial development and in basic research. Technological applications include e.g. controlled oxidation reactions in the petrochemical industry. Promising candidates for high temperature membranes include perovskite type oxides. In order to obtain a better understanding of the oxygen transport in these materials, we have initiated a study, where in-situ synchrotron X-ray powder diffraction plays a crucial role.

The present in-situ experiment was designed for mapping the oxygen stoichiometry through a working oxygen permeable membrane at temperatures between 600 and 900°C using high energy X-ray powder diffraction from small, well defined volume elements. The material studied was a chromium substituted strontium iron oxide, $\text{SrFe}_{0.97}\text{Cr}_{0.03}\text{O}_{3-\delta}$ ($0.15 < \delta < 0.5$), which display high oxygen ion conductivity at temperatures between 600 and 1000°C. Oxygen non-stoichiometry and defect chemistry in these materials are crucial for the oxygen transport mechanisms.

We have performed in-situ synchrotron studies leading up to the present experiment during the last year:

- In-situ experiments studying the kinetics of oxidation/reduction processes at elevated temperatures. Unit cell and symmetry variations during oxidation were determined with a time resolution down to 100ms.
- In-situ experiments determining the structural phase diagram of $\text{SrFe}_{0.97}\text{Cr}_{0.03}\text{O}_{3-\delta}$ (Unit cell/symmetry as a function of temperature and composition (Oxygen stoichiometry)).

From the structural phase diagram we are able to derive the oxygen stoichiometry from knowledge of temperature and unit cell. Thus, by mapping the unit cell of the membrane material through a working membrane in an oxygen partial pressure gradient, the variation of the oxygen stoichiometry can be determined. This can then be compared with theoretical values based on oxygen transport modelling.

Membranes of chromium substituted strontium iron oxide perovskite, $\text{SrFe}_{0.97}\text{Cr}_{0.03}\text{O}_{2.84}$, were prepared from pressed pellets. The membranes had a diameter of 10 mm and a thickness of 2-3 mm.

The cell used for the in-situ X-ray diffraction studies was a modified version of an electrochemical cell used for e.g. ion conductivity measurements, Figure 1. (NorCell, ref 1) The membrane was sealed to an alumina tube using a gold ring in order to prevent gas leakages. The partial pressure of O_2 is 1 atm. on one side of the membrane, while the other side is flushed with a argon. The cell was enclosed in a resistance furnace (600-900°C) with two vertical slits to enable powder diffraction data to be collected.

The principle of the diffraction experiment is shown in Figure 2. In order to obtain information about the variations of the material through the membrane, penetrating X-ray radiation (60-100 keV) must be used. The radiation must be able to penetrate the quartz glass tubes and up to 10 millimetres of membrane material. In order to obtain the spatial resolution needed for mapping the height of the incoming as well as the detected beam must be small (20-75 μm) and very well collimated using two sets of double slits. This ensures that only diffraction from a very small volume element is detected. With a 2-3000 μm thick membrane and a spatial resolution of 50 μm , a good mapping of the unit cell changes through the membrane can be obtained.

The oxygen gradient over the membrane results in a transport of oxygen through the membrane. The measurements were performed under steady state conditions. In order to be able to map the interior of the membrane, a high resolution translating stage was used for vertical translation of the cell. The cell was mounted upside-down on a large goniometer, allowing controlled tilting of the cell with respect to the incoming beam.



Figure 1

From the in-situ powder diffraction data, the cubic unit cell parameter was determined as a function of depth of the membrane. using the previous mentioned relation between unit cell, temperature and oxygen stoichiometry, the oxygen content of the perovskite material through the membrane was determined

Determination of compositional gradients, e.g. oxygen non-stoichiometry, in membranes at operating conditions is important for understanding transport mechanisms. However, until now only predicted gradients from theoretical calculations have been available. Figure 4 shows the variation in the unit cell through the membrane at 750 and 850°C. The corresponding stoichiometry change was smaller than expected. This was caused by cracking of the membrane due to thermal stress, resulting in gas leaks and a smaller oxygen gradient across the membrane.

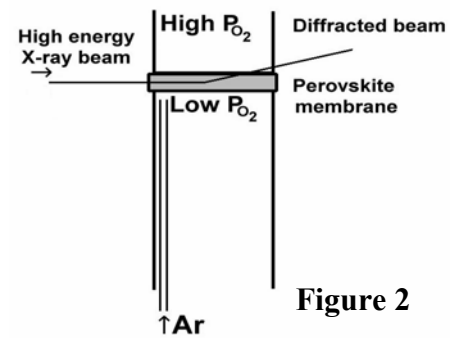


Figure 2

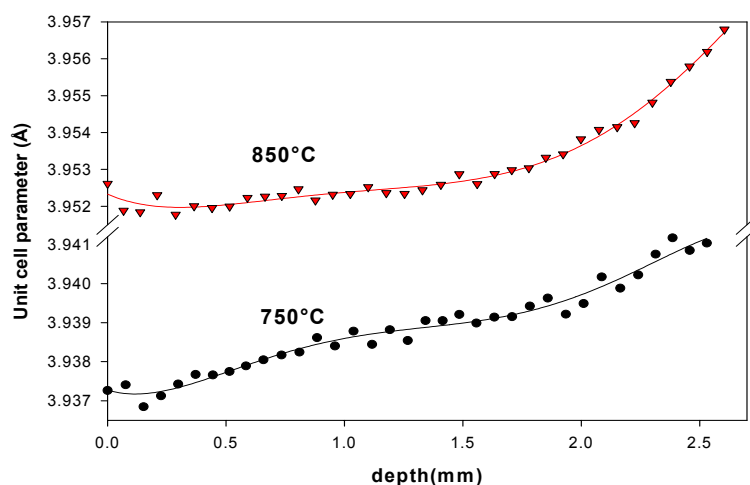


Figure 4

Figure 3



1. ProboStat from NorECs (Norwegian Electro Ceramics AS)

2. P.Norby, H. Fjellvåg and H. Emerich "Fast time resolved *in-situ* powder diffraction experiments: *In-situ* studies of high temperature oxidation/reduction reactions" ESRF Highlights 2001.

3. Rita Glenne "Preparation and Transport Properties of SrFeO_3 based materials with controlled microstructure." Dr. Ing. thesis, 2001, NTNU, Trondheim, Norway.