# Correlation between oxygen transport properties and microstructure in $La_{0.5}Sr_{0.5}FeO_{3-\delta}$

Stefan Diethelm [a,*], Jan Van herle [a], Joseph Sfeir [b,1], Philippe Buffat [c]

[a] Laboratory for Industrial Energy Systems (LENI), STI, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland
[b] HTceramix, EPFL Science Park, PSE-A, CH-1015 Lausanne, Switzerland
[c] Interdisciplinary Centre for Electron Microscopy (CIME), SB, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

Available online 23 March 2005

## Abstract

The effect of the bulk microstructure (grain size distribution, grain boundary composition) on the oxygen transport properties of $La_{0.5}Sr_{0.5}FeO_3$ membranes was investigated. For this purpose, samples with different microstructures were prepared by modifying the sintering duration and/or temperature. The average grain sizes, ranging from 0.20 to 1.43 μm, were determined from SEM analysis. The oxygen transport properties of these samples were characterised by permeation measurement. The fluxes presented a change in the activation energy which was attributed to a change in the rate limiting step, from bulk diffusion at lower temperature ($<850\,°C$) to surface limitations at higher temperature ($>900\,°C$). Only the transport through the bulk was influenced by the microstructure, with the highest flux for the smallest grains. This would imply that oxygen transport occurs more rapidly along the grain boundaries than through the bulk. Grain and grain boundary compositions were analysed by TEM.
© 2005 Elsevier Ltd. All rights reserved.

*Keywords:* Grain growth; Grain size; Grain boundaries; Ionic conductivity; Perovskites

## 1. Introduction

Perovskite-type mixed conducting oxides have been intensively studied in view of their application as oxygen separation membranes[1] or cathodes in solid oxide fuel cells.[2] In particular, the oxygen transport properties of a large variety of compositions have been investigated. However, a review of this abundant literature data often reveals important discrepancies, especially for identical compositions.[3] These discrepancies are believed to arise from differences in the microstructure of the samples. The influence of the microstructure on the oxygen transport properties of mixed conducting oxides has often been ignored, but recently, several studies have pointed out its importance. The microstructure, i.e. grain size distribution, inhomogeneous grain composition or grain boundary composition, depends significantly on the preparation method and the sintering procedure. As an example, Zhang et al.[4,5] have obtained samples of $SrFe_{0.2}Co_{0.8}O_{3-\delta}$ with grain sizes comprised between 2 and 15 μm by varying sintering temperature between 930 and 1200 °C. Permeation measurements showed that the oxygen flux could be increased by a factor 3 simply by decreasing the grain size. They suggested that the grain boundaries provided high diffusivity paths due to higher defect concentrations. The opposite trend was observed by Kharton et al.[6] in $La_{0.3}Sr_{0.7}CoO_{3-\delta}$. For instance, the permeability through a 80 μm grained sample was five times higher than through a 20 μm grained sample. This pointed to grain boundary resistance to oxygen ion transport. Nevertheless, fast diffusion along the grain boundary was also reported for a 3–4 μm grained sample, which had undergone liquid phase sintering, giving grain boundaries of distinctly different composition than that of the bulk. The influence of the powder synthesis method on the microstructure was further investigated by Qi et al.[7] Although different microstructures were thus obtained (with average grain size varying from 1 to 5 μm), little flux variation was noticed. Therefore, grain boundaries can either

---

* Corresponding author. Tel.: +41 216935968; fax: +41 216933502.
  *E-mail address:* stefan.diethelm@epfl.ch (S. Diethelm).
[1] Present address: Laboratory For High Performance Ceramics, EMPA, Dübendorf, Ueberlandstrasse 129, CH-8600 Dübendorf, Switzerland.

act as high diffusivity paths or barriers for oxygen transport depending on their structure and composition.

In this study, we examine the effect of microstructure on the oxygen transport properties of $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ samples. In particular, the influence of the grain size and the grain boundary length (GBL) on the oxygen permeation flux is investigated.

## 2. Experimental

### 2.1. Sample preparation

The nanometric $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ powder ($\sim$100 nm average grain size) was provided by HTceramix SA (Switzerland). Disc-shaped samples (30 mm diameter) were produced by uni-axial compaction of the powder at 50 MPa and sintered in air. The temperature and duration of the sintering were varied between 1175 and 1300 °C, respectively, 0.5 and 68 h, in order to control the microstructure. The density of the sintered samples was measured by the Archimedes method.

### 2.2. Permeation measurements

The oxygen transport through the dense samples was characterised by permeation measurements. A $\sim$24 mm diameter dense sample was clamped between two alumina tubes using gold rings and paste as sealing.[8] Air was flushed in the lower compartment and argon in the upper one. Oxygen was separated from air by solid-state diffusion through the membrane and released in the argon side due to the oxygen partial pressure gradient. The extremities of the tubes were sealed in the cold. The outlet gas composition was analysed with a gas chromatograph from Varian Inc. equipped with a molecular sieve 5 Å capillary column. The outlet flux was measured on-line by a bubble-meter. Any leakage could be detected by the presence of $N_2$ in the outlet gas.

### 2.3. TEM observations

The sample was first mechanically polished down to approximately 20 μm using the tripod method. It was then thinned by ion milling under grazing incidence with full sample rotation in a Fischione apparatus at low temperature (close to liquefied nitrogen). The process started with a 5 mA beam of 6 keV $Ar^+$ ions. To reduce the milling artefacts, the ion en-

ergy was reduced to 3.0 keV for 30 min followed by 20 min at 0.5 keV at the end of the thinning process.

All TEM observations were done on a Philips CM300 FEG/UT microscope, with a field emission gun operated at 300 kV and a reduced illumination intensity (spot size 5 and above). The EDS standardless microanalysis was performed with an INCA/Oxford spectrometer.

## 3. Results and discussion

### 3.1. Grain growth

The microstructure of the samples, principally the grain size, was controlled by varying the sintering parameters, i.e. temperature and duration. The grain size distributions were estimated from SEM micrographs of the surface of the samples, using the following approach: the 2D surface area and periphery of the individual grains were first calculated with a graphical integrator software (DigitalMicrograph 3.4). Then, for the sake of simplicity, the grains were assimilated to cubes so that their characteristic dimension was taken as the side of a surface-equivalent-square. The grain boundary length was estimated from half of the perimeter of the grains per surface area and is thus expressed in $\mu m/\mu m^2$. It is evident that estimating the size of 3D grains from their planar section leads to an underestimation. It is, sometimes, possible to recover the real 3D grain-size distribution whenever the shape of the grain is known.[9] In this work, however, we shall remain with the 2D approximation. The resulting data is summarized in Table 1, for five different samples. In the remaining of this paper, the samples will be referred to by the following code: LSF-1200-1/2 corresponds to the $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ sample, sintered at 1200 °C for half an hour, LSF-1250-15 corresponds to the $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ sample, sintered at 1250 °C for 15 h, etc.

As the grain growth results from the free-energy difference across a curved grain boundary, its rate is expected to be inversely proportional to grain size and thermally activated in such a way that the grain size ($d$) can be expressed as[10]

$$d - d_0 = \sqrt{2r_0} \exp\left(-\frac{E_A}{RT}\right) \sqrt{t} \tag{1}$$

where $d_0$ is the initial grain size; $r_0$, pre-exponential factor of the rate of grain growth; $E_A$, activation energy; $T$, absolute temperature and $t$, sintering duration. In Fig. 1, the average grain size is plotted as a function of the sintering temper-

Table 1
Sintering parameters with the resulting grain size and grain boundary length

| Sample | Sintering temperature (°C) | Sintering duration (h) | Average grain size[a] (μm) | GB length (μm/μm²) |
|---|---|---|---|---|
| LSF-1200-1/2 | 1200 | 0.5 | 0.20 (0.10) | 8.69 |
| LSF-1200-2 | 1200 | 2 | 0.31 (0.15) | 5.51 |
| LSF-1200-20 | 1200 | 20 | 0.63 (0.26) | 2.92 |
| LSF-1250-15 | 1250 | 15 | 1.43 (0.64) | 1.21 |
| LSF-1275-15 | 1275 | 15 | 2.74 (1.15) | 1.06 |

[a] Side of an area equivalent square. The standard deviation is given between parenthesis.